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PAPER

Assessing the risk to firefighters from chemical vapors and gases during vehicle fire suppression†

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Despite the frequent occurrence of vehicle fires, very few studies investigating firefighters' potential inhalation exposures during vehicle fire suppression have been conducted. In this paper, we present an assessment of firefighters' health risk from vehicle fire suppression that accounts for the mixture of gases and vapors likely to be found in these fires. Summa canisters were used to collect emissions from the engine and cabin fires of a single vehicle and were analyzed for 75 volatile organic compounds (VOCs). Firefighters' breathing zone concentrations (BZCs) of aromatic hydrocarbons, aldehydes, isocyanates, and carbon monoxide were measured during the suppression of three vehicle fires. The Summa canister and BZC data were used to develop a simple model for predicting BZCs for the compounds that were not measured in the firefighters' breathing zones. Hazard quotients (HQs) were calculated by dividing the predicted and measured BZCs by the most conservative short-term exposure limits (STELs) or ceiling limits. Hazard indices (HIs) were determined by adding HQs for compounds grouped by the target organ for acute health effects. Any HIs above unity represented unacceptable risks. According to this mixture analysis, the estimated 95th percentile of the exposure distribution for the study population represents ≥9.2 times the acceptable level of risk to the respiratory tract and eyes. Furthermore, chemicals known or reasonably anticipated to be human carcinogens contributed to >45% of these HIs. While STELs are not usually based on carcinogenicity, maintaining exposures below STELs may protect individuals from the biological stress that could result from short-term exposures to carcinogens over time. Although vehicle fires are suppressed quickly (<10 min), this assessment suggests that firefighters have the potential to be overexposed to acute toxins during vehicle fire suppression and should therefore wear self-contained breathing apparatus at all times during vehicle fire response.

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Introduction

According to a report by the US Fire Administration,[1] from 1996 to 1998, there were an average of 377 000 highway vehicle fires per year, and nearly one-quarter of all fire department responses during that time were to vehicle fires—more than the responses to residential property fires. Similarly, according to a report by the National Fire Protection Association,[2] in 2002, public fire departments responded to 329 500 vehicle fires, accounting for 20% of all reported fires. Since 1980, reported vehicle fires have

Environmental impact

Vehicle fires are a common occurrence; yet, firefighters do not always wear self-contained breathing apparatus during vehicle fire suppression. Although vehicle fires are suppressed quickly, our findings suggest that firefighters can be overexposed to acutely toxic chemicals during vehicle fire suppression that could adversely affect the respiratory tract and eyes. Many of these chemicals are also known or reasonably anticipated to be human carcinogens, and over time, could lead to higher cancer risks than equivalent doses from chronic exposures. To reduce the risk of adverse health effects from chemical exposures, firefighters should wear self-contained breathing apparatus at all times during vehicle fire suppression. This practice should become written policy at all fire departments.

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fallen only 30%, compared to a 51% drop in reported structural fires and a 44% drop in fires of all types.

Despite the frequent occurrence of vehicle fires, only a few studies characterizing the emissions from vehicle fires have been conducted.[3–5] Lonnermark and Blomqvist[3] reported potentially harmful levels of hydrogen chloride, sulfur dioxide, hydrogen cyanide, aromatic hydrocarbons (*e.g.*, benzene), polycyclic aromatic hydrocarbons (PAHs), aldehydes (*e.g.*, formaldehyde), dioxins and furans, and isocyanates in the emissions of vehicle fires conducted in a controlled setting. Because the data were presented as mass of contaminant over mass of material burned and were not necessarily representative of personal exposures, the results cannot be compared directly to occupational exposure limits (OELs). Recently, Underwriters Laboratory (UL) Inc. published a report of firefighter exposures to gases, vapors, and particulates during different fire events, which included an engine fire and cabin fire for vehicles that were burned under a calorimeter hood inside a large room.[4] Most of the measured contaminant concentrations were greater for the engine fire than the cabin fire. Investigators measured peak concentrations exceeding short-term exposure limits (STELs) or ceiling limits of carbon monoxide (CO), hydrogen chloride, ammonia, and butanol in the smoke plume of the engine fire; and of sulfur dioxide, nitrogen dioxide, hydrogen sulfide, and CO in the breathing zones of the firefighters during overhaul, which is the period of time that follows knockdown when firefighters search for and suppress residual flames or flare-ups. Benzene, naphthalene, and formaldehyde were detected near the front of the engine that was burned, but were below their respective STELs and ceiling limits.

Many more studies investigating firefighter inhalation exposures during structural fires have been conducted.[6–11] High levels (in excess of STELs) of CO, formaldehyde, acrolein, hydrogen chloride, hydrogen cyanide, hydrogen sulfide, and hydrogen fluoride have been reported during knockdown of structural fires.[10] Similarly, high levels of CO, formaldehyde, acrolein, glutaraldehyde, benzene, nitrogen dioxide, sulfur dioxide, and PAHs have been reported during overhaul of structural fires when self-contained breathing apparatus (SCBA) are commonly removed.[7]

Firefighters' exposures during vehicle fires are likely to be different than their exposures during structural fires for a number of reasons. First, firefighters commonly do not wear SCBA when responding to vehicle fires. According to an analysis by Austin *et al.*,[12] firefighters in Montreal were estimated to wear SCBA approximately 50% of the time at structural fires, but only 6% of the time at all fires (which included vehicle fires). Possible reasons for not wearing an SCBA during vehicle fires include the following: vehicle fires tend to be suppressed within minutes and inhalation exposures are assumed to be minimal, donning an SCBA takes time and is cumbersome to wear, and the belief that breathing air should be saved for more intense fires when it is really needed. Even when SCBA are worn for vehicle fires, they may be removed during overhaul. Another reason that firefighters' exposures during vehicle fires are likely to be different than their exposures during structural fires is that vehicle fires are typically fought outdoors where the weather can influence the intensity and duration of the exposures. For example, firefighters generally attack vehicle fires from an upwind position to minimize their exposures and maximize their field of vision. This approach may work well on days with strong straight winds but not so well on days with swirling or still wind conditions. Lastly, vehicles have many materials not typically found in structures (*e.g.*, rubber belts, rubber tires, oil, gasoline, and batteries), as well as materials that are often present in structures (*e.g.*, foams, plastics, carpeting, and steel).

A need exists to characterize the chemical gas, vapor, and particle exposures to firefighters during vehicle fire suppression due to the higher frequency of these fires, the potential for hazardous emissions from these fires, and the fact that firefighters do not always wear SCBA when responding to these fires. We addressed this need by conducting a health hazard evaluation of firefighters' inhalation exposures during vehicle fire suppression training as requested by management at a small municipal fire department. A report summarizing our findings was published in July 2010 and is available online at www.cdc.gov/niosh/hhe.

This paper provides an in-depth analysis of the chemical gas and vapor exposures and related health risks from vehicle fire suppression. In this paper we present an approach to assessing firefighters' risk from vehicle fires that accounts for the mixture of chemical vapors and gases likely to be present in these fires. Because we collected breathing zone concentrations (BZCs) for only a few chemicals, we estimated BZCs of other contaminants present using data acquired from evacuated canister samples of volatile organic compounds (VOCs) in the smoke plume. This approach is seldom undertaken in the industrial hygiene field, but can be valuable for estimating health risk from exposure to complex mixtures, and more importantly, for making decisions regarding exposure controls.

Materials and methods

Study population

Nineteen firefighters, including the Fire Chief and Assistant Fire Chief, from a small municipal fire department in Southwest Ohio were involved in the evaluation. The majority of the firefighters were volunteer (not full-time employees). Fifteen of the firefighters were male. Participation in the evaluation (wearing sampling pumps, *etc.*) was voluntary. Because this evaluation was in response to a health hazard evaluation request from the fire department and utilized standard industrial hygiene methods, human subject review board approval was not needed according to federal regulations.[13]

Vehicle fires

Vehicle fire suppression training is conducted at the fire department two to three times per year. Salvaged vehicles were used in the training exercises, which took place in abandoned parking lots. The training had three phases: (1) startup—when the fire was ignited and allowed to build, (2) knockdown—when the fire was suppressed with water, and (3) overhaul—when the firefighters searched for and suppressed residual flames or flare-ups. Vehicle engines and cabins were separately set on fire with flares and accelerated with gasoline. The firefighters waited 2–5 min to let the fires build before knockdown with water. Exposure times for each phase averaged 30 s for startup (when the firefighters approached the fires), 2 min for knockdown, and 2 to 3 min for

overhaul. Thus, the total exposure time for the engine and cabin fire of one vehicle averaged ~10 min.

Three firefighters were involved in suppressing the vehicle fires: a nozzle operator, a backup fighter, and an officer. The nozzle operator aimed the stream of water, the backup fighter assisted with holding the hose, and the officer managed the other firefighters and assisted where needed. In addition, another firefighter assisted with the particle sampling described elsewhere[14] by holding a sampling duct near the breathing zone of the nozzle operator. These firefighters' exposures were included in the risk assessment. Each of the firefighters wore full turnout gear and an SCBA the entire time they fought the fires, including during overhaul.

On the first sampling visit, the engine and cabin of a 1991 Dodge Dynasty sedan were set on fire. Prior to the fire, most of the belts and the battery were removed and the gas tank emptied but the cabin interior was relatively unaltered. According to the National Weather Service (http://www.nws.noaa.gov), during this exercise, the wind was from the southwest (away from firefighters attacking the fires) and averaged 23 km h^{-1}, the ambient temperature was 27 °C, and the relative humidity was 30%.

On the second sampling visit, the engines and cabins of three vehicles were set on fire: a 1994 Ford Aerostar minivan, a 1986 Toyota Corolla sedan, and a 1986 Toyota Celica coupe. The belts, fluids, batteries, cushions, and upholstery were present in each vehicle, but the gas tanks had been emptied. According to a weather station (HOBO®, Onset Computer Corp., Bourne, MA) setup by National Institute for Occupational Safety and Health (NIOSH) investigators at the training ground, the wind direction during this exercise varied but was predominately southerly with an average speed of 4.2 km h^{-1}. The firefighters attacked the fires mostly from the south or southeast direction. Thus, the wind tended to blow away from the firefighters. The ambient temperature increased slightly throughout the day (24–26 °C), while the relative humidity remained steady (average of 33%). According to thermal images (IR FlexCam Ti55, Fluke®, Everett, WA), the cabin fires were hotter than the engine fires, and the temperatures of some metal parts of the vehicles remained elevated (>93 °C) after knockdown. All but one fire exceeded 540 °C.

Air sampling

First sampling visit. The primary purpose of the first sampling visit was to identify the main VOCs in the vehicle fire emissions. A firefighter in turnout gear and SCBA collected samples of the emissions from the engine and cabin fires using 1 litre evacuated stainless steel Summa canisters. The firefighter collected the samples by holding the canister in the smoke plume and opening the valve, which allowed the canister under vacuum to draw in 1 litre of the emissions in <30 s. Particulate screens (7 μm pore size) prevented particles from entering the canisters. Six samples were collected in conjunction with startup, knockdown, and overhaul for each fire. The Summa canister samples were quantitatively analyzed for 75 VOCs according to the EPA TO-15 Method by Columbia Analytical Services (Simi Valley, CA).[15]

Second sampling visit. The primary purpose of the second sampling visit was to quantify BZCs of specific chemical vapors. Based on the results of the first evaluation, as well as an extensive literature review, we decided to sample for specific aromatic hydrocarbons, aldehydes, isocyanates, and CO. Aromatic hydrocarbons, aldehydes, and CO are common byproducts of organic material combustion. Isocyanates are used in the manufacture of polyurethane materials and are released during combustion. Each of the four firefighters wore three sampling trains and direct-reading CO detectors (GasAlert Extreme, BW Technologies Ltd., Calgary, Canada) that were set to record levels every 5 s. Calibrated Pocket Pumps® (SKC Inc., Eighty Four, PA) were used for each sampling train. Sampling times ranged 14–18 min for the isocyanate samples (which were replaced between the engine and cabin fires) and 32–55 min for the aromatic hydrocarbon and aldehyde samples. The sampling times are greater than the exposure times (~10 min) because it took several minutes to hang and remove sampling trains and because of the intermission (~5 min) between the engine and cabin fires.

Benzene, ethylbenzene, naphthalene, styrene, toluene, and xylenes were sampled with charcoal tubes (100 mg front section 50 mg back section) at a flow rate of 200 cm^3 min^{-1} and analyzed with NIOSH Method 1501.[16] Formaldehyde and acrolein were sampled at a flow rate of 100 cm^3 min^{-1} with XAD-2 tubes treated with 2-hydroxymethyl piperazine (120 mg front section 60 mg back section) and analyzed by NIOSH Method 2541.[16] However, to achieve better sensitivity, the XAD-2 tube samples were analyzed by gas chromatography equipped with a nitrogen phosphorus detector instead of the flame ionization detector as stated in NIOSH Method 2541. The charcoal tubes and XAD-2 tubes were analyzed by Bureau Veritas North America (Novi, MI).

The sampling and analytical method used to measure isocyanates is described elsewhere.[17] The sampling media consisted of a denuder—a polypropylene tube (7 cm long, 0.8 cm diameter)—attached to a 13 mm diameter polypropylene cassette. The inner wall of the denuder was coated with a dibutyl amine (DBA) impregnated glass fiber filter (2.5 × 6 cm). The polypropylene cassette held a DBA impregnated glass fiber filter (13 mm diameter, 0.3 μm pore size). We sampled at a flow rate of 200 cm^3 min^{-1}. In theory, most gases, vapors, and aerosols are collected and derivatized in the filter cassette. However, methyl isocyanate reacts too slowly with the reagent (DBA) to be collected solely with the filter cassette.[17] Thus, the primary purpose of the denuder was to act as a sampler for the low molecular weight monoisocyanates (*e.g.*, methyl isocyanate, ethyl isocyanate, isocyanic acid) and to enhance the derivatization efficiency by continuously replenishing the filter cassette with the reagent.[17]

These samples were analyzed by the Institutet för Kemisk Analys Norden AB (Hässleholm, Sweden) under the direction of Dr Gunnar Skarping according to the methodology described elsewhere.[17] Isocyanates that were analyzed included: toluene diisocyanate, methyl bisphenyl isocyanate, hexamethylene diisocyanate, phenyl isocyanate, methyl isocyanate, ethyl isocyanate, propyl isocyanate, isophorone diisocyanate, and isocyanic acid. However, the results are reported as total reactive isocyanate groups (TRIG), which is the sum of masses of all isocyanate functional groups in a sample.

In this paper, we present BZCs as time weighted average (TWA) concentrations over 15 min because we believe it is

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reasonable to assume that most exposures occurred during the engine and cabin fires (~10 min of total exposure time for each vehicle burned) and possibly the few minutes before and after the suppression of these fires. However, because TRIG was not detected during engine fire suppression, we only report BZCs of TRIG measured during the cabin fires. These also are presented as 15 min TWA concentrations. Although we have real-time CO data and could potentially report levels for every 5 s of exposure, for consistency, we report the average BZCs for the engine and cabin fires combined.

Predicting BZCs

Because we only measured BZCs for a few select compounds, we established a simple model for predicting BZCs for the other contaminants found in the smoke plume using Summa canisters. This model makes the following assumptions: (1) the Summa canister sampling data can be used to estimate the average VOC concentrations in the emissions, (2) the wind will carry a percentage of the emissions into the breathing zones of the firefighters, (3) this percentage can be estimated for the study population using the ratio between the measured BZCs and the VOC concentrations in the emissions, (4) exposures are log-normally distributed, and (5) the 95th percentile of the exposure distributions (X95) for the VOCs can be estimated using the geometric standard deviation (GSD) for the measured BZCs.

We calculated a TWA concentration for each VOC in the emissions (TWA-Es) by multiplying the chemical concentrations for each phase of the fire response (measured with Summa canisters) by the respective exposure times and dividing the result by the total exposure time for all phases combined (see Table 1). Measurements of benzene, toluene, xylenes, and ethylbenzene were common to both the Summa canister samples and personal air samples and were detectable in ≥2 personal air samples. We calculated the median ratio between geometric mean (GM) BZCs and TWA-Es for these compounds (median = 0.080, range = 0.032–0.20). This ratio suggests that, on average, 8% of the emissions were carried into the firefighters' breathing zones. We multiplied the TWA-Es by 0.080 to predict the task-based GM BZCs for all VOCs collected with the Summa canisters.

Maximum likelihood estimation was used for the non-detectable BZCs, after which the GM, GSD, and X95 were calculated for exposure distributions. The X95 was calculated according to the following equation described in Bullock and Ignacio.[18]

$$X95 = GM \times GSD^{1.645} \quad (1)$$

The median GSD for the BZCs with greater than 30% detection rate (*i.e.*, toluene, benzene, formaldehyde, and TRIG) was determined (median = 2.0, range = 1.3–4.8) and used along with the predicted GMs to calculate theoretical X95s for the VOCs collected with the Summa canisters. Although formaldehyde, CO, and TRIG were not measured by the Summa canisters, we included them in the risk assessment because they were measured in the personal air samples. Measured data for benzene, toluene, xylenes, and ethylbenzene from personal air samples were used instead of predicted data based on the Summa canisters because we have more confidence in the measured data (provided some of the data are above the detection limit).

Mixture analysis/risk assessment

The American Conference of Governmental Industrial Hygienists (ACGIH) additive mixture formula[19] was used for this risk assessment. This formula is similar to the dose addition formula established by the US Environmental Protection Agency (EPA).[20] Hazard quotients (HQs)—the ratio between the BZC and applicable occupational exposure limit (OEL)[19,21]—were calculated for all predicted (or measured) BZCs. Because the BZCs represent exposures during 15 min time periods, their summary statistics were compared directly to STELs or ceiling limits as specified by ACGIH.[19] We compared the BZCs to the most conservative Occupational Safety and Health Administration (OSHA) permissible exposure limits (PELs),[22] NIOSH

Table 1 Ordered list of the 15 most abundant VOCs measured with Summa canisters (mg m^{-3}) in the emissions from vehicle fires that were used to calculate time weighted average concentrations (mg m^{-3}) for each chemical in the emissions (TWA-E) over the exposure period

	Engine fire			Cabin fire			
Compound	Startup	Knockdown	Overhaul	Startup	Knockdown	Overhaul	TWA-E[a]
Dichlorodifluoromethane	5.1	2.4	48	<0.087	<0.027	0.0059	10
Benzene	5.2	1.6	11	60	1.4	0.38	6.2
Toluene	1.4	9.3	3.8	10	4.6	0.95	4.4
Propene	3.3	0.91	11	18	1.4	0.16	3.8
m,*p*,*o*-Xylenes	0.35	9.1	1.4	1.1	2.7	0.45	2.8
Styrene	0.83	3.3	1.6	14	2.3	0.45	2.3
Acetone	0.40	0.84	3.8	12	1.9	0.30	2.0
Acrylonitrile	0.32	<0.026	0.77	27	0.38	0.066	1.6
1,3-Butadiene	2.3	0.40	4.8	6.8	0.25	0.049	1.6
Naphthalene	2.4	0.93	1.2	10	0.60	0.17	1.2
Acrolein	0.56	0.35	1.4	15	0.18	0.048	1.2
1,2,4-Trimethylbenzene	0.070	4.2	0.38	0.15	0.70	0.10	1.1
Acetonitrile	0.28	0.12	0.70	14	0.12	0.034	0.9
Chloromethane	0.33	0.17	1.2	11	0.19	0.046	0.89
Ethylbenzene	0.15	2.2	0.41	1.4	0.70	0.12	0.78
Exposure time for each phase/min	0.5	2	2	0.5	2	3	10

[a] TWA-Es were calculated by multiplying the chemical concentrations for each phase of the fire response by the respective exposure times and dividing the result by the total exposure time (10 min).

recommended exposure limits (RELs),[22] or ACGIH threshold limit values (TLVs).[19] Because there are no STELs for TRIG in the United States, we used the STEL established in Sweden.[23] Compounds without STELs or ceiling limits (*e.g.*, dichlorofluoromethane, propene, trimethylbenzenes, *etc.*) were not included in the risk assessment.

The HQs were added together to provide hazard indices (HIs). According to the EPA, a hazard index (HI) is a numerical indication of the nearness to acceptable limits of exposure or the degree to which acceptable limits are exceeded.[20] On an additive basis, any HI exceeding unity represents unacceptable level of risk from exposure.[19–21] According to ACGIH[19] and EPA,[20,21] the additive mixture formula is most properly applied to compounds that induce similar health effects. Hence, HIs were calculated for chemicals grouped by the primary target organs for acute health effects using predicted or measured GM and X95 BZCs. The primary target organs for the acute health effects were determined using International Chemical Safety Cards.[24] The chemicals were also identified as known or reasonably anticipated to be human carcinogens as established by the National Toxicology Program.[25]

Results

Table 1 provides the 15 highest TWA-Es and corresponding Summa canister data. Forty eight of 75 VOCs analyzed were detected with the Summa canisters. Dichlorofluoromethane, a refrigerant no longer manufactured in the United States,[26] was measured in the highest concentrations overall. The source of this compound was most likely the coolant in the vehicle, which would explain why so little was detected during the cabin fires. Benzene was measured in the second highest concentrations overall. For the cabin fire, we measured the highest VOC concentrations during start-up and the lowest during overhaul, except for xylene and trimethylbenzene, which were highest during knockdown. However, for the engine fire, only the concentration of naphthalene was highest during startup; the highest concentrations of the other VOCs were nearly split between knockdown and overhaul.

A summary of the BZCs measured during the second sampling visit is provided in Table 2. These BZCs were compared to the most conservative STELs or ceiling limits because they represent short exposure periods (≤15 min). Formaldehyde was the only chemical measured at BZCs above its ceiling limit. The BZCs of naphthalene, styrene, and acrolein were below the respective minimum detectable concentrations of 2.1, 10.3, and 0.36 mg m^{-3}. Two samples of toluene and one sample of ethylbenzene had evidence of significant breakthrough, where the back section of the charcoal tube collected >10% of the front section. TRIG was only detected during the cabin fires. This is not surprising since isocyanates are a component of foams present in the interior of the cabin but not the engine.

The risk assessment is summarized in Table 3 for the 10 compounds with the highest HQs. It is important to note that the HIs calculated using all detectable compounds (data not shown) did not differ substantially from the HIs calculated using these 10 compounds. Thus, these compounds were the main contributors to the HIs. We estimated unacceptable risks to the respiratory tract and eyes when we compared GMs to STELs (HI = 1.8) and X95s to STELs (HI ≥ 9.2). The HIs based on X95s represent risks according to the estimated 95th percentile of the exposure distribution for the study population, and hence, are appropriate for making decisions regarding exposure controls. The HIs based on X95s for chemicals affecting the central nervous system, liver/kidney, and blood were all <0.40 and therefore represent acceptable exposures to these target organs. Chemicals known or reasonably anticipated to be human carcinogens contributed to >45% of the HIs.

Discussion

The primary purpose of this work was to characterize the potential exposures and health risks to firefighters during vehicle fire suppression. There are several limitations to the simplistic model we developed for predicting BZCs. This model relied heavily upon Summa canister data collected from one vehicle fire during the first sampling visit. Although VOC concentrations in the smoke plume have some spatial and temporal variability, because only one Summa canister was collected for each phase, we were unable to analyze this variability and obtain better estimates of mean VOC concentrations. Moreover, it is unlikely that this one vehicle fire is representative of all vehicle fires. For example, the gas tank in this vehicle was empty; whereas, most automobiles have some fuel in them when they catch fire and therefore might release different emissions. Similarly, it is unlikely that the BZCs we measured are representative of the

Table 2 Summary of 15 min TWA BZCs (mg m^{-3}) measured during the suppression of three separate vehicle fires

Compound	*N*	Non-detects[a]	Min	Max	GM	GSD	X95[b]	Lowest STEL or ceiling limit (C)/ mg m^{-3}
Benzene	12	8	<0.21	0.33	0.20	1.5	0.38	3.2 C[f]
Ethylbenzene	12	10	<0.14	0.33	0.052	3.1	0.33	545[f,g]
Toluene	12	1	<0.17	13	0.90	4.8	12	560[f]
Xylenes	12	10	<0.34	0.56	0.26	1.5	0.52	655[f,g]
Formaldehyde	12	7	<0.14	0.67	0.11	2.5	0.52	0.12 C[f]
CO[c]	12	0	0.030	25	3.3	6.2	65	230 C[f]
TRIG[d]	10[e]	7	<0.018	0.030	0.017	1.3	0.027	0.044[h]

[a] Values below the minimum detectable concentration were assigned values using maximum likelihood estimation. [b] 95th percentile of the exposure distributions where X95 = GM × GSD$^{1.645}$. [c] The average CO concentration for the engine and cabin fires combined (~10 min of sampling time). [d] TRIG concentrations measured during cabin fire suppression only. [e] Two TRIG samples were excluded due to the sampling pump error. [f] NIOSH REL. [g] ACGIH TLV. [h] Sweden OEL.

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Table 3 Hazard indices (HI) by target organ for the 10 compounds with the highest hazard quotients (HQs)

Compound	TWA-E	Predicted or measured BZC/mg m^{-3} GM	X95	STEL or ceiling limit (C)	HQ by GM	HQ by X95[f]	Target organ for acute health effects: Respiratory tract	Eyes	Central nervous system	Liver/kidney	Blood	Human carcinogen[g]
Formaldehyde[a]	NA	0.11	0.52	0.12 C[b]	0.92	4.3	X	X				Reasonably anticipated
Acrolein	1.2	0.094	1.1	0.25[c]	0.38	3.9	X	X				
TRIG[a]	NA	0.017	0.027	0.044[d]	0.39	0.61	X	X				
CO[a]	NA	3.3	65	230 C[b]	0.014	0.28	X				X	
Benzene[a]	6.2	0.20	0.38	3.2[b]	0.063	0.12	X	X	X			Known
1,3-Butadiene	1.6	0.12	1.4	11[e]	0.011	0.12	X	X	X			Known
Acrylonitrile	1.6	0.13	1.5	22 C[b]	0.0059	0.061	X	X	X			Reasonably anticipated
1,2-Dichloroethane	0.4	0.034	0.38	8[b]	0.0042	0.044	X	X	X	X		Reasonably anticipated
1,4-Dioxane	0.10	0.0081	0.093	3.6 C[b]	0.0023	0.023	X	X	X			Reasonably anticipated
Toluene[a]	4.4	0.90	12	560[b]	0.0016	0.021	X	X	X			
				HI based on GM			*1.8*	*1.8*	*0.086*	*0.0042*	*0.014*	
				HI based on X95			*9.5*	*9.2*	*0.34*	*0.044*	*0.28*	

[a] Measured BZCs (not predicted). [b] NIOSH REL. [c] ACGIH TLV. [d] Sweden OEL. [e] OSHA PEL. [f] 95th percentile of the exposure distribution where X95 = GM × GSD$^{1.645}$. [g] Carcinogenicity as established by the National Toxicology Program.

exposures to all firefighters who suppress vehicle fires because firefighters may differ in their proximity to the source and the amount of time spent on the different phases of the fire response.

Our model was built on the premise that the smoke generated from vehicle fires is transported by the wind into the breathing zones of the firefighters. The ratio between GM BZCs and TWA-Es was 0.080. Thus, in essence, we estimated that the wind carried the smoke into the firefighters' breathing zones 8% of the time. Due to the significant breakthrough on charcoal tubes presumably caused by elevated temperatures,[27] we likely underestimated the actual BZCs of aromatic hydrocarbons. Hence our estimate of 8% may underestimate the actual exposure potential to firefighters. Although the wind was not particularly strong during the second sampling visit (4.2 km h^{-1}), the prevailing winds were at the firefighters' backs. Higher exposure potentials are conceivable under different weather conditions (*e.g.*, still conditions or swirling winds) or scenarios where firefighters must attack vehicle fires from downwind positions (*e.g.*, upwind position is blocked). Moreover, our model was based on data from a small number of compounds and did not account for the variability in the factors used to build the model. Both factors used in the model were highly variable; the ratio between measured BZCs and TWA-Es ranged more than 6-fold and the GSDs for the measured BZCs ranged more than 3.5-fold. Hence, actual GMs and X95s could vary substantially from our predictions.

In addition to the limitations of the prediction model, we did not measure all the harmful substances emitted in vehicle fires and thus, our HIs probably underestimate the actual health risk from suppressing vehicle fires. For example, sulfur dioxide, nitrogen dioxide, hydrogen chloride, hydrogen sulfide, and hydrogen cyanide, which were not measured, are likely to be present in the vehicle fire smoke[3,4] and could contribute significantly to the HIs. The latter two compounds, like CO, are chemical asphyxiants. Chemical asphyxiants have been associated with acute cardiovascular deaths.[28] This is important to note because sudden cardiac deaths account for nearly half of all on-duty firefighter deaths,[29] most of which occur during or soon after fire suppression activities.[30]

The HIs we calculated are rough estimates of potential toxicity. As more HIs for different effects exceed unity, the potential for human toxicity increases. However, this potential for risk is not the same as probabilistic risk; a doubling of an HI does not necessarily indicate a doubling of the risk for toxic effects.[21] In addition, as the number of compounds in the mixture increases, the uncertainty associated with the risk assessment increases.[20] Because vehicle fires produce a multitude of chemicals, there is a great deal of uncertainty surrounding the HIs we calculated.

Another limitation is that the sampling media we used is designed to sample gases and vapors and not aerosols. Thus, this risk assessment did not account for particulate exposures. (Although, particle sizes and other particle characteristics were measured and are presented elsewhere.[14]) Lastly, the BZCs used in the risk assessment are not ideal for comparison against ceiling limits because a ceiling limit is an exposure that should not be exceeded at any point in time. Thus, averaging over 15 min may diminish the actual risk posed by compounds with ceiling limits. For example, the maximum direct-reading BZC of CO (220 mg m^{-3}, data not shown) was substantially greater than the

X95 of CO (65 mg m^{-3}) that was used in the risk assessment. This maximum direct-reading BZC was just below the NIOSH ceiling limit of 230 mg m^{-3}.

Despite these limitations, our results suggest a potential for overexposure to acute toxins. According to the mixture analysis, average BZCs encountered during vehicle fire suppression present an unacceptable risk for acute health effects to the respiratory tract and eyes of firefighters (HI = 1.8). These HIs are considerably higher (*i.e.*, ≥9.2) for the estimated 95th percentile of the exposure distribution for the study population. While studies of health effects to the eyes of firefighters are lacking, acute decreases in pulmonary function have been observed in firefighters who did not wear SCBA during firefighting activities.[31,32] Chemicals known or reasonably anticipated to be human carcinogens accounted for >45% of these HIs. The effect of intermittent short-term exposures to carcinogens is not well understood, but depending on the life stage when exposure occurs and the mechanism of carcinogenesis, it could lead to higher cancer risks than equivalent doses from chronic exposures.[33–36] Although STELs are usually not based on carcinogenicity, an argument can be made that intermittent exposures to carcinogens should be kept below STELs to adequately protect workers from the biological stress of the carcinogens. A recent meta-analysis of epidemiological studies determined that firefighters have a probable increased risk of multiple myeloma, non-Hodgkin lymphoma, prostate, and testicular cancer.[37]

The HIs we calculated assume that the toxicological effects of the chemicals are additive. However, it is possible that chemicals can have synergistic effects, where one chemical enhances the toxicity of another chemical. This is possible for both acute and chronic health effects. We did not consider the chronic health effects in the mixture analysis because vehicle fires represent short-term exposures. However, if we adjust the 15 min TWA BZCs for an 8 h workday by assuming zero exposure for the other 465 min and compare the 8 h TWA BZCs to their corresponding work-shift OELs, we would calculate an overall HI based on X95s of <0.4. This is an acceptable risk for chronic health effects if firefighters only respond to one vehicle fire in a day but often firefighters have several different responses in a day.

The goal of an occupational safety and health program should be to protect the most exposed individuals. The HIs based on X95s (*e.g.*, 9.5 for respiratory tract) suggest the need for NIOSH approved respirators with assigned protection factors ≥ 10. However, respirators with much higher assigned protection factors are advisable given the uncertainty associated with this risk assessment. It is conceivable that air purifying respirators could be used if the canisters in them were effective against all possible exposures. However, when investigators recently evaluated the effectiveness of air purifying respirators equipped with chemical, biological, radiological, and nuclear canisters they found that these respirators were effective for most combustion products except CO.[38] Because BZCs of CO could exceed the NIOSH ceiling limit, these respirators should not be used for vehicle fires. Until an air purifying respirator/canister combination is found that provides adequate protection against all combustion products, firefighters should wear SCBA during vehicle fire suppression.

For the cabin fire, the highest VOC concentrations occurred during start-up or knockdown, with relatively low concentrations occurring during overhaul (Table 1). In contrast, for the engine fire, some of the highest VOC concentrations occurred during knockdown and overhaul (Table 1). Opening the hood during knockdown and smoldering after knockdown likely contributed to these higher concentrations. These findings are similar to the findings in the UL study.[4] According to real-time air sampling in the UL study, the highest area air concentrations occurred before knockdown for the cabin fire. However, for the engine fire, some chemicals (*e.g.*, methane, ethylene, and hydrogen chloride) were at their highest area air concentrations during knockdown or overhaul.[4] Because higher concentrations of some chemicals can be released during overhaul of an engine fire than startup or knockdown, firefighters suppressing vehicle fires should only doff SCBA when overhaul is completed. This was the standard procedure at the fire department we evaluated.

The predominant contributors to the HIs were formaldehyde, acrolein, TRIG, CO, and benzene. Even though acrolein was not detected in any of the personal air samples, it was one of the primary contributors to the HIs. The predicted GM BZC for acrolein was 0.094 mg m^{-3}, which was lower than the minimum detectable concentration for acrolein (0.36 mg m^{-3}) in the personal air samples, and thus, may be a reasonable estimate of exposure. Nevertheless, we have greater confidence in the measured BZCs than we do in the predicted BZCs. Considering only the measured BZCs (*i.e.*, formaldehyde, TRIG, CO, benzene, and toluene), we would calculate HIs (based on X95s) for the respiratory tract and eyes of 5.4 and 5.1, which represent unacceptable risk.

Because most vehicle fires take place outdoors, this evaluation is more representative of what firefighters would encounter during vehicle fires than the UL study[4] that took place under a calorimeter hood inside a 3600 ft^2 room. Many of the compounds measured in the UL study were not measured in this evaluation. Measurements of benzene, naphthalene, styrene, formaldehyde, and CO were common to both studies. Of these compounds, only CO was measured in the breathing zone of the firefighters in both studies. Peak BZCs of CO reported in the UL study during overhaul ranged from 13 to 610 mg m^{-3}. The X95 BZC of CO in our study (65 mg m^{-3}) was at the lower end of this range, while the maximum direct-reading of CO (220 mg m^{-3}, data not shown), which is a more appropriate comparison, was toward the middle of this range. However, our highest readings occurred during suppression; whereas the UL study only measured BZCs of CO during overhaul. The area air concentrations of benzene, naphthalene, and formaldehyde measured during the engine fire in the UL study were 2 to 10 times lower than the GM BZCs we measured or predicted in this study. Human movement in concert with the transport of exposures over time may lead to a dissonance between BZCs and area air concentrations. For example, the wind and movement of firefighters around the vehicle fires in this study may have led to higher BZCs than the area air concentrations reported in the UL study.

This mixture analysis provides us with a better understanding of the exposures and health risks from vehicle fire suppression than a hazard analysis that only considers individual compounds. On an individual basis, formaldehyde was the only chemical measured at BZCs that exceeded STELs. Yet, if we remove formaldehyde from the mixture analysis, we still calculate an unacceptable level of risk (*i.e.*, HI of 5.2 based on X95s). In addition, the mixture analysis provides concise quantitative information for making health and safety decisions. For example, our findings suggest that firefighters

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suppressing vehicle fires should be monitored for health effects to the respiratory tract and eyes.

In summary, this assessment attempts to quantify the health risk to firefighters from inhalation exposure to chemical vapors during vehicle fire suppression. Emissions from vehicle fires are probably composed of thousands of different compounds in gaseous and particulate forms. Not all of these compounds were quantified in this evaluation. Nevertheless, the mixture analysis we conducted with limited data suggests that firefighters have the potential to be overexposed to acute toxins during vehicle fire suppression. A more thorough evaluation of firefighters' exposures during vehicle fire suppression that addresses the limitations of this study is warranted.

Conclusion

The intensity of exposures to chemical vapors from vehicle fires will depend on the direction and speed of the wind. Although firefighters in this evaluation attacked the fires from the upwind position and suppressed the fires quickly (<10 min), for the most exposed firefighters, we measured short-term exposures to chemicals affecting the eyes and respiratory tract that were ≥9.2 times the acceptable levels. Many of these chemicals are also known or reasonably anticipated to be carcinogenic to humans and, over time, could lead to higher cancer risks than equivalent doses from chronic exposures. To reduce their risk of adverse health effects, firefighters should don SCBA when they arrive at the vehicle fire scene and doff SCBA only after overhaul is completed.

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References

1 USFA, *Topical Fire Research Series, vol. 2, issue 4: Highway Vehicle Fires*, US Fire Administration (USFA), Emmitsburg, MD, 2002.
2 M. Ahrens, *US Vehicle Fire Trends and Patterns*, Fire Analysis and Research Division, National Fire Protection Association, Quincy, MA, 2004.
3 A. Lonnermark and P. Blomqvist, *Chemosphere*, 2006, **62**, 1043–1056.
4 T. Fabian, J. L. Borgerson, S. I. Kerber, P. D. Gandhi, C. S. Baxter, C. S. Ross, J. E. Lockey, and J. M. Dalton, *Firefighter Exposure to Smoke Particulates, Final Report*, Underwriters Laboratory Inc., Northbrook, IL, 2010.
5 H. Wichmann, W. Lorenz and M. Bahadir, *Chemosphere*, 1995, **31**, 2755–2766.
6 C. C. Austin, D. Wang, D. J. Ecobichon and G. Dussault, *Journal of Toxicology and Environmental Health, Part A*, 2001, **63**, 437–458.
7 D. M. Bolstad-Johnson, J. L. Burgess, C. D. Crutchfield, S. Storment, R. Gerkin and J. R. Wilson, *AIHAJ*, 2000, **61**, 636–641.
8 P. W. Brandt-Rauf, L. F. Fallon, Jr, T. Tarantini, C. Idema and L. Andrews, *Br. J. Ind. Med.*, 1988, **45**, 606–612.
9 A. Gold, W. A. Burgess and E. V. Clougherty, *Am. Ind. Hyg. Assoc. J.*, 1978, **39**, 534–539.
10 J. Jankovic, W. Jones, J. Burkhart and G. Noonan, *Ann. Occup. Hyg.*, 1991, **35**, 581–602.
11 R. D. Treitman, W. A. Burgess and A. Gold, *Am. Ind. Hyg. Assoc. J.*, 1980, **41**, 796–802.
12 C. C. Austin, G. Dussault and D. J. Ecobichon, *Am. J. Ind. Med.*, 2001, **40**, 683–692.
13 Code of Federal Regulations (CFR), *42 CFR 85*, US Government Printing Office, Office of the Federal Register, Washington, DC, 1984.
14 D. E. Evans and K. W. Fent, *Ultrafine and Respirable Particles during Vehicle Fire Suppression*, in preparation.
15 EPA, *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Center for Environmental Research Information*, Office of Research and Development, US Environmental Protection Agency (EPA), Cincinnati, OH, 1999.
16 NIOSH, *NIOSH Manual of Analytical Methods*, ed. P. C. Schlecht and P. F. O'Connor, US Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health (NIOSH), Cincinnati, OH, 4th edn, 2003, suppl. 3.
17 A. Marand, D. Karlsson, M. Dalene and G. Skarping, *J. Environ. Monit.*, 2005, **7**, 335–343.
18 W. H. Bullock and J. S. Ignacio, *A Strategy for Assessing and Managing Occupational Exposures*, Fairfax, VA, 3rd edn, 2006.
19 ACGIH, *Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*, American Conference of Governmental Industrial Hygienists (ACGIH), Cincinnati, OH, 2010.
20 EPA, *Guidelines for the Health Risk Assessment of Chemical Mixtures, Risk Assessment Forum*, US Environmental Protection Agency (EPA), Washington, DC, 1986.
21 EPA, *Supplementary Guidance for Conducting Health Risk Assessment for Chemical Mixtures, Risk Assessment Forum*, US Environmental Protection Agency (EPA), Washington, DC, 2000.
22 NIOSH, in *NIOSH Pocket Guide to Chemical Hazards*, ed. M. E. Barsen, US Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health (NIOSH), Cincinnati, OH, 2005.
23 Sweden Occupational Exposure Values, *Arbetarskyddsstyrelsens forfattningssamling, AFS 2000:3*, Liber, Stockholm, 2000.
24 IPCS, *International Chemical Safety Cards: US National Version*, World Health Organization, International Programme on Chemical Safety (IPCS), http://www.cdc.gov/niosh/ipcs/icstart.html, accessed 2010.
25 NTP, *Report on Carcinogens*, US Department of Health and Human Services, Public Health Service, National Toxicology Program (NTP), Research Triangle Park, NC, 11th edn, 2005.
26 P. G. Le Prestre, J. D. Reid and E. T. Morehouse, *Protecting the Ozone Layer: Lessons, Models, and Prospects*, Kluwer, Boston, 1998.
27 J. Roh, Y. J. Park, C. N. Kim, N. G. Lim, S. H. Lee, J. S. Song, J. U. Won and G. Talaska, *AIHAJ*, 2000, **61**, 405–409.
28 P. D. Thompson, B. A. Franklin, G. J. Balady, S. N. Blair, D. Corrado, N. A. M. Estes, J. E. Fulton, N. F. Gordon, W. L. Haskell, M. S. Link, B. J. Maron, M. A. Mittleman, A. Pelliccia, N. K. Wenger, S. N. Willich and F. Costa, *Circulation*, 2007, **115**, 2358–2368.
29 R. F. Fahy. *US Firefighter Fatalities Due to Sudden Cardiac Death, 1995–2004*, Fire Analysis and Research Division, National Fire Protection Association, Quincy, MA, 2005.
30 S. N. Kales, E. S. Soteriades, C. A. Christophi and D. C. Christiani, *N. Engl. J. Med.*, 2005, **356**, 1207–1215.
31 J. L. Burgess, C. J. Nanson, D. M. Bolstad-Johnson, R. Gerkin, T. A. Hysong, R. C. Lantz, D. L. Sherrill, C. D. Crutchfield, S. F. Quan, A. M. Bernard and M. L. Witten, *J. Occup. Environ. Med.*, 2001, **43**, 467–473.
32 P. W. Brandt-Rauf, B. Cosman, L. F. Fallon, Jr, T. Tarantini and C. Idema, *Br. J. Ind. Med.*, 1989, **46**, 209–211.
33 R. L. Kodell, D. W. Gaylor and J. J. Chen, *Risk Anal.*, 1987, **7**, 339–345.
34 J. J. Chen, R. L. Kodell and D. W. Gaylor, *Risk Anal.*, 1988, **8**, 223–230.
35 D. J. Murdoch, D. Krewski and J. Wargo, *Risk Anal.*, 1992, **12**, 569–577.
36 N. C. Halmes, S. M. Roberts, J. K. Tolson and C. J. Portier, *Toxicol. Sci.*, 2000, **58**, 32–42.
37 G. K. LeMasters, A. M. Genaidy, P. Succop, J. Deddens, T. Sobeih, H. Barriera-Viruet, K. Dunning and J. Lockey, *J. Occup. Environ. Med.*, 2006, **48**, 1189–1202.
38 J. Currie, D. Caseman and T. R. Anthony, *Ann. Occup. Hyg.*, 2009, **53**, 523–538.