Published in final edited form as:

J Environ Monit. 2008 March ; 10(3): 305–314.

Assessment of diesel particulate matter exposure in the workplace: freight terminals†

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Abstract

A large study has been undertaken to assess the exposure to diesel exhaust within diesel trucking terminals. A critical component of this assessment is an analysis of the variation in carbonaceous particulate matter (PM) across trucking terminal locations; consistency in the primary sources can be effectively tracked by analyzing trends in elemental carbon (EC) and organic molecular marker concentrations. Ambient samples were collected at yard, dock and repair shop work stations in 7 terminals in the USA and 1 in Mexico. Concentrations of EC ranged from 0.2 to 12 $\mu\text{g m}^{-3}$ among the terminals, which corresponds to the range seen in the concentration of summed hopanes (0.5 to 20.5 ng m^{-3}). However, when chemical mass balance (CMB) source apportionment results were presented as percent contribution to organic carbon (OC) concentrations, the contribution of mobile sources to OC are similar among the terminals in different cities. The average mobile source percent contribution to OC was $75.3 \pm 17.1\%$ for truck repair shops, $65.4 \pm 20.4\%$ for the docks and $38.4 \pm 9.5\%$ for the terminal yard samples. A relatively consistent mobile source impact was present at all the terminals only when considering percentage of total OC concentrations, not in terms of absolute concentrations.

Introduction

Significant health effects have been associated with diesel exhaust exposure in highly impacted micro-environments.^{1–4} An important component of understanding exposure to diesel exhaust is the determination of its contribution to carbonaceous fine particulate matter (PM)

†Electronic supplementary information (ESI) available: Supplementary information including air toxin sources and concentrations, Tables S1 and S2, Fig. S1 and S2. See DOI: 10.1039/b715429a

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concentration in heavily impacted micro-environments, such as diesel freight terminals.^{5,6} Ambient studies in urban centers have been able to effectively track diesel exhaust contributions,^{7,8} however, it is not known whether these methods will translate well to micro-environments with potentially high diesel emissions. Additionally, the variability of diesel exhaust contributions to PM concentrations in diesel freight terminals across North America is not known.

In an environment with a variety of PM sources, tracers are needed to track the contribution of diesel particulate matter. Particulate matter in diesel exhaust is primarily composed of carbonaceous material,^{9,10} containing different mixtures of elemental and organic carbon, which vary according to engine operating conditions.^{9,11-13} Although elemental carbon (EC) is often used as a marker for particulate diesel exhaust in the atmosphere,^{11,14} this may not be appropriate for assessing the overall carbon contribution (EC and OC) from diesel in micro-environments with significant diesel activity. Additionally, within the trucking terminal there may be work stations which are heavily impacted by diesel engines operating under conditions not well represented by published diesel emission profiles. Issues of variable diesel operating conditions and the potential for additional sources make apportionment of diesel exhaust in a micro-environment more complicated than simply measuring EC or even total particulate carbon.

An initial study has been completed assessing the trucking industry worker's exposure to fine PM, elemental and organic carbon at 36 locations around the US.⁶ Measurements were made to assess differences in exposure by job title including: clerks, dockmen, combo workers, pickup and delivery (P&D) drivers, long haul (LH) drivers, hostlers (yard drivers), and mechanics. Significant differences in PM concentrations were shown based upon terminal location and work station, with the highest measurements in the repair shops.^{5,6}

The overall objective for this particular paper is to quantify the dominant sources of carbonaceous particulate matter in the different work stations within freight terminals using molecular markers and source apportionment and to assess the variability of these sources between terminals. Organic tracer source apportionment modeling has previously helped to distinguish these sources in the ambient atmosphere, and will be used to assess diesel sources within the micro-environment of the trucking terminals.^{8,15-18} This paper also provides a more comprehensive portrayal of the composition of organic PM, including PM source tracers and PM air toxics, in the freight terminal environment, for use in wider epidemiological assessments of the trucking industry.

Methods

Sampling

Seven different terminal locations in the US and one in Mexico¹⁹ were chosen for detailed organics analysis; not all 36 sites reported by Smith *et al.* have been characterized in this study.⁶ Table 1 contains the sample locations and dates of the sampling events discussed in this paper. A limited number of sites were chosen for detailed organic characterization; these sites were randomly chosen to represent the range in terminal locations across the US in the companies participating. In addition, a terminal from Mexico City was included for comparison.

A complete description of the sampling instrumentation and strategy has been reported previously.⁶ However, a brief description of the range of sampling conducted in the larger study will be given here. Particulate matter samplers were placed at central locations in the freight dock area and the repair shop. In order to account for the background levels of PM, a sampler was also placed at an upwind location in the yard. PM_{2.5} (PM ≤ 2.5 μm aerodynamic

diameter) for mass measurements was collected on 37 mm Teflon filters, while elemental and organic carbon measurements were conducted on PM₁ (PM ≤ 1.0 μ m aerodynamic diameter) collected on 22 mm quartz fiber filters. The samples used in this paper were collected over 8–12 h using a 16.7 lpm PM_{2.5} sampler with 47 mm quartz filters. A feasibility study showed that within the freight terminal environment, PM₁ comprised 90–98% of the PM_{2.5} mass.⁶ The higher volume samplers were necessary to achieve the higher OC loadings used for the detailed organic characterization.

Carbon analysis

Elemental and organic carbon analysis of the PM₁ samples was done by thermal evolution and combustion using the NIOSH 5040 method.²⁰ Field blanks were collected in parallel to the terminal samples and were used for blank subtraction of the EC and OC and detailed organic components. The average OC loading for the field blanks was 0.58 μ g per filter, which represents roughly 8% of the average filter loading. There was a very small amount of EC in the blank filters, 0.02 μ g, which was 2% of average EC loading.

Composites were made for detailed organics analysis of the PM samples used for the initial study. These composites were designed to assess the average carbonaceous PM concentrations and emission sources in the dock area and the repair shop, taking into account the background values as measured by the yard samples. For each composite, 5–8 filters from the yard, dock or repair shop at each of 8 terminals were combined for analysis (Table 1). The soxhlet extraction protocol used in this study has been described previously.²¹ Briefly, the combined filters are spiked with labeled internal standard and extracted by soxhlet, first with dichloromethane (DCM) for 12 h and then by methanol for 12 h. The DCM and methanol extracts are each concentrated by rotary evaporation and then combined before being further concentrated by nitrogen blow down to 250–500 μ L. At this point, each extract is then derivatized using diazomethane to convert all acids to their methyl esters. Each methylated extract is then run by gas chromatography mass spectrometry (GCMS) and quantified using calibration curves of quantification standards run with the same internal standard. The labelled internal standards used in this study included ¹³C-Levogluconan and the following deuterated compounds: eicosane, heptadecanoic acid, 4,4'-dimethoxybenzophenone, chrysene, octacosane, $\alpha\alpha\alpha$ 20R-cholestane, cholesterol, dibenz[ah]anthracene and hexatriacontane.

Chemical mass balance model

A chemical mass balance model (CMB8) was used for source apportionment in the freight terminal environment using recently published profiles of mobile sources,¹¹ which includes 3 profiles used in this study: gasoline, high load diesel exhaust and lubricating oil-impacted exhaust. Although the lubricating oil-impacted profile was derived from spark ignition exhaust, in the present study, which focuses on micro-environments impacted by diesel exhaust, this profile would include diesel exhaust, which can contain significant lube oil as well. Because of collinearity between the gasoline and lube oil-impacted profiles in the repair shop model runs, a composite profile was created using the 5 repair shop composites. The shop profile is a weighted average of all the repair shops with the OC adjusted for wood smoke, cigarette smoke and natural gas OC contribution. The profile is included in the ESI (Table S1[†]).

The remaining profiles used in the CMB model include: cigarette smoke,^{22,23} a west coast wood smoke average using published wood smoke profiles²⁴ and natural gas combustion.²⁵ The source profiles used in this study were compiled from studies employing similar organic

[†]Electronic supplementary information (ESI) available: Supplementary information including air toxin sources and concentrations, Tables S1 and S2, Fig. S1 and S2. See DOI: 10.1039/b715429a

analysis techniques. Uncertainties of 20% of the reported value were input into the source apportionment model for the above profiles.

Results and discussion

Detailed organic speciation

Molecular markers—Seven different terminal locations in the US and one in Mexico were chosen for detailed organics analysis to begin to understand the potential range in worksite concentrations and source contributions in trucking terminals (Table 1). The freight terminal locations represent a variety of locations across North America. The sampling seasons range from February to November in order to give an initial idea of seasonal impacts on the freight terminal micro-environment.

For the seven sites, a variety of individual organic compounds were quantified; Table S2[†] (in the ESI) contains the select concentrations of resolved organic compounds and compound classes in ng μg^{-1} OC. Measured concentrations were normalized to their respective OC concentration in order to determine whether compounds and tracers are present in similar proportions across terminals. Table S2[†] is split into known air toxics, as identified by the US EPA,²⁶ and compound classes used as quantitative molecular markers or qualitative tracer species.^{18,22,27-29} Fig. 1 shows the work station concentrations of a few of the compounds from Table S2[†], without normalization by OC.

Of the compounds listed as markers or tracers, the hopanes and steranes are commonly used as markers for gasoline and motor vehicle exhaust in source apportionment modeling.^{8,16} These compounds are emitted from the tailpipe due to the presence of lubricating oil in the engine. Isoprenoids and cycloalkanes have also been proposed as tracers for gasoline and diesel exhaust^{10,30} and are included in the speciation analysis, but not the CMB modeling. Higher molecular weight polycyclic aromatic hydrocarbons (PAHs), including indeno[*cd*]pyrene and benzo[*ghi*]perylene, are emitted by mobile sources^{11,31,32} and are key tracers in molecular marker CMB for distinguishing gasoline exhaust.^{11,32} The combination of hopanes, steranes and PAHs with mobile source elemental carbon concentrations are used to differentiate among gasoline, lube oil-impacted exhaust and diesel exhaust in the CMB model.^{16,33} Although the work station concentrations of hopanes vary by almost a factor of 40 for the repair shops in Fig. 1, the OC-normalized values in Table S2[†] are separated by a factor of 8 (0.07 to 0.55 ng μg^{-1} OC). This indicates that although there is a large range in the absolute concentration of motor vehicle tracers between terminals, when considered as a fraction of total OC, the contribution of motor vehicles is similar among the terminals.

The high molecular weight iso- and anteiso-alkanes are emitted in cigarette smoke and have been used as markers in CMB models.^{22,34} These have only been detected in two of the repair shop composites and the yard and dock samples from Mexico. Nicotine, a semi-volatile organic compound, is a commonly used marker for cigarette smoke. However, semi-volatile organic compounds can be present in both the gas and particle phase in the atmosphere and the analysis methods used in this study focus on molecular markers which are present primarily in the particle phase. With these caveats, quantification of the nicotine present in the filter composites (particle phase nicotine) shows the same trend as the iso- and anteiso-alkanes (Fig. S1[†]). Cigarette smoke contribution to organic PM would not be expected to be consistent throughout the work stations given their large volume,⁵ however, it may still be important when attempting to identify the OC sources impacting the PM samples collected at certain locations.

There are several additional organic tracers which have been included in Fig. 1 and Table 2 and are used in the CMB modeling later in the paper. Levoglucosan is a marker for biomass smoke and would also be present in cigarette smoke. Cholesterol, present in varying

concentrations in most of the samples, can be used as a marker for meat charbroiling, but may also be present in bioaerosols.^{21,35,36} Plant waxes have a known odd over even predominance, often quantified as the carbon preference index; this predominance is exploited in the vegetative detritus emission profile which includes high molecular weight alkanes^{18,29}

Measured concentrations of EC, OC have also been included in Fig. 1 in order to address the issue of bulk carbonaceous aerosol trends at the worksite. The highest OC concentration correlates with the highest levels of hopanes and steranes, but not PAH. The EC : TC ratio ranges from 0.02 at the site 5 yard to 0.45 at the site 3 repair shop (Table S2[†]). This range represents the range seen for cold start and idle conditions in Shah *et al.*⁹ and light load conditions in Kweon *et al.*¹³ but may also represent dilution of the diesel exhaust particles with low EC particles from other sources. However, if the work stations are considered separately, the EC : TC ratio is much narrower: 0.05 – 0.16 for the docks and 0.13 – 0.45 for the repair shop. This may indicate that different mobile source operating conditions dominate in the different work stations. In Fig. 1, the shop samples appear to have a high degree of consistency among terminals for most of the compounds shown.

The Detroit site (site 11) appears to have a unique background source contributing very high quinolines, PAHs, oxygenated PAHs, and methyl-PAHs compared to the rest of the composites in this study (Fig. 1, yard). These compound classes would all be of potential concern from a health perspective. From a source attribution perspective, the presence of these compounds indicates an auxiliary source of organic carbon which needs to be accounted for in the carbon budget for Detroit. The terminal was located in an industrial area with numerous large industrial complexes which could be impacting air quality.³⁷ Dilution of this background or yard source is apparent in the dock composite for Detroit, but the source is still present. The high levels of oxygenated and methyl PAH(s) indicate contribution from natural gas combustion and/or diesel fuel. It is apparent in Table S2[†], however, that it is predominantly the lower molecular weight PAHs that are disproportionately impacted by this off-site source, particularly fluoranthene and pyrene. These species are typically not included in particle-phase CMB models. This example shows how a large unusual source can distort the pattern of chemical species.

Air toxics—Diesel exhaust is a suspected carcinogen, but other, more specific air toxics were also measured within the freight terminals and in the background PM including: quinolines, phthalates, dibenzofuran, and substituted and un-substituted PAHs. These particle phase air toxics are not necessarily important on a total mass basis, but are valuable for worksite exposure assessment. Fig. 1 also illustrates the differences in exposure to measured air toxics at the different sites. The phthalates do not trend with the motor-vehicle exhaust markers, cigarette smoke markers, biomass smoke markers or the overall OC concentrations. Within the terminals, packages of small items are commonly wrapped with PVC film, which often contain phthalates as plasticizers. For bis(2-ethylhexyl)phthalate, measured exposure ranges from <1.92 to 110 ng m⁻³. Phthalates have been characterized as endocrine disrupters,³⁸⁻⁴¹ with several possible pathways of exposure including inhalation.⁴² The phthalate concentrations measured in this study are not above the risk-based concentrations (RBC) suggested by the EPA. However, concentrations at the Detroit dock exceeded the EPA RBC's for quinoline, benz[a]anthracene, benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and dibenz[a,h]anthracene.⁴³ These concentrations represent ambient concentrations in the terminal, not necessarily individual exposure. RBC's are calculated for 25 years of occupational exposure (technical background information from US EPA) and would be dependent upon the constancy of the source. These air toxics could be emitted from propane or natural gas powered equipment, including forklifts, cigarette smoke and other background sources, but are not present in large quantities in diesel exhaust. Thus the location of the freight terminals within an urban environment seems to impact occupational exposure to air toxics in freight terminals.

Regression plots and source analysis

Fig. 2 has EC concentration plotted *versus* OC for the yard, dock and repair shop. In Fig. 3-4 and S2[†], select organic tracers are plotted against OC and EC concentrations at the three trucking terminal work stations: yard, dock and repair shop. Regression lines were calculated for all of the dock and repair shop relationships (Table 2), but only those with correlation coefficients greater than 0.40 were plotted in Fig. 2-4 and S2[†]. Emission profile relationships have been included in the shop plots in Fig. 2-4 and S2[†] for reference.

EC and OC—The EC *versus* OC plots show a fairly consistent relationship across the 3 terminal work stations (yard, dock and repair shop). These are also composite samples of 5–8, 8–12 h filter samples, which means that average trends are being measured. Interestingly, there is no stronger correlation for the indoor work station plots (dock and shop) than for the yard; all are roughly $r^2 = 0.7$ (Table 2). The Salt Lake City (site 3) repair shop is not in line with the trend for the remaining shops in Fig. 2, as originally indicated in Fig. 1; it has a much lower OC : EC ratio.

PAHs as organic tracers—PAHs are often reported for diesel exhaust.⁴⁴⁻⁴⁶ Many combustion sources emit PAHs and it is questionable whether this could confound the tracking of PAHs emitted by diesel exhaust in a micro-environment. The same can be said for PAHs emitted by gasoline exhaust. As suggested by Fig. 1, there is no clear relationship between PAH concentration and total OC concentration for the yard (Fig. 3). The PAHs plotted range from molecular weight 252–276, which is the upper limit for natural gas combustion²⁵ and are the species less impacted by the low molecular weight PAH source at Detroit (Table S2[†]).

For the dock samples, the only PAH species which shows a good correlation with OC is benzo[ghi]perylene ($r^2 = 0.77$, Table 2). This compound has been used to distinguish gasoline exhaust in CMB models.³² High molecular weight PAHs, including indeno[1,2,3-cd]pyrene, benzo[ghi]perylene and others, are typically not reported in diesel exhaust,^{10,12,47} but are present nonetheless in many of the trucking terminal samples.

In contrast, all of the shop PAHs are strongly correlated with OC in Fig. 3 (Table 2); the correlation coefficients are all above 0.9 ($r^2 = 0.92–0.95$). Thus the source of the PAHs in the repair shop is the diesel source driving OC concentrations in repair shops across the terminals.

Hopanes and steranes—There is a noticeably stronger correlation for hopanes and steranes than PAHs in the dock area (Fig. 3 and 4) and the slopes for each regression line are pretty similar (Table 2). Interestingly, the data from the Mexico terminal fits nicely into the plot and is indistinguishable from the US values for these compounds. This indicates that the exhaust conditions for these various fleets are equivalent when normalized by OC.

The repair shop plot (Fig. 4) was similar to the shop PAHs plot, in that the 3 hopanes and the sterane were very well correlated with OC. However, the slopes were split distinctly with norhopane and hopane at roughly 0.2 and trisnorhopane and sitostane with slopes of 0.03. The strong correlation between individual hopane and sterane concentrations and OC concentrations (Fig. 4) seems to indicate that one type of lube oil-impacted motor vehicle exhaust is the controlling emission source for organic carbon, particularly in the repair shop.

Correlation between the individual hopanes and sterane and EC is not as strong as the relationship with OC (Fig. 4 and S2[†] in the ESI). Again, norhopane and hopane have some of the highest correlations for the repair shop (Table 2), while Sitostane has the highest r^2 (0.69) for the dock samples. Hopanes and steranes are part of the OC fraction of the diesel exhaust. The correlation between EC and OC (Fig. 2) is not as strong as the correlation between OC

and select hopanes, so it should not be expected that the correlation between select hopanes and EC would be as high as with OC (Fig. S2[†]). This illustrates that the ratio between organic tracers and elemental carbon is not consistent among different diesel operating conditions.^{11,12} It is also apparent that Salt Lake City (site 3), which had the highest EC : TC ratio (Table S2[†]), is anomalous with respect to the remaining repair shops; this point lies far below the regression lines for four compounds.

The most striking aspect of the correlation plots is the consistently high correlation for PAH, hopanes and OC in the repair shops (Fig. 3 and 4). This is strong evidence for a single consistent motor vehicle OC source in repair shops among the sampled terminals which cover locations across the US and Mexico.

Chemical mass balance modeling

A CMB model was used to apportion OC in the terminals to specific emission sources. Three different mobile source profiles were initially used in the model: high load diesel exhaust, gasoline exhaust and lubricating oil-impacted exhaust.^{11,48} Because the dock and repair shop samples represent micro-environments, where the emissions are high and the impact of individual trucks on the total OC concentration is expected to be much higher than in ambient samples, it was unknown how well the published profiles would fit the worksite concentrations. In this study, the diesel exhaust profile should be considered high load diesel, as it is predominantly EC⁴⁶ and the lubricating oil-impacted profile probably also represents low load, lubricating oil-impacted diesel exhaust.^{12,46}

After an initial model run it was apparent that the published mobile source emission profiles would not be sufficient to characterize the diesel source in the repair shops; the spark ignition and lube oil-impacted exhaust profiles were collinear for all but the Burnsville (site 15) repair shop. Additionally, the combined source left much of the OC unapportioned in the repair shops. This contradicted the very strong correlations seen in Fig. 3-4 and S2[†] which indicate a single strong motor vehicle source in the shops (with the Salt Lake City shop, site 3, an exception). To investigate this further, the 3 published emission profile values were included in Fig. 2-4 to assess whether any of the 3 matched the shop profile. None of the 3 profiles consistently match the slopes for the tracers and OC : EC seen in the shops. The gasoline profile is very similar for the OC : EC (Fig. 2) and hopane : OC relationships (Fig. 4), but does not match the PAH : OC relationship (Fig. 3). Interestingly, the hopane : OC relationship is matched well by both the lube oil-impacted and gasoline profiles for norhopane and hopane, while the high load diesel profile better matches the trisnorhopane : OC and sitostane : OC relationships in the shop. Because the shop profile did not match any of the published profiles for EC, PAH and hopanes, a shop profile was calculated using a weighted average of the 5 shop tracer concentrations as described in the ESI (Table S1[†]).

Fig. 5 shows the fraction contribution for each emission source across the 3 work stations at the 8 different terminals with high load diesel, gasoline and lube oil-impacted exhaust profiles used for the yard and dock samples and high load diesel and the shop profile used as the mobile source profiles in the shop samples. The yard samples are the closest approximation to background conditions, but are still heavily impacted by mobile sources (Fig. 5). Stafford and Detroit yards have very low apportionment to high load diesel, but this is confirmed by very low EC concentrations in Fig. 1. Because these are effectively background samples with greater impact from off-site sources, a high degree of consistency among terminals is not expected. However, to assess the consistency of work station samples among the different terminals, averages of the fraction contribution to OC for each emission source are included in Table 3; a sum of all the mobile sources is included, as well as the average unapportioned OC contribution. Despite the large deviation among terminals for the separate mobile sources in the yard, the summed mobile contribution is relatively consistent at $38.4 \pm 9.5\%$.

The lube oil-impacted exhaust profile is the dominant OC contributing source among the different terminals for the dock work station. The lube oil-impacted source contributes an average of $57.2 \pm 20.1\%$ of the OC in the dock area, while the high load diesel contributes an average of $3.4 \pm 2.5\%$ to the OC. The mobile source impacts in the dock areas would include the propane-powered forklifts and diesel tugs used in the yard to move trailers plus any background inputs. The propane-powered forklift emissions would be best approximated by the gasoline or lube oil-impacted emission profile. There is high variability in fractions of unapportioned OC among terminals for the dock samples (Table 3, Fig. 5). There is not an obvious seasonal, spatial or urban/rural trend to this pattern (Table 1).

The correlation plots were very supportive of 1 major source of motor vehicle OC in the repair shops among all terminals (Fig. 3-4 and S2[†]). The calculated shop source dominated the OC contribution in Kansas City, Detroit and Tonawanda and accounted for roughly 50% of the OC in Salt Lake City and Burnsville. All the OC was apportioned in Kansas City and Detroit, while the unapportioned OC ranged from 16–50% at the remaining 3 sites. Kansas City and Detroit repair shops were also the only 2 samples which had significant cigarette smoke OC contribution and were both sampled during the winter when lower air ventilation was likely.^{5,6} Although Salt Lake City had a higher percentage of high load diesel emissions, as indicated earlier by higher EC concentrations, the summed mobile source contribution average was fairly consistent across the 5 repair shops at $75.3 \pm 17.1\%$.

There are limitations to the CMB analysis. For example, a natural gas combustion profile was included in this study, but a specific propane-powered vehicle emission profile was not available. This may inhibit the apportionment of OC to this source in the dock areas where this equipment is the most prevalent. However, natural gas and propane combustion does not typically emit high levels of particulate matter, but may be important for the emission of specific air toxics. Resuspended dust may be an important source of organic carbon at these locations, particularly at Strafford (site 5), where there are few measured organic tracers. Secondary organic aerosol (SOA) may also be important in some of these composites, but the organic acid indicators measured by this method do not display a seasonal trend among the terminals. Wood smoke did not contribute more than a $1.5 \mu\text{g m}^{-3}$ in any of the composites and the average OC fraction contribution was 2–8% for the three freight terminal work stations.

Conclusion

From an occupational exposure perspective, it is important to be able to accurately assess the diesel emissions in the freight terminal. The results from this study indicate that there is some consistency among terminals in the fraction contribution of different mobile emission sources accounting for at least 65–75 % of the OC in the dock and shop work stations, respectively. The key is that there is much higher variability in absolute concentrations than in concentrations normalized by OC. The OC concentration in 4 of the 5 repair shops is dominated by a single mobile source which can be tracked effectively by measuring hopanes, with the fifth shop split between high load diesel as tracked by EC and the calculated shop OC source. The emission profile of this source does not exactly match previously reported diesel and gasoline exhaust profiles,¹¹ but is still consistent within the terminals sampled in this campaign. In the end, most of the particulate carbon in the shops can be attributed to diesel sources, with some contribution from cigarette smoke and unapportioned OC (potentially from outside the shop).

The dock samples were more variable among the different terminals and were likely impacted by ventilation and differences in the mobile source profiles. However, the lube oil-impacted exhaust profile accounted for the largest portion of the apportioned OC. This particulate OC source was originally reported for gasoline-powered motor vehicles which were operating under conditions of high lubricating oil in the emissions (*i.e.* smoking vehicles),¹¹ but is likely

representing the diesel and possibly forklift emissions in the terminals which are impacted by engine lubricating oil.

Concentration of organic tracers for cigarette smoke and biomass burning vary significantly throughout the terminal environment, indicating that these sources also vary significantly in their contribution to the measured OC. The air toxics are shown to not correlate with any particular source or bulk parameter, but to vary independently. This has implications for epidemio-logical studies attempting to correlate health endpoints with bulk parameters, such as OC and EC alone.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

This work was supported by NIH/NCI R01 CA90792 and HEI 4705-RFA03-1/04-1. We wish to gratefully acknowledge the contributions of the participating companies and workers represented by the International Brotherhood of Teamsters. We would also like to acknowledge the work of Erin Bean at the Wisconsin State Laboratory of Hygiene in the GCMS analysis.

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Fig. 1. Worksite concentrations of air toxics, key molecular markers, EC and OC (elemental and organic carbon).

Fig. 2. Correlation plots for worksite concentrations of EC and OC (elemental and organic carbon) with published relationships for gasoline, high load diesel and lubricating oil-impacted exhaust included in the repair shop plot.

Fig. 3. Correlation plots for key mobile source PAH (polycyclic aromatic hydrocarbons) with OC (organic carbon) including published relationships for gasoline, high load diesel and lubricating oil-impacted exhaust in the repair shop plot.

Fig. 4. Correlation plots for key mobile source hopanes and sterane with OC (organic carbon) including published relationships for gasoline, high load diesel and lubricating oil-impacted exhaust in the repair shop plot.

Fig. 5. CMB (chemical mass balance) source apportionment results of worksite OC (organic carbon) presented as a fraction of the measured OC.

Table 1
Information on the terminal locations, sampling dates and sampling locations within the terminal^a

Sample code	Urban/rural	City	State	Country	Sampling month	Worksite sampling locations		
						Yard	Dock	Shop
03	Rural	Salt Lake City	UT	USA	May, 2002		X	X
05	Rural	Strafford	MO	USA	July, 2002	X	X	
07	Urban	Seattle	WA	USA	September, 2002	X	X	
08	Urban	Kansas City	MO	USA	November, 2002	X	X	X
11	Urban	Detroit	MI	USA	February, 2003	X	X	X
14	Urban	Tonawanda	NY	USA	May, 2003		X	X
15	Urban	Burnsville	MN	USA	June, 2003		X	X
MEX	Urban	Mexico City	DF	Mexico	October, 2002	X	X	

^aUT – Utah, MO – Missouri, WA – Washington, MI – Michigan, NY – New York, MN – Minnesota, DF – Federal District and State of México.

Table 2

Regression statistics

	EC ^a regressions				OC ^b regressions			
	Intercept	Unc	Slope	R ²	Intercept	Unc	Slope	R ²
Yard								
OC	6.45	1.07	1.35	0.71^c				
Dock	5.62	1.63	3.85	0.73				
17a (H)-22,29,30	0.09	0.11	0.20	0.63	-0.16	0.14	0.05	0.74
Trisnorhopane								
17b(H)-21a(h)-Norhopane	0.82	0.36	0.40	0.38	0.02	0.36	0.12	0.74
17a(H)-21B(H)-Hopane	0.60	0.29	0.41	0.49	0.07	0.40	0.10	0.59
20R,5a(H),14b(H),17b(H)-	0.02	0.13	0.27	0.69	-0.32	0.15	0.07	0.82
Sitostane								
Benzo(b)fluoranthene					0.44	0.27	0.03	0.18
Benzo(a)pyrene					0.37	0.25	-0.01	0.02
Indeno(1,2,3-cd)pyrene					0.20	0.20	0.00	0
Benzo(g,h,i)perylene					-0.30	0.19	0.07	0.77
Shop								
OC	3.84	5.87	2.38	0.71	-0.11	0.12	0.03	0.92
17a (H)-22,29,30	0.10	0.29	0.07	0.46				
Trisnorhopane								
17b(H)-21a(h)-Norhopane	-0.06	1.19	0.43	0.67	-0.87	0.13	0.19	1
17a(H)-21B(H)-Hopane	-0.60	1.24	0.50	0.72	-1.40	0.14	0.21	1
20R,5a(H),14b(H),17b(H)-	0.23	0.22	0.05	0.43	0.07	0.11	0.03	0.88
Sitostane								
Benzo(b)fluoranthene					-2.00	1.05	0.34	0.94
Benzo(a)pyrene					-1.78	1.01	0.38	0.95
Indeno(1,2,3-cd)pyrene					-1.05	1.01	0.30	0.93
Benzo(g,h,i)perylene					-0.51	1.23	0.35	0.92

^aEC = elemental carbon.

^bOC = organic carbon.

^cAll correlation coefficients which are in bold are greater than 0.40 and are displayed in Fig. 2-4.

Table 3
Average percent contribution for each emission source by work-site across terminals with standard deviation

	Yard		Dock		Shop	
	Ave	Std dev	Ave	Std dev	Ave	Std dev
Cigarette	0.5%	1.0	0.3%	0.7	8.6%	12.4
Wood smoke	7.8%	6.0	5.8%	5.9	2.0%	1.9
Natural gas	0.1%	0.1	0.1%	0.2	0.0%	0.0
High load diesel	5.4%	5.0	3.4%	2.5	5.0%	11.1
Spark ignition	13.1%	12.8	4.6%	4.1	0.0%	0.0
Lube oil-impacted	19.9%	12.7	57.2%	20.1	0.0%	0.0
Shop source	0.0%	0.0	0.0%	0.0	70.3%	22.8
Summed mobile sources	38.4%	9.5	65.2%	20.4	75.3%	17.1
Unapportioned	53.3%	12.6	28.6%	21.9	14.1%	26.3