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I, Barbara M Alexander , hereby submit this original work as part of the requirements for the degree of Master of Science in Industrial Hygiene (Environmental Health).

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Student's name: **Barbara M Alexander**

This work and its defense approved by:

Committee chair: Carol Rice, PhD

Committee member: Charles Stuart Baxter, PhD

Committee member: Marepalli Rao, PhD

Committee member: Tiina Reponen, PhD



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Contamination of Firefighter Personal Protective Gear

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By

Barbara M. Alexander

B.S., Michigan State University, 1977

M.S., University of Cincinnati, 1981

Ph.D., Carnegie Mellon University, 1984

Committee Chair: Carol Rice, Ph.D., CIH

Abstract

The hazards of firefighting include heat, smoke and the risk of building collapse. However, the most frequent cause of on-duty firefighter deaths is not trauma but cardiac arrest. Firefighters also face a high risk of chronic illnesses, including an elevated risk of several cancers. These adverse effects may result from chemical exposures incurred during firefighting. This research aims to characterize chemical contamination on firefighter personal protective gear as a surrogate for the risk of dermal exposure.

Methods: Chemical contamination on firefighter personal protective gear was characterized by taking wipe samples from the inside of firefighter self-contained breathing apparatus (SCBA) facepieces and by cutting swatches from unused and used firefighter hoods, gloves and one coat. Wipe samples and swatches were extracted with methylene chloride and analyzed by EPA method 8270 for the presence of semivolatile contaminants, including 20 polycyclic aromatic hydrocarbons (PAHs) and 6 phthalates.

Results: This is the first time that wipe samples from firefighter facepieces have been reported. Low levels of di-(2-ethylhexyl) phthalate (DEHP) were consistently measured on the facepieces (range: <LOD to 17 micrograms/facepiece; n=29). Swatches from gloves, hoods and one coat, that were discarded after a period of use, exhibited a wide array of PAH and phthalate contamination. Levels of DEHP contamination (range: 50 to 7280 micrograms/swatch; n= 8) were from 52 to 875 times higher than the level of the highest PAH on each sample. The adverse human health effects of DEHP exposure are poorly understood, but DEHP has been implicated in heart disease, cancer and reproductive disorders. Dermal exposures to firefighters could be reduced by prompt washing following fireground exposure, the use of undergloves, and frequent laundering

of personal protective gear such as gloves, hoods and coats. Further research is needed to better isolate the source of DEHP during different types of fires and different firefighting activities (e.g., knockdown vs. overhaul) in order to reduce exposures.

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I. Significance and Background

Firefighters are exposed to hazardous chemicals when fighting structure and vehicle fires. Assessment of these exposures is complicated by the high temperatures encountered during firefighting as well as the unpredictable nature of fires. The exposure routes for firefighters may include dermal exposures as well as inhalation. Many of the chemicals to which firefighters are exposed are very lipophilic, and may absorb well through the skin, especially when skin temperature is elevated, as in a firefighting situation. In this study, contamination levels of firefighter personal protective gear are measured as a surrogate for risk of dermal and respiratory exposure.

A. Hazards of Firefighting

1. Cardiovascular Effects

The hazards of firefighting include heat, smoke and the risk of building collapse. However, the most frequent cause of on-duty firefighter deaths is not trauma but cardiac arrest. In 2010, the most recent year for which statistics are available, 34 of the 72 on-duty firefighter deaths were classified as sudden cardiac deaths. The number of firefighter deaths reported by the National Fire Protection Association (NFPA) in 2010 was the lowest recorded since record-keeping began in 1977. However, the fraction of these deaths due to cardiac arrest has remained steady for many years.(Fahy et al., 2011)

Although firefighting is a hazardous profession, many of the risk factors for heart disease faced by firefighters are the same factors found in the general population. In a study published in 1996, a cohort of 806 Cincinnati firefighters was studied for an average of 6.4 years. At enrollment, the firefighters underwent urinalysis, blood tests for hematocrit, blood sugar and lipid profile, an electrocardiogram and blood pressure measurements. Lifestyle and inherited factors,

such as cigarette smoking and family history of early-onset coronary heart disease (CHD), were recorded. As a result of these measurements, the firefighters' risk of developing CHD was determined. Those with high risk underwent further testing, and were counseled on lifestyle changes that could lower their risk score.

Seven firefighters suffered myocardial infarction during the course of this study. An additional 15 firefighters developed CHD. Significant risk factors for developing CHD were found to be higher age, cigarette smoking, high blood pressure and a family history of early CHD. CHD rates in firefighters did not differ significantly from those in the general population. Those firefighters who developed CHD did not differ significantly from those who did not develop CHD in their history of suffering smoke inhalation. (Glueck, 1996)

In a 2011 study, it was reported that nearly 1 in 1000 US firefighters are impacted by fatal or nonfatal cardiovascular events each year. The high incidence of cardiovascular problems is attributed to chemical and particulate exposures, exertion, stress and shift work, among other factors. Although active fire suppression is only 1 to 5% of firefighters' on-duty time, the exertion of active fire suppression accounts for 32 to 43% of on-duty cardiovascular events. However, on-duty cardiovascular events and retirements due to heart disease are frequently linked to other known risk factors for cardiovascular disease.

The study, involving male firefighters from 11 fire departments in 3 Midwestern states, found highly significant associations between a firefighter's cardiorespiratory fitness level and age, body mass index (BMI), blood pressure, heart rate, percent body fat, triglycerides, total cholesterol, low density lipoproteins, high density lipoproteins and blood sugar. Less than half of the study participants met or exceeded the cardiorespiratory fitness standards of the National Fire Protection Association (NFPA). Nearly 90% of participants had a BMI that put them in the

category of overweight or obese, while nearly 40% could be classified as obese.(Baur et al., 2011)

Occupational exposures that also increase firefighters' risk of sudden cardiac events are listed in an alert issued by the National Institute for Occupational Safety and Health (NIOSH), published in 2007. These include exposures to smoke, exertion, heat stress, shift work and noise. While over 25 studies had been published before that date, examining whether fire fighting increased risk of heart disease, results were contradictory. (National Institute for Occupational Safety and Health, 2007) Nevertheless, the evidence for the connection between the profession of firefighting and cardiovascular disease is convincing enough that 37 states and 2 Canadian provinces require benefits to be paid to firefighters who develop certain cardiovascular diseases. (Kales et al., 2007)

Odds ratios for death from coronary heart disease, calculated in a study published in 2007, showed that certain firefighter duties led to a higher risk of death. Four hundred and forty-nine on-duty firefighter deaths from coronary heart disease, occurring between 1994 and 2004, were studied. Estimates of the proportion of firefighter time spent on various activities were used in calculating odds ratios. The highest risk of death from a coronary heart event was observed during fire suppression activities. Deaths were 12 to 136 times as likely to occur during fire suppression as during non-emergency duties. Significantly increased risk was also observed during alarm response, alarm return and physical training.(Kales et al., 2007)

2. Elevated Cancer Rates

The NFPA study reports solely on firefighter fatalities related to acute events occurring in connection with fire department duties, both routine and non-routine. However, the NFPA recognizes that counting only these fatalities omits deaths from chronic illnesses that result from

years of fire department service. (Fahy et al., 2011) In the category of chronic illnesses, firefighters are believed to experience an elevated risk of several cancers.

Increasing use of plastic materials in homes and vehicles in recent years has led to concerns over a rise in firefighter exposure to carcinogens. In 1990, Howe and Burch published a meta-analysis of epidemiological studies of firefighters and cancer. They found no excess risk of death from all cancers. They concluded that studies of lung cancer and colon cancer in firefighters showed no consistent evidence of increased risk. The only exception was a study of Buffalo firefighters that showed some increased risk with years of service for colon cancer.

A significantly elevated risk of brain cancer was observed. The authors applied modified Bradford-Hill criteria to judge a probable causal relationship. Known occupational causes of brain cancer are work in the rubber industry and exposure to vinyl chloride monomer. For this reason, it was considered that some evidence exists that firefighter chemical exposures could have contributed to an increased risk of brain cancer, even though an increased risk with years of service was not observed.

There was a weak association with malignant melanoma, but causality was unlikely because of a lack of known chemical exposures that cause melanoma. Multiple myeloma also showed a weak association. Chemical exposures are a known contributor to multiple myeloma, so a causal relationship with firefighter exposures was a possibility.

All of the studies reviewed were limited by the small number of fatalities. The healthy worker effect also contributes, but its effect is generally less for cancer than for other diseases. The effect also decreases with increasing time since the end of employment, and epidemiological studies cover long periods of time. It is considered unlikely that the healthy worker effect obscured any association between service as a firefighter and primary site cancer. Because

these studies relied on death certificates, misclassification of occupation could limit the accuracy of the results, but a more serious limitation is the lack of good exposure data for firefighters.

The authors recommend that studies of the incidence of cancers, rather than mortality studies would be helpful in evaluating rates of cancers of low to moderate lethality. They also advocate studies of specific exposures and practices among firefighters. (Howe & Burch, 1990)

A retrospective cohort mortality study of Philadelphia firefighters was published in 2001. Causes of death were determined for 7,789 Philadelphia firefighters. Excess cancer risks were noted for colon cancer and ischemic heart disease. Firefighters with more than 20 years of service also showed excess risks of kidney cancer, non-Hodgkin's lymphoma and multiple myeloma. (Baris et al., 2001) As this was a mortality study, elevated risks of highly curable cancers, such as testicular cancer, could not be studied. However, a German case-control study published in 2003 found an increased odds ratio for testicular cancer. (Stang et al., 2003)

A meta-analysis of 8 studies in which standardized mortality ratios (SMRs) were calculated for firefighters was performed by Haas in 2003. No increased risk of all-cause mortality, all cancer, coronary artery disease or respiratory disease was found. Consistently high SMRs were found for brain cancer, but only one study showed increased risk with increasing years of service or increasing latency. He found that the studies were limited by their reliance on employment records and death certificates for information. This information was unverified. There were no exposure records and minimal exposure/response data. Also, non-occupational risk factors, such as smoking, were not taken into account.

Several Canadian provincial governments have passed legislation establishing six cancers as occupational diseases of firefighters, given that they have worked a minimum number of years in that career. These are cancer of the brain, kidneys, bladder and colon, non-Hodgkin's lymphoma and leukemia. A Canadian study evaluated the risks of these six cancers and found

risks very similar to those of the general population until duration of employment was taken into account. Accounting for duration of employment, the risks of five of the six cancers were elevated. The elevation in risk for non-Hodgkin's lymphoma was not found to be statistically significant.(Youakim, 2006)

A retrospective cohort study of 36,813 professional firefighters in Florida, published in 2006, found reduced risks in male firefighters for certain cancers, including brain and lung, but elevated risks for bladder, testicular and thyroid cancers. The cancer risk for all cancers was significantly elevated in female firefighters. Specific cancers showing elevated risks in female firefighters included cervical cancer, Hodgkin's disease and thyroid cancer. Breast cancer rates were similar to those in the general population.(Ma et al., 2006)

A registry-based case-control study published in 2007 examined California cancer registry records to assess the increased risk of cancer in male firefighters. Firefighting was listed as the occupation on 3,659 of the 804,000 records. An increased risk was found for testicular, esophageal, brain and prostate cancer, leukemias and melanoma. The risk of thyroid cancer was also possibly elevated. Scant evidence of any increased risk of bladder cancer, non-Hodgkin's lymphoma, multiple myeloma, colorectal or lung cancer was found. Limitations of the study included a lack of information on duration of employment.(Bates, 2007)

LeMasters et al., in a meta-analysis published in 2006, performed a detailed analysis of 32 studies of firefighters and cancer. Most studies used death certificates for determining a diagnosis of cancer. The meta-analysis rated elevated risk of testicular and prostate cancer, non-Hodgkins lymphoma and multiple myeloma in firefighters as "probable". In addition, they report an elevated risk of malignant melanoma and brain cancer as "possible".

The only known exposures causing elevated risk of multiple myeloma are occupational exposures to substances such as paints, herbicides, insecticides, engine exhaust and organic

solvents. Firefighting could possibly result in similar exposures. The risk of non-Hodgkin's lymphoma is difficult to assess because it is reported as several cancer types, having five different possible codes.(LeMasters et al., 2006)

A study published in 2008 used the Massachusetts Cancer Registry to evaluate the risk of cancer in white male firefighters. Firefighting was listed as the occupation on 2,125 of the 258,964 cases studied. Controls were taken from white, male cancer patients listing a career in law enforcement or corrections. A second comparison group was made up of all white, male patients in the registry, listing any occupation other than firefighting, who had a cancer diagnosis of a type of cancer not previously found to be elevated in firefighters. Moderately elevated risks of colon and brain cancer for firefighters were found in this study. Slightly elevated risks of bladder and kidney cancer and Hodgkin's disease were observed. Differences were noted between this study and an earlier study using the same cancer registry. In the earlier study, risks of melanoma, bladder cancer and Hodgkin's disease were observed to be higher. The reasons for these changes are unknown. (Kang et al., 2008)

3. Other Health Effects

Firefighters are subjected to a high risk of other chronic diseases, including respiratory diseases such as chronic obstructive pulmonary disease (COPD), reproductive effects, hearing loss and occupational stress. They may suffer burns or trauma. Exposure to blood-borne pathogens, tuberculosis, anthrax and other communicable diseases may also be a threat.(National Institute for Occupational Safety and Health, 2004)

Finding the cause of sudden cardiac death and elevated rates of cancers in firefighters is complicated by the fact that firefighters are exposed to such a wide array of different hazardous substances in smoke. These include irritants, carcinogens and ultrafine particulate matter. Interactions between chemicals and particulates may contribute to adverse health effects. The

exposures may also vary greatly between different fires, depending on what materials are burning, ventilation and the temperature of the fire.(Underwriters Laboratories Inc, 2010)

The NFPA recognizes current limitations in measurement of firefighter exposure to hazardous substances and in relating chronic illness in firefighters to occupational exposures. NIOSH is currently studying the cancer risk for 18,000 active and retired firefighters, using fire department health records. Findings are projected to be available in 2013.(Fahy et al., 2011)

B. Hazardous Exposures during Firefighting

Actual firefighter exposures have rarely been measured. Years of employment as a firefighter have been used as a surrogate for exposure, but this may not be an accurate measurement. Fire department duties vary widely, from personnel who have no smoke exposure at all to front line firefighters. Misclassification of fire department personnel as being exposed, when they have no exposure, could lead to underestimates of the disease risk caused by actual firefighting exposures.

In a study published in 2001, Austin studied fire response by the Montreal Fire Department for 12 months. Firefighter exposure groups were classified by job title, firehouse assignment and time spent at fires. Only 66% of fire department employees were front-line firefighters. Ten percent of employees had no smoke exposure.

The use of breathing air in the fire department was also tracked and related to time spent at fires. Only a small percentage of a firefighter's duties were spent in actual firefighting. About 20% of emergency calls received by firefighters were actually for fires. Of these fires, 41% were structure fires, 17.2% were vehicle fires and 41.8% were other fires, such as garbage fires. Nearly all the fires were small (one-alarm fires).

There were large differences between different firehouses in the number of fires to which they responded. The busiest firehouses responded to over 3 times as many fires as the least busy firehouses. SCBA gear was not always being worn during smoke exposure, as smoke inhalation accounted for over 10% of fireground injuries. Firefighters used SCBAs for at least 50% of the time at structure fires, but only 6% of the time spent at all fires. This reflects the fact that SCBA was not worn for overhaul activities and probably was not used for small fires. (Austin et al., 2001)

The elevated risk of adverse health effects in firefighters may be due to exposure to toxic substances while fighting fires. Early efforts to characterize firefighter exposures were concentrated on the risk of inhalation of toxic gases such as carbon monoxide. A study of Dallas firefighters published in 1985 used personal sampling to evaluate firefighter exposures during structure fires. Colorimetric tubes specific for carbon monoxide, hydrogen cyanide, formaldehyde and hydrochloric acid were used, as well as charcoal tubes and gas grab samples. Readings were compared to ACGIH threshold limit values (TLVs) for short-term exposure limits (STELs), to IDLH (immediately dangerous to life and health) levels and to a concentration called the short-term lethal concentration (STLC). Carbon monoxide was the chemical most often found in concentrations exceeding the STEL. The other chemicals were often found in measurable quantities.

The authors did not find a pattern of toxic gas concentration depending on the materials burned, but did find differences associated with the intensity of the fire. Benzene was found in fires based on natural as well as synthetic combustibles. The production of benzene when burning both types of fuels was attributed to free radical rearrangements, leading to benzene formation. (Lowry et al., 1985)

A study of Buffalo fire fighters published in 1988 used personal sampling with colorimetric tubes, charcoal tubes and filter cassettes to evaluate fire fighter exposures. Significant concentrations of carbon monoxide, benzene, sulfur dioxide, hydrogen cyanide, formaldehyde, aldehydes, hydrogen chloride, dichlorofluoromethane and particulates were found. In many cases of these exposures, the visual appearance of smoke did not correlate with the exposure. In other words, smoke did not have to appear thick and black to contain high levels of toxic gases. This resulted in personal protective equipment not being worn during some of the worst exposures, due to a perception of low exposure. Some of the chemicals of exposure have been implicated in causing cardiovascular and respiratory disease or cancer. Many factors were noted as determining which chemicals are produced during a specific fire, including the materials being burned, the temperature of the fire and the amount of oxygen present.(Brandt-Rauf et al., 1988)

More recent studies, instead of simply focusing on irritants and asphyxiants, have considered firefighter exposures to other agents, such as polycyclic aromatic hydrocarbons (PAHs), particulates, fibers and even exposures found inside the firehouse, such as exposures to diesel exhaust and to asbestos found in old facilities. (Actual measurement of firefighter exposure is rare, and exposure will depend on job task and use of respiratory protection.) Golden et al., in 1995, published a survey of the literature on firefighter exposures and cancer. They reported that benzene has been frequently measured in the atmosphere at fire scenes.(Golden et al., 1995)

In a study by Jankovic et al., fibers were collected on cellulose ester filters at several fire scenes, and examined by phase contrast microscopy. Types of fires included training fires, residential fires and one vehicle fire. Fiber counts were higher during overhaul than during knockdown.(Jankovic et al., 1991) In a study by Markowitz et al., of New York City firefighters, lung abnormalities associated with asbestos exposure were found in a percentage of firefighters

not otherwise exposed to asbestos. There is concern that firefighters in an urban setting may have significant asbestos exposure.(Markowitz et al., 1991)

Jankovic et al. also measured fourteen PAHs in the air at fire scenes. Higher levels were found during knockdown than during overhaul. Levels during overhaul approximated ambient levels. (Jankovic et al., 1991) Formaldehyde and other aldehydes have been measured at fire scenes by several researchers, especially during knockdown. Measureable levels of formaldehyde have also been reported inside the mask. Significant levels of diesel exhaust particulate have been measured in the air inside firehouses. Other agents of possible concern for firefighter exposures include PCBs, furans, styrene and methylene chloride.(Golden et al., 1995)

In a 2001 study, Summa canisters were used to collect an atmospheric sample inside 9 different burning buildings, at a time when firefighters might be removing their SCBAs. Gas chromatography-mass spectroscopy was used to analyze the samples for the presence of nonpolar volatile organic compounds (VOCs). The mixture of VOCs found in the different fires was quite similar. Benzene, propylene and 1,3-butadiene were found in every fire. Other compounds frequently observed were substituted benzene compounds such as styrene, xylenes and ethylbenzene. The maximum level of benzene measured exceeded the STEL. The researchers did not observe any compounds that would not have been produced by burning solely natural materials. They concluded that exposures from the burning of synthetic materials may not be different from exposures found in fires decades ago.(Austin et al., 2001)

Many researchers have studied firefighter exposures during the knockdown phase, but very few have characterized exposures during overhaul, when firefighters are likely to work without respiratory protection. In 2000, Bolstad-Johnson et al. published the results of a study in which 12 firefighters in Phoenix, Arizona were trained to perform air monitoring. Sampling equipment was staged on the HazMat response truck, so that sampling could be performed during

structure fires. The trained firefighters did not carry out overhaul duties, but rather monitored the firefighters who were doing overhaul. Personal sampling was performed for several toxic chemicals and for respirable dust during the overhaul phase of 25 different structure fires. A gas monitor was used to continuously measure levels of carbon monoxide, hydrogen cyanide, nitrogen dioxide and sulfur dioxide. Area samples were collected for asbestos, metals and total dust.

In several of the fires, exposure limits were exceeded for some of the contaminants of interest. Ceiling values were exceeded for acrolein, CO, formaldehyde and glutaraldehyde. STELs were exceeded for benzene, nitrogen dioxide and sulfur dioxide. Levels of individual PAHs were relatively low, but the sum of PAH exposures exceeded the NIOSH Recommended Exposure Limit (REL) for coal tar pitch volatiles. A correlation coefficient was calculated between the initial 10-minute CO concentration and concentrations of other contaminants, but the CO concentration did not predict the concentrations of other products of combustion. CO should not be used as an indicator gas for other contaminants. One problem noted with the study was that the gas-powered ventilation fans used to clear the structure of smoke were found to generate measurable quantities of CO.

There was a tremendous variation in contaminant concentrations from fire to fire, but certain contaminants, such as formaldehyde, were found at elevated concentrations at a majority of fires. It was noted that adverse health effects may occur from exposure to a mixture of chemicals, even if the individual chemicals do not exceed exposure limits. Also, airborne respirable particulate may be a vehicle to carry other contaminants into the lungs. (Bolstad-Johnson et al., 2000)

A study published in 1973 looked at soot produced by the burning of polyethylene and PVC. The soot was examined by electron microscopy, and found to be agglomerates of spherical

particles of a diameter ranging from 0.03 to 0.11 microns. X-ray diffraction of the soot revealed no crystallinity. The measured properties of the soot compared closely to those of certain carbon blacks. It was observed that the soot was capable of transporting hydrogen chloride, some of which was loosely bound and could be removed by nitrogen purge. In the size range of this soot, 20 to 40% would be expected to be retained in the alveolar sacs. (Stone et al., 1973)

Only recently have firefighter dermal exposures been studied, even though studies of dermal exposure to PAHs in other industries have shown that it may be the most important route of exposure. (Knipp, 2010)

In Finland, firefighter exposure to toxic substances during training exercises was studied. The study focused on trainers because of their high exposure. Different burning materials, protective turnout gear and use of undergloves were studied. Biomonitoring, air sampling and dermal wipes were utilized. Dermal samplers were worn on the chest and back. Hands were rubbed with sunflower oil and wiped off on towels as another measure of dermal contamination. Fifteen PAHs were measured on the towels and dermal samplers. Area sampling was conducted for PAHs, hydrogen cyanide (HCN), other cyanides, formaldehyde and VOCs.

It was demonstrated that burning of natural wood produced far less HCN and benzene than burning of plywood, particle board or polystyrene. Benzene exposures were reduced even further when propane was burned instead of wood. Formaldehyde levels were actually much higher when burning propane, probably due to the mineral oil used to create artificial smoke in the simulator. High formaldehyde levels have also been measured in wildland fires.

Measurements of dermal exposure to PAHs showed that exposures could be reduced greatly by burning propane instead of wood products. Also, the ratio of pyrene to carcinogenic benzo(a)pyrene was much higher in the artificial smoke used during the burning of propane. Wearing of undergloves reduced PAH contamination on trainers' hands by nearly 80%.

Biomonitoring of trainers immediately after training exercises showed a much higher urinary level of muconic acid when exercises used plywood, compared with natural wood or gas. This indicates benzene exposure, most likely during the overhaul phase of firefighting. Excretion of 1-hydroxypyrene, showing PAH exposure, was increased after exercises where plywood and particle board were burned, but not after the burning of natural wood or propane. However, urinary levels of 1-naphthol, a biomarker of naphthalene exposure, were higher after the burning of natural wood, than after the burning of propane. (Laitinen et al., 2010)

Despite the common occurrence of vehicle fires (estimated at 20-25% of fire department fire responses), they also have been seldom studied. Because of the short duration of vehicle fire suppression (usually about 10 minutes), respiratory protection is usually not used. In 2008 and 2009, NIOSH performed a Health Hazard Evaluation (HHE) for firefighter inhalation exposures during vehicle fire suppression training for a small town fire department. The fire department conducts such training 2 to 3 times a year.

Summa canisters were used to collect smoke from one vehicle fire, and this smoke was analyzed for the presence of 75 VOCs. The refrigerant, dichlorofluoromethane, was present in the highest concentration overall, followed by benzene. In all, measurable concentrations of 48 different VOCs were detected.

Personal breathing zone measurements were subsequently collected during fire suppression training involving three different vehicles. The only measurement above a ceiling exposure limit was for formaldehyde. However, exposures to acrolein, isocyanates, CO and benzene were anticipated to pose a possible risk to human health. Several limitations to the study were noted. Significant breakthrough was observed on charcoal tubes due to the high air temperatures sampled. Also, chemicals adsorbed to particulate matter could not be measured by the chosen techniques. (Fent & Evans, 2011)

C. Exposures Known to Cause Cardiovascular and Carcinogenic Effects

1. Polycyclic Aromatic Hydrocarbons

Several PAHs, semivolatile chemicals formed by incomplete combustion, are known carcinogens, acting by forming DNA adducts in the human body. Some studies linking PAH exposure to increased risk of prostate cancer have shown unclear and contradictory results. It is postulated that inconsistent results due to PAH exposure might be explained by a threshold level of exposure being necessary in order to increase prostate cancer risk. Individual genetic variation is likely also a factor. Measurement of PAH-DNA adducts in human cells may be a better means of quantifying PAH exposure than traditional methods of self-reporting. (Rybicki et al., 2008)

Prostate cancer has the highest prevalence of any non-skin cancer in the world and is found across the globe. The risk of contracting prostate cancer increases significantly with age and family history. (Bostwick et al., 2004) Other causes of prostate cancer are poorly understood. Some research has linked an increased risk of prostate cancer to factors including consumption of animal fat, smoking, cadmium exposure, agricultural jobs and motor exhaust. Smoking and motor exhaust are known sources of PAH exposure. Certain studies have found links between occupations with probable exposure to PAHs and prostate cancer. These occupations include employment in the rubber industry, the foundry industry and firefighting. (Seidler et al., 1998)

Prostate tumors have been induced in rats by exposure to benzo(a)pyrene, a PAH. Benzo(a)pyrene is fat-soluble and requires metabolic activation for its carcinogenic activity. Metabolism in human prostate epithelial cells may activate this carcinogenicity. Increased tumor production was observed when the carcinogen was followed by a hormone such as testosterone. (Grover & Martin, 2002)

PAH-DNA adducts in firefighters were studied in a 1989 case-control study. Forty-three active Washington, DC firefighters from busy firehouses were matched with forty non-firefighter controls. They filled out questionnaires on demographic factors, medical history, non-occupational exposures and firefighting activity. Blood samples were obtained for measurement of PAH-DNA adducts and sister chromatid exchange, a measure of DNA damage. After adjusting for consumption of charcoal-broiled food, white firefighters showed a statistically significant increase in PAH-DNA adducts over controls.(Liou et al., 1989)

In a case-control study published in 1998, patients who had undergone prostate biopsies were studied. Those whose biopsies showed prostate cancer were compared to those whose biopsies were negative. Cases and controls filled out surveys concerning their occupations and probable exposures to heavy metals, cutting oils, paints and pigments, asbestos, fuels and exhaust, pesticides, PAHs, polychlorinated biphenyls (PCBs), soot, tar, mineral oil and solvents. Dose-years of exposure were estimated based on theoretical levels of exposure. The statistical analysis was adjusted for age, smoking status and home region. The association between dose-years of exposure to diesel fuel or exhaust, and prostate cancer, was the only exposure found to be statistically significant. PAHs are the primary carcinogenic constituents of diesel exhaust. Their influence on prostate cancer may be attributed to induction of certain enzymes in the prostate. Hormonal effects of PAHs may also play a role. (Seidler et al., 1998)

Some studies have also linked occupational PAH exposure to the development of bladder cancer.(Geller et al., 2008) A sweeping study of occupation and cancer incidence in five Nordic countries found an increased incidence of bladder cancer in chimney sweeps, who have high PAH exposures. This same study showed no significant link between occupation and prostate cancer. It should be noted that firefighters in this study were included in a larger category

including all public safety workers.(Pukkala et al., 2009) PAH exposure has also been linked to increased risk of brain cancer and kidney cancer.(Golden et al., 1995)

PAH exposure was studied as part of a survey of dust exposures in relation to heart disease, published in 1997. This survey was prompted by observations of increased deaths from heart disease during severe urban pollution episodes. Occupations with significant PAH exposures included chimney sweeps, auto mechanics and aluminum potroom workers. Chimney sweeps were found, in both a Danish and a Swedish study, to have an increased risk of death from ischemic heart disease (IHD). Similarly, a Norwegian and a Canadian study found an increased risk of IHD in potroom workers. A cohort of Danish auto mechanics was also found to have an elevated risk of IHD. The mechanism is hypothesized to be inflammation caused by long-term inhalation of fine particulate matter, leading to IHD. (Sjogren, 1997)

Heart-rate variability was related to a biomarker of PAH exposure in a study published in 2011. 1-hydroxypyrene (1-HP) was measured in the urine of a cohort of boilermakers both pre- and post-shift during boiler repair work. Electrocardiograms of the workers showed decreased heart variability with post-shift increases in 1-HP, indicating an imbalance in cardiac autonomic control.(Lee et al., 2011)

2. Di-(2-ethylhexyl) Phthalate

Di-(2-ethylhexyl) phthalate (DEHP) is a diester of phthalic acid. It is one of a group of chemicals called phthalates. DEHP is used commercially as a plasticizer, added to polyvinyl chloride (PVC) to impart flexibility, and can constitute up to 40% of the weight of the PVC. It is not tightly bound to the polymer, and is readily leached. In Western countries, annual DEHP production is estimated as 1 – 4 million pounds. (Pflieger-Bruss et al., 2004)

DEHP is a nearly-colorless and –odorless, oily liquid, with a melting point of -55°C and a boiling point of 384°C. It is only slightly soluble in water, but is soluble in blood and in fluids containing

lipoproteins. DEHP is classified as Group B2, a probable human carcinogen, by the US Environmental Protection Agency (EPA), due to its carcinogenic effects in laboratory animals. The American Conference of Governmental Industrial Hygienists (ACGIH) classifies DEHP as Group A3, a confirmed animal carcinogen with unknown relevance to humans. The National Toxicology Program of the US Department of Health and Human Services classifies DEHP as “reasonably anticipated to be a human carcinogen”. (National Library of Medicine Hazardous Substances Data Bank, 2010) The International Agency for Research on Cancer (IARC) classifies DEHP as Group 3, “not classifiable as to its carcinogenicity to humans”, because the peroxisome proliferation seen in rodent liver cells is not documented in human liver cells. (International Agency for Research on Cancer, 2010)

DEHP is found in products such as vinyl flooring, wire and cable coatings, toys, wall coverings, shower curtains and medical IV bags and tubing. Because of the wide distribution of products containing DEHP, exposure to the chemical is common both in an occupational setting and in the general public. (International Agency for Research on Cancer, 2010) The major route of exposure in the general public is considered to be ingestion. DEHP contamination is found in many different types of food, often arising from materials used in processing and packaging. (Wittassek et al., 2011)

Inhalation and dermal absorption may be more significant routes of exposure occupationally, but they have been only rarely studied. Due to the low vapor pressure of DEHP, inhalation exposures are primarily in aerosol form. (International Agency for Research on Cancer, 2000) Dirven et al. documented a significant pre-shift to post-shift increase in the concentration of four metabolites of DEHP in the urine of workers in a PVC boot factory. However, six workers at a PVC cable factory showed no significant increase in urinary metabolite concentrations, even though both populations of workers were exposed to a maximum of 1.2 mg/m^3 of airborne

DEHP. Boot factory workers worked with DEHP on a more regular basis than the cable workers, leading investigators to conclude that continuous exposure might create higher levels of DEHP or its metabolites in a body compartment such as fatty tissue.(Dirven et al., 1993)

In 1988, Elsisi et al. performed a dermal absorption study of phthalate esters. They recognized factors with known effects on dermal absorption, including dose, location and surface area of the exposure, and skin temperature and damage. Radiolabeled phthalates were applied to the skin of shaved rats. The rats were restrained, and the area of application was covered with a circular plastic cap, so grooming by the animal was not a factor. Urine and feces were collected and radioactivity measured to determine absorption. The rate of DEHP excretion was very slow, showing slow dermal absorption. After 7 days, 86% of the original dose was found, unabsorbed, at the site of application. Forty percent of the excreted DEHP activity was found in the feces and sixty percent in the urine.(Elsisi et al., 1989)

Scott et al. studied dermal absorption of phthalates through samples of human and rat skin in vitro. The epidermis only was used. Researchers applied pure, radio-labeled phthalates to samples mounted in diffusion cells, and measured the radioactivity passing through into a 50% aqueous solution of ethanol at 30°C. As the chain length and lipophilicity of the ester increased, decreased permeation was observed. This is contrary to the expected increase in absorption with increased lipophilicity. Other chemical properties may cause the decreased absorption. Measured DEHP absorption rates were low in both rat and human skin samples.(Scott et al., 1987)

The adverse health effects of DEHP exposure in rodents are attributed to the metabolites of DEHP. DEHP is rapidly hydrolyzed in the lung and intestines after uptake. Hydrolysis products are mono-(2-ethylhexyl) phthalate (MEHP) and 2-ethyl hexanol, but these products are also further metabolized to more polar species. The lipase that hydrolyzes DEHP to MEHP is found

in many tissues in the rat, but primarily in the pancreas. This enzyme does not hydrolyze MEHP to phthalic acid. The only enzyme that will further hydrolyze MEHP is found in the rodent liver.

Twenty separate metabolites produced from the original metabolite, MEHP, have been identified in the urine of rats. The aromatic ring is not metabolized in mammals, but the ethylhexyl side chain of MEHP is acted upon by monooxygenases in the second stage of DEHP metabolism.(Albro, 1986) MEHP is absorbed to a greater extent in the human body than DEHP. DEHP and MEHP can potentially interact with 183 genes and proteins in the body. When the toxicities of these genes and proteins were analyzed, the top three categories for toxic effects were heart, liver and kidney toxicity. A simulation identified the most likely diseases to result from DEHP exposure as cardiovascular, liver, urologic, endocrine and genital diseases. (Singh & Li, 2011)

Phthalates as a class are known to be endocrine-disrupting compounds (EDCs). EDCs interfere with normal production of human hormones, especially those involving reproduction. In men, EDC exposure may lead to infertility or increased risk of prostate or testicular cancer. Exposure assessment has been problematic, but there is growing evidence for EDC exposure as a cause of poor semen quality, sperm abnormalities or changes in hormone levels.(Meeker et al., 2009)

A study published in 2004 reports that rates of male infertility and testicular cancer are rapidly rising. Lab experiments on animals have shown that substances with estrogenic effects may cause poor sperm density and increased testicular tumors. Data for humans are lacking. No estrogenicity has to date been demonstrated for DEHP. However, its adverse reproductive effects in laboratory animals are well-documented. Its first metabolite, MEHP, appears to be responsible for the toxic effects of DEHP.(Pflieger-Bruss et al., 2004)

Experiments in vitro have demonstrated kidney toxicity from DEHP exposure. Studies at doses similar to those found in the general public have been shown to cause subtle reproductive

effects in male rodents.(Singh & Li, 2011) Reproductive effects observed include testicular dysgenesis, Leydig cell dysfunction, cryptorchidism, and hypospadias. (International Agency for Research on Cancer, 2010)

Recent animal experiments have shown toxic effects of DEHP in the pancreas and the testicles. Pancreatic acinar cell adenomas were observed in male rats only, not in females, following DEHP exposure. Male rats exposed to DEHP also exhibited testicular atrophy and aspermatogenesis at some doses. Chronic exposure to a 300 mg/kg dose of DEHP caused liver tumors, but testicular tumors developed earlier in life, and increased in number with time. Although peroxisome proliferator-activated receptor (PPAR) agonists, like DEHP, are believed to induce testicular tumors by inhibiting testosterone synthesis or increasing estradiol levels, DEHP was shown to induce high levels of gonadotropin-luteinizing hormone, estradiol and testosterone.(International Agency for Research on Cancer, 2010) Elevated concentrations of testosterone may increase the risk of prostate cancer, but findings have been inconsistent.(Bostwick et al., 2004)

Little is known about the cardiac toxicity of DEHP, even though this toxicity has been studied for almost 40 years. A 1973 experiment showed that chick cardiomyocytes stopped beating after DEHP exposure. Another early study showed decreased heart rate, cardiac flow and pressure in isolated, perfused rat hearts after DEHP exposure. Twenty years ago, an arrhythmogenic effect of DEHP or its metabolites was proposed, but little follow-up work was performed. Recent experiments in vitro, using neonatal rat cardiomyocytes have shown that DEHP exposure adversely affects electrical conduction and mechanical movement of cardiomyocytes. (Gillum et al., 2009)

MEHP has been shown to induce peroxisome proliferation, which has a role in metabolic disorders such as atherosclerosis, hyperlipidemia and obesity. These conditions also contribute

to heart disease. Peroxisome proliferation in the rodent liver is thought to be primarily responsible for the liver cancer seen with DEHP exposure. Peroxisome proliferation in the human liver is less likely, because peroxisome proliferator-activated receptor alpha (PPARA) is not expressed to the extent that it is in the rodent liver. (Singh & Li, 2011)

However, the most current evidence proposes several different mechanisms of DEHP carcinogenesis, including increased cell proliferation, reduced apoptosis and DNA damage, which may be more relevant to human pathways. The PPARA-mediated mechanism has also been called into question. Experiments in which wild-type and PPARA-deficient mice were exposed to DEHP showed a lower incidence of liver tumors in the wild-type mice. Relevance to carcinogenesis in humans is unclear. (Ward et al., 2010)

D. Contribution of Firefighter Practices to Exposures

1. Use of Personal Protective Equipment

a. Description of Personal Protective Equipment

Typical “bunker gear” worn by a firefighter might include a short-sleeved cotton T-shirt and pants. When called out to a fire, a firefighter will don “turnout gear” consisting of a coat and pants. The coat and pants are constructed from multiple layers of fire-resistant fabric, such as Nomex[®], to confer insulation and water-resistance. Rubber boots with a steel shank and steel toe box are also worn. Firefighting gloves are made of multiple layers of material, as well, to be resistant to cuts and water, as well as providing insulation. Helmets are worn for protection from falling objects. A typical firefighting helmet will be made of leather or fiberglass, with an attached face shield. A Nomex[®] hood covers all exposed areas of the head and neck not covered by the self-contained breathing apparatus (SCBA) facepiece.

SCBA consists of a bottle of compressed breathing air, a backpack assembly and a facepiece.(City of Davis California Fire Department, 2012) The bottle is typically made of aluminum or fiberglass. The SCBA facepiece is constructed of hard rubber and polycarbonate. The SCBA, minus the facepiece, is referred to as the “air mask”. The SCBA typically provides 30-45 minutes of breathing air when in use, depending on the individual using it.

b. Use of Personal Protective Equipment

SCBA is commonly worn during the knockdown phase of firefighting, when water hoses are used to bring flames under control. This protects the firefighter from inhaling toxic chemicals and particulate matter. However, SCBA is often not utilized during the overhaul phase of firefighting, when smoldering materials are broken up, turned over and spread out. Exposure to toxic chemicals and fine particulate matter can still occur during this phase. SCBA is also seldom worn during response to short-duration events such as car fires.(Austin et al., 2001)

2. Firefighter Procedures

In a study performed by Stull et al. in 1996, it was noted that exposures to hazardous chemicals do not necessarily end when the firefighter leaves the fireground. Firefighter protective clothing can become contaminated with a wide variety of toxic compounds during use. Soiled protective clothing may be viewed, among firefighters, as a “badge of honor”, but it can be a source of continuing exposure to toxic and carcinogenic substances. Soiled turnout gear also offers a lesser amount of thermal protection, is more electrically conductive and could potentially ignite, also increasing risk for the wearer.

Chemicals may soak into the fabric of protective gear or may be carried on porous particles of soot. These materials may end up on the firefighter’s skin or may later be inhaled. Cleaning practices varied widely between fire departments surveyed by Stull et al. They ranged from no cleaning to hand or machine washing to professional cleaning. Most frequently, cleaning was

performed “as needed”, using a residential-style washing machine. Severely contaminated gear might be professionally cleaned or discarded.

Samples were cut out of three heavily-used turnout coats, extracted with methylene chloride and analyzed for contamination by semivolatile contaminants, using EPA method 8270. Contamination by metals was assessed using atomic absorption. Several PAHs and phthalates were found on the samples tested. Fabric spiked with contaminants of interest was cleaned by several techniques. Most techniques had limited effectiveness in removing semivolatile contaminants such as PAHs. However, simple aeration at a slightly elevated temperature was shown to be more effective, in many cases, than most of the conventional techniques, with the exception of dry cleaning.(Stull et al., 1996)

A recently-published study by Underwriters Laboratories (UL) found that gloves and protective hoods worn by firefighters at residential fires become contaminated with a wide range of organic and inorganic compounds, some of which are known to be carcinogens. Some of the organic chemicals found in the largest quantities on firefighter gloves and hoods were PAHs and phthalates, especially DEHP. (Underwriters Laboratories Inc, 2010) The PAHs, benz[a]anthracene and benzo[a]pyrene, also found on firefighters’ gloves and hoods in the UL study, are classified as probable human carcinogens by the US EPA.(US Environmental Protection Agency, 2011)

Contamination may accumulate on the inside of SCBA facepieces due to poor fit during use or due to cleaning and handling practices. Poor fit may be caused by inadequate tightening of straps, incomplete seating of the facepiece or seal damage. Facepieces might be loosely attached to the outside of protective clothing when not being used, as during overhaul, allowing contamination to accumulate. Failure to clean the facepiece after each use, as recommended by the manufacturer, may contribute to the presence of contamination on the facepiece.

Contamination may also occur during storage, by resuspension of fine particulate on coats, gloves and pants stored next to the facepiece. A 1985 study of beryllium dust contamination on workers' protective clothing showed that dust could resuspend, potentially leading to worker exposures.(Bohne & Cohen, 1985)

II. Objectives

A. Characterize Contamination of Firefighter Personal Protective Gear

The objective of this thesis research is to characterize some of the firefighter exposures that could contribute to their high risk of sudden cardiac death and to the elevated rates of certain cancers. DEHP and PAHs are specifically of interest, due to their classification by the EPA as probable human carcinogens, and to the known cardiac effects of DEHP. Some possible routes of exposure that have not been investigated fully include dermal exposures as well as possible inhalation of contamination re-aerosolized from the inside of SCBA facepieces.

The purpose of this investigation is to characterize the extent of contamination of firefighters' protective clothing and equipment as a way of approximating skin contamination. Wipe samples were taken inside firefighters' SCBA facepieces. Contamination on the inside of the mask may occur due to poor fit of the facepiece or to contamination that occurred while the SCBA was not being worn. This contamination may be re-aerosolized during the high-heat conditions of firefighting, allowing it to be inhaled or deposited on the skin.

Contamination was also extracted from used firefighter protective clothing for analysis. Clothing items such as gloves are constructed of several layers. Contamination in each layer of the glove was assessed separately to evaluate whether contamination penetrated the clothing layers next to firefighters' skin.

B. Assess Relevance of Firefighter Procedures to Exposure

Firefighters wear SCBA units during the knockdown phase of structural firefighting, but only rarely during the overhaul phase of structural firefighting or during short-duration events such as vehicle fires. This presents the risk of inhalation exposures when SCBA is not being used.

During training exercises, firefighters were observed doffing their SCBA using their bare hands. This is presumably done because the small buckles on the helmet chinstrap and on the SCBA facepiece are extremely difficult to undo while wearing a bulky firefighting glove. The result of this practice is the transfer of soot, ash and other chemicals released during the fire, from the firefighter's personal protective gear to the firefighter's hands. Chemicals may then be absorbed through the skin and/or transferred to other areas of the body, increasing exposures.

Personal protective gear is seldom cleaned. Rewearing contaminated gear may also contribute to firefighter exposures to hazardous chemicals. Particulate contamination may be released from contaminated gear, and spread contamination within vehicles and living areas at the firehouse and even in the home. Volunteer firefighters, may store their protective clothing in their personal vehicles and launder it at home, potentially increasing exposure of their families.(Stull et al., 1996)

C. Hypothesis

The study hypothesis was that the quantity of PAH and DEHP contamination found on used firefighter gear would be significantly higher ($p < 0.05$) than that found on unused gear.

To test this hypothesis, the following specific aims were accomplished.

1. Specific Aims

- a. Aim 1: Survey fire department personal protective equipment use and maintenance procedures.
- b. Aim 2: Characterize contamination on inside surfaces of firefighter SCBA facepieces.
- c. Aim 3: Characterize contamination on samples of used firefighter protective clothing.

In addition, contamination was extracted from samples of used firefighter clothing for later use in toxicological experiments.

III. Materials and Methods

A. Investigation of Fire Department Policies and Procedures

Fire department standard operating procedures were investigated to determine current practice in the wearing, donning, doffing and cleaning of protective clothing and equipment. A survey instrument was developed (See Appendix A.) to systematically evaluate written programs and observed implementation of the work practices in the program.

B. Wipe Sampling of SCBA Facepieces

1. Sample Collection

SCBA facepieces in current use at an area fire department were wiped so that contamination on the internal surfaces of the facepiece could be characterized. Detailed specifications of the sampling materials used are listed in Table 1.

To wipe the interior of a facepiece, a piece of gauze was dampened with tap water by dipping the lower quarter of the gauze into a jar of tap water. The gauze was folded over and pressed together to distribute the water throughout the gauze. All inner surfaces of a facepiece were wiped including flanges making contact with the face during use. The surfaces wiped, in order, were:

- Inside surface of nose cup, including inhalation and exhalation valve area, speaking diaphragm and underside of the nose cup flange
- Flange of nose cup, which rests against the face during use
- Clear lens of facepiece
- Underside of facepiece flange
- Exterior of nose cup
- Flange of facepiece, which rests against the face during use

Table 1. Sampling Materials used for Facepiece Wipes

Material	Manufacturer	Description
Nitrile powder-free exam gloves	Kimberly-Clark (Irving, TX)	Purple Nitrile, powder-free exam gloves, Size M, Model 55082, acrylonitrile butadiene, powder-free, latex-free, ambidextrous, 3.5 – 5.9 mil thickness
Gauze pads	Dental Health Products, Inc. (New Franken, WI)	Health-Tec all gauze sponges, #250-1925, 4" x 4", 12 ply, non-sterile, USP Type VII gauze
Jars, glass, 2 oz.	Quality Environmental Containers (QEC) (Beaver, WV)	2 oz. clear jar, #2114-0002. lot #O-1-129-01DB, specially cleaned using USEPA procedures to limit concentrations of many organic compounds, pesticides/PCBs and elements, including bis(2-ethylhexyl) phthalate (CRQL 5.0 µg/L)
Jars, glass, 4 oz.	Quality Environmental Containers (QEC) (Beaver, WV)	4 oz. clear jar, #2114-0004. lot #G-1-284-05DB, specially cleaned using USEPA procedures to limit concentrations of many organic compounds, pesticides/PCBs and elements, including bis(2-ethylhexyl) phthalate (CRQL 5.0 µg/L)

Facepieces used by the fire department are shown in Figure 1. Data noted for each wipe were the date and location of collection, and an identifier for each facepiece.

A media blank, consisting of a sample of dampened gauze, was collected at each location where facepieces were wiped. Several special wipe samples were also obtained. A new, unused SCBA facepiece, a facepiece cleaned according to the manufacturer's specifications,



Figure 1. Fire Department SCBA Facepieces, FireHawk[®] MMR 4500 Ultra Elite[®]

and the exterior of an uncleaned facepiece, were wiped for comparison. After a facepiece was wiped, the wipe material was inserted into a glass jar and stored in a department freezer at a temperature of -20°C until it could be transferred to the analytical laboratory to be analyzed for the presence of PAHs and phthalates. An example of a wipe sample in a sample collection jar is shown in Figure 2.



Figure 2. Facepiece Wipe Sample Collected 1/31/2012

2. Analytical Methods

Gauze wipe samples were analyzed at ALS Datachem for the presence of 26 semi-volatile organic compounds - polynuclear aromatic hydrocarbons (PNAs, also known as PAHs) and phthalates - according to EPA method 8270. Wipe samples were extracted using methylene chloride for analysis. The list of compounds for which analysis was performed is given in Appendix B. Appendix B refers to DEHP as bis(2-ethylhexyl) phthalate, the name used in the analytical reports.

C. Extracting Samples of Used Firefighter Protective Clothing

1. Sample Collection

Unused and used firefighter clothing, including gloves, coats and protective hoods, has been donated to the University of Cincinnati by several fire departments. Detailed descriptions of the gear sampled are given in Table 2. Cloth samples were cut from the protective gear as described below.

Table 2. Firefighter Gear Sampled

Gear	Manufacturer	Description and Material
Protective Hoods (n = 3)	American Firewear (Dayton, OH)	Style HD 300 22887FNF, material - Nomex [®]
Coat (n = 1)	Honeywell First Responder (Dayton, OH)	Morning Pride, Nomex [®] wristlets
Structural Gloves (n = 2)	American Firewear (Ohatchee, AL)	Model 6500, outer layer – kangaroo leather, middle layer - Pyroprotect [®] , inner layer - Kevlar [®] /Nomex [®] , cuff - Nomex [®]

Samples from different types of personal protective clothing were obtained as follows. Hoods are composed of a double layer of one type of material. A 4" by 4" hood sample was removed from the area of the chin, keeping both layers of fabric together. Unused and used hoods are shown in Figures 3 and 4, showing the area of sample removal. Samples were cut in half, from the chest edge to the chin edge.



Figure 3. Unused Firefighter Hood, American Firewear Style HD 300 22887FNF, showing square area of sample removal.

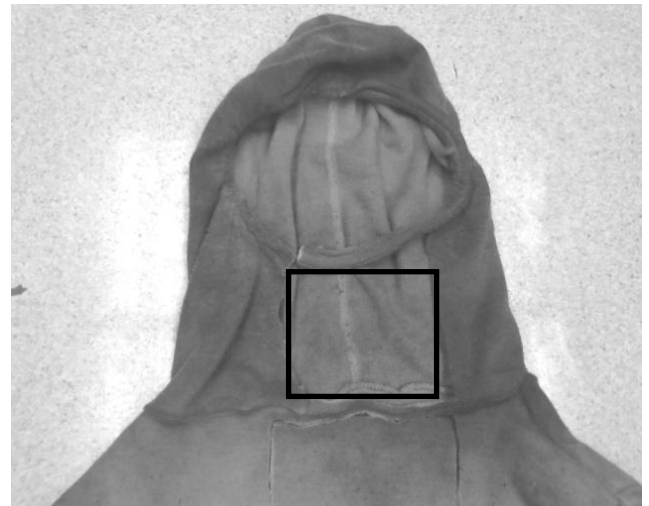


Figure 4. Used Firefighter Hood 1, showing square area of sample removal.

The coat is fitted with double wristlets at the end of each sleeve. The entire right inner wristlet, which included a thumb loop, was removed from the coat. The firefighter coat sampled is shown in Figure 5.



Figure 5. Firefighter Coat 1, showing right inner wristlet removed

The gloves are made up of three layers of different fabrics. A sample approximately 4" by 4" in size was cut from the palm of the glove. Unused and used gloves are shown in Figures 6 and 7.



Figure 6. Unused firefighter glove, showing area sampled.



Figure 7. Used Firefighter Glove 1, showing 3 layers sampled. The inner layer remains in the glove.

Samples from the gloves, and the coat wristlet, were cut in half, from the finger edge to the wrist edge, and the halves placed in separate glass jars. One half was sent to the analytical lab and one half was reserved for extraction with solvent.

The middle layer of the glove was actually larger in dimensions than the inner and outer layers when flattened, because an oversized amount of this non-stretchable moisture barrier material was incorporated into the glove. The layers were separated for later extraction or analysis.

Equipment and supplies used are listed in Table 3.

2. Sample Preparation

The sample halves were weighed on an analytical scale. (See Table 3.) One piece was to be analyzed at an analytical lab for contaminants and one piece was to be extracted with solvent for later application to cell cultures. The halves were placed in separate glass jars and stored in a freezer at -10°C until sent out for analysis or extracted. The half of the wristlet that included the thumb loop was sent out for analysis.

The clothing samples to be extracted were placed into a round-bottom flask containing 40 ml of hexane, to extract the contamination from the gear sample. The vial was shaken gently for 30 minutes in a wrist-action shaker, and left to soak for at least 12 hours. The solvent was withdrawn and evaporated to near dryness in a Buchler Evaporator. The extracts were then stored in a glass developing vial. Two milliliters of petroleum ether were used to rinse the round-bottom flask, and the resulting extract was again evaporated to reduce volume. The vials were saved for future use with cell cultures.

Table 3. Equipment and Supplies used for Samples of Firefighter Gear

Equipment/Supplies	Manufacturer	Description
Nitrile powder-free exam gloves	Kimberly-Clark (Irving, TX)	Purple Nitrile, powder-free exam gloves, Size M, Model 55082, acrylonitrile butadiene, powder-free, latex-free, ambidextrous, 3.5 – 5.9 mil thickness
Jars, glass, 4 oz.	Quality Environmental Containers (QEC) (Beaver, WV)	4 oz. clear jar, #2114-0004. lot #G-1-284-05DB, specially cleaned using USEPA procedures to limit concentrations of many organic compounds, pesticides/PCBs and elements, including bis(2-ethylhexyl) phthalate (CRQL 5.0 µg/L)
Electronic Balance	Ohaus Corp. (Pinewood, NJ)	Scout Pro 200g (±0.1 g)
Hexane	Fisher Scientific, Inc. (Fair Lawn, NJ)	Fisher H303-4, hexane Optima grade, lot #880979
Petroleum Ether	Fisher Scientific, Inc. (Fair Lawn, NJ)	Fisher P-480, petroleum ether, pesticide grade, lot #723113
Wrist-Action Shaker	Burrell Scientific (Pittsburgh, PA)	Model 75 Wrist Action Shaker (Setting 1.5)
Buchler Evaporator	Buchler Instruments (Ft. Lee, NJ)	Buchler Flash Evaporator
Water Bath	Buchler Instruments (Ft. Lee, NJ)	Buchler Thermo-Lift
Developing vial	SKC (Eighty-Four, PA)	3.7 ml developing vial, SKC model #226-02A, with Teflon-lined septum cap

3. Analytical Methods

The other half of selected clothing samples was transferred to ALS Datachem to be analyzed for the presence of 26 semi-volatile organic compounds (PAHs and phthalates), according to EPA method 8270. Samples were extracted using methylene chloride for analysis. (See Appendix B for the list of analytes.)

D. Statistical Analysis Methods

A statistical power calculation was performed prior to the start of this study, using a value for DEHP contamination on an unused facepiece of 0.01 mg, and a value for the contamination on a used facepiece of 0.05 mg. Using a value of 0.0125 for the standard deviation of the mean contamination of a used facepiece, and a sample size of 5 per group, yielded a statistical power of 0.98. A total of 29 wipe samples were subsequently collected from facepieces in current use, at three different locations.

An analysis of variance (ANOVA) was performed on the natural log of DEHP levels of wipe samples from the three different locations, to test whether the samples obtained from the three different locations were significantly different from one another. The residuals of the log DEHP levels were calculated, and the normality assumption was tested.

A histogram was created for the 29 wipe samples. Boxplots of the wipe samples were constructed for the three different locations and for three levels of visual “griminess” observed. All statistical calculations and plots were performed using SAS version 9.2. A P-value of less than 0.05 was used to determine statistical significance.

IV. Results

A. Fire Department Policies and Procedures

Fire department policy calls for the SCBA facepiece to be cleaned after each use. A proprietary detergent solution supplied by the SCBA manufacturer is provided in spray bottles at the fire houses, along with soft disposable cloths, for this purpose. Minor facepiece repairs are handled at the 5th & Central firehouse. Only rarely does a facepiece need to be discarded and replaced due to damage.

A firefighter's SCBA air bottle, harness and regulator is positioned on his or her seat on the fire truck when the firefighter is on duty, so that the harness can be donned while traveling to the fire. Facepieces are the property of the individual firefighter. Storage conditions may vary from one firehouse to another. All facepieces in the fire department were replaced in January/February, 2012, after about 6 years of use. The new facepieces have a heads-up display (HUD) that shows more information than the old models. The firefighter, as well as those around him, will be able to see the amount of breathing air remaining in the SCBA bottle. Under some conditions, facepieces may be used up to 15 years.

Firefighter protective clothing is laundered on an "as-needed" basis at the Central Supply facility. At the same facility, minor repairs are made. If heavily contaminated or significantly damaged, protective clothing is discarded and replaced. Department policy is to inspect turnout coats and pants twice per year, and to clean them at least once a year.

Firefighters are offered a free annual physical, but it is only mandatory for the hazardous materials response team. Results of the physical are not reported to the fire department.

B. Facepiece Wipes

A total of 35 facepiece wipe samples were obtained, including 3 blanks and 3 special wipe samples. The wipe samples were obtained at the following locations on the given dates:

- Firehouse at W. 5th St. & Central Ave., primarily from the Heavy Rescue Unit, on November 7th, 2011
- Price Hill Firehouse on December 13th and 15th, 2011
- Fire Department Warehouse on Spring Lawn Ave., where discarded facepieces were stored, on January 31st, 2012.

Of the 26 semivolatile chemicals for which the analysis was run, only one chemical was detected on the facepieces, DEHP. DEHP is referred to as bis(2-ethylhexyl) phthalate in the laboratory reports in the appendices. Results of analysis of the wipe samples for facepieces in current use, by EPA Method 8270, are shown in Table 4. A sticky microscope slide was used to lift a sample of the contamination from the inside of a used facepiece. A mixture of irregularly-shaped particles and fibers was observed. (See Figure 8.)



Figure 8. Photograph of contamination from a used firefighter SCBA facepiece, at 400X magnification

Table 4. SCBA Facepiece interior wipe results for DEHP by EPA Method 8270, showing date, location and field notes.

Sample	Date	Location	DEHP weight (µg/facepiece)	LOD* (µg)	Notes
1	11/7/2011	5th & Central	14	1	Entered a fire on 11/4/11
2	11/7/2011	5th & Central	6.9	1	
3	11/7/2011	5th & Central	8.1	1	
4	11/7/2011	5th & Central	17	1	
5	11/7/2011	5th & Central	5.1	1	
6	11/7/2011	5th & Central	5.7	1	
7	11/7/2011	5th & Central	5.5	1	
8	11/7/2011	5th & Central	9.7	1	
9	11/7/2011	5th & Central	7.5	1	
10	11/7/2011	5th & Central	14	1	
11	12/15/2011	Price Hill	5	1	Exceptionally grimy
12	12/13/2011	Price Hill	4.1	1	
13	12/15/2011	Price Hill	2.7	1	Responded to a fire 12/14/11
14	12/13/2011	Price Hill	1.7	1	Entered a fire 12/12/11
15	12/13/2011	Price Hill	1.5	1	
16	12/15/2011	Price Hill	2.9	1	Grimy
17	12/15/2011	Price Hill	1.3	1	
18	12/15/2011	Price Hill	ND	1	
19	12/15/2011	Price Hill	3.4	1	
20	1/31/2012	Warehouse	ND	1	Barely visible dirt
21	1/31/2012	Warehouse	1.5	1	Very grimy
22	1/31/2012	Warehouse	3.3	1	Barely visible dirt
23	1/31/2012	Warehouse	3.7	1	Very grimy
24**	1/31/2012	Warehouse	3	1	Moderate grime
25	1/31/2012	Warehouse	ND	1	Barely visible dirt, newer looking mask, webbing is clean
26	1/31/2012	Warehouse	ND	1	Moderate grime
27	1/31/2012	Warehouse	3.3	1	Moderate grime
28	1/31/2012	Warehouse	2.5	1	Very grimy
29	1/31/2012	Warehouse	2.5	1	Very grimy

*LOD = Limit of Detection

**Re-wipe of Sample 10.

ND = below the limit of detection.

Results of analysis of special wipe samples of facepieces, and of blanks, by EPA Method 8270, are shown in Table 5.

Table 5. Special Wipe Samples and Blanks, Analyzed for Semivolatile Contaminants by EPA Method 8270.

Sample	Date	Location	DEHP weight (µg/facepiece)	LOD (µg)	Notes
2-clean	11/7/2011	5th & Central	ND	1	Just cleaned according to department procedure
3-outside	11/7/2011	5th & Central	4.8	1	Outside surface of facepiece 3 from previous table
Unused	11/7/2011	5th & Central	1.1	1	Never-used facepiece
Media Blank 1	11/7/2011	5th & Central	ND	1	
Media Blank 2	12/15/2011	Price Hill	ND	1	
Media Blank 3	1/31/2012	Warehouse	ND	1	

A histogram was prepared of the log DEHP levels on the 29 facepiece wipes obtained from the interior of facepieces in active use, using SAS version 9.2 with PROC UNIVARIATE. (See Figure 9.)

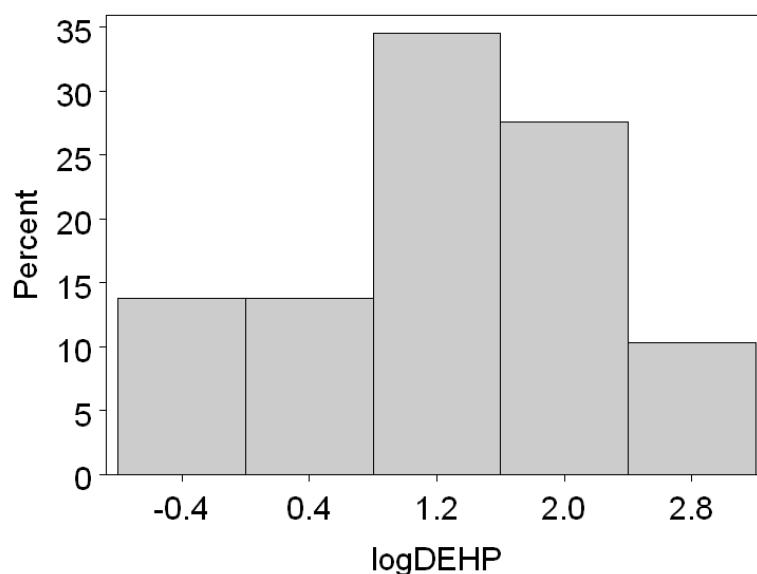


Figure 9. Histogram of natural log of DEHP levels (micrograms per facepiece) on 29 wipes of SCBA facepieces in current use.

A statistical power calculation was performed on the 29 facepiece wipes obtained from the interior of facepieces in active use, using SAS version 9.2. The analysis was run on the log of the DEHP level, because the distribution was observed to be lognormal. The power of this study to show that the mean of the 29 facepiece wipes was different from the LOD is $>.999$.

An ANOVA procedure was performed on the log of the DEHP level, with the Tukey's studentized range test, to check whether the means of the contamination levels on the facepiece wipe samples obtained at the three different locations differed significantly from one another. The Tukey test showed that the facepiece wipes from the 5th & Central firehouse (location 1) were significantly different from those obtained at the two other locations ($P<0.05$). The wipe samples obtained at the Price Hill firehouse (location 2) and at the fire department warehouse (location 3) were not significantly different from each other. A boxplot of log DEHP level vs. location is shown in Figure 10. The residuals were calculated for the 29 log DEHP levels, and the assumption of normality was verified.

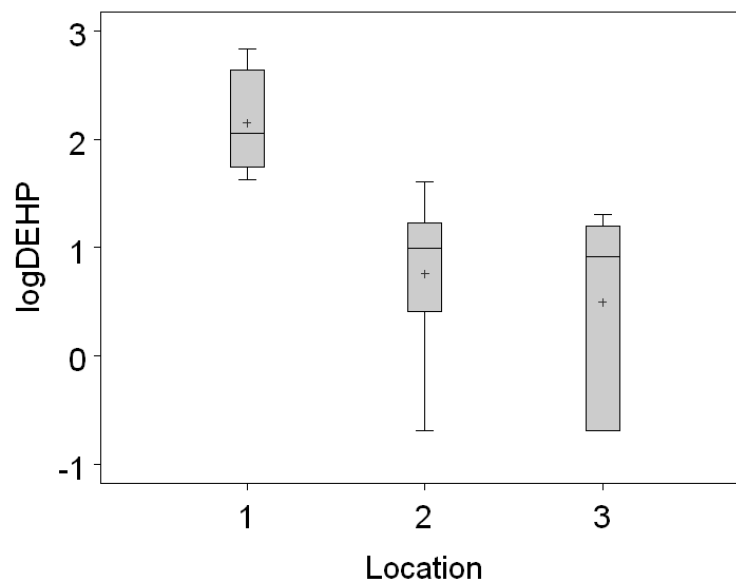


Figure 10. Boxplot of natural log of DEHP level (micrograms/facepiece) on firefighter SCBA facepieces vs. location of wipe sampling (1 = 5th & Central, 2 = Price Hill, 3 = fire department warehouse.)

A two-sided t-test was performed on the wipe sample results for each location individually, to test whether the means of the samples collected were significantly different from the LOD. Results are summarized in Table 6. All means were significantly different from the LOD ($P < 0.05$).

Table 6. Results of t-test procedures on facepiece wipe sample locations (1 = 5th & Central, 2 = Price Hill, 3 = fire department warehouse).

Location	Number of samples	Mean DEHP Level on wipe samples($\mu\text{g}/\text{facepiece}$)	95% confidence interval of the mean	P-value
1	10	9.35	6.34 – 12.36	0.0001
2	9	2.57	1.45 – 3.68	0.0119
3	10	2.13	1.22 – 3.04	0.0205

An ANOVA procedure was also performed for the 12 wipe samples for which the “griminess” of their appearance had been noted, to test whether a grimy appearance was associated with a higher level of DEHP contamination. Those samples noted as “Barely visible dirt” were coded “1”, those with “Moderate grime” or “Grimy” were coded “2”, and those noted as “Very grimy” or “Exceptionally grimy” were coded “3”. No significant difference in contamination level with griminess was found. A boxplot of log DEHP concentration vs. griminess is shown in Figure 11.

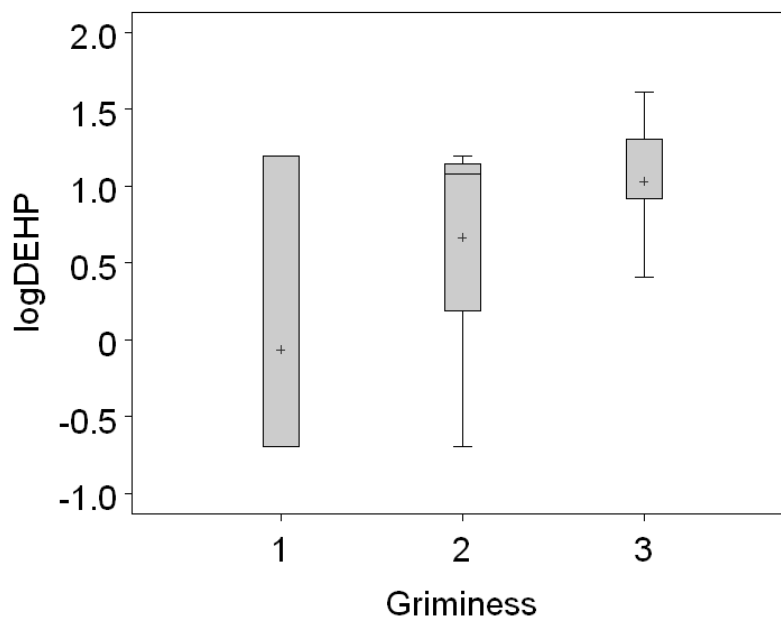


Figure 11. Boxplot of natural log of DEHP level on firefighter SCBA facepiece wipes (micrograms/facepiece) vs. grimy appearance of the wipe sample.

C. Protective clothing samples

Of the 26 semivolatile chemicals for which the analysis was run, 22 of the chemicals were detected on at least one protective clothing sample. The results of analysis of protective clothing samples are shown in Table 7. The limit of detection for each analyte was 1 microgram.

Table 7. Weights (micrograms/swatch) of analytes on protective clothing samples[†]

Sample	Unused glove inner	Unused glove middle	Unused glove outer	Unused glove cuff	Unused hood	Hood 1	Coat wristlet 1. worn with Hood 1	Hood 2	Glove 1 inner	Glove 1 middle	Glove 1 outer	Glove 2 inner	Hood 3
1-Methyl naphthalene						4.6							
2-Methyl naphthalene						4.6							
Acenaphthylene						11.8	3.9						
Anthracene						3.0							
Benzo(a) anthracene						4.6				3.5	7.3		1.3
Benzo(a) pyrene							2.6			1.3			
Benzo(b) fluoranthene							2.6	1.3		3.1			
Benzo(g,h,i) perylene							1.6				2.7		
Benzo(k) fluoranthene							4.9			1.2			
Butyl benzyl phthalate			2.2				46.8		2.0	11.2		1.2	5.7
Chrysene						4.3		1.0		5.4	8.3		
Di(2-ethylhexyl) phthalate*	2.1	4.9	23.4	1.8		1111.8	1287.0	487.9	454.4	1278.2	7280.0	50.1	162.5
Dibenzo(a,h) anthracene						2.6							
Diethyl phthalate			2.2							1.7	2.2		
Di-n-butyl phthalate			2.2					1.6	3.1	14.0		1.4	
Di-n-octyl phthalate			1.0				10.5	1.7	1.8	1.8	33.8	2.7	
Fluoranthene							3.0	1.1	1.1	12.2	8.3		
Fluorene						2.5							
Indeno(1,2,3-cd) pyrene							1.3				2.6		
Naphthalene						10.1	1.1						
Phenanthrene							22.2	1.0		6.6	3.6		3.1
Pyrene										12.9	7.8		
Sample Weight (g)	1.5	1.1	5.2	3.5	2.3	3.3	5.9	2.9	1.4	1.5	5.2	1.7	2.9

[†]An empty cell denotes a result below the level of detection.

*DEHP

V. Discussion

A. Fire Department Policies and Procedures

At the time that facepiece wipes were collected, a variety of storage conditions were noted for the facepieces. Some facepieces were stored in a separate fabric bag, while others were found in a backpack with other items of protective clothing, placed inside a boot or simply clipped by means of a buckle to the outside of the turnout coat. New facepieces received in January and February were intended to be delivered along with a fabric bag for storage. This method of storage may help the facepieces to stay cleaner than when stored in close contact with other pieces of protective gear.

Although fire department policy calls for facepieces to be cleaned every time they are used, cleaning does not often happen, according to anecdotal information. Similarly, the mandated semiannual inspections and annual cleaning of turnout coats and pants do not always happen. Soiled turnout gear may still be viewed as a “badge of honor”, and there may be some reluctance to have a favorite set of gear cleaned or inspected if that might lead to the gear being replaced.

Because not all firefighters take advantage of the annual physical, and results of firefighters’ physicals are not reported to the fire department; firefighters with cardiopulmonary disease may still be performing the physically demanding job of firefighter.

B. Facepiece Wipes

SCBA facepieces in current use at an area fire department were wiped so that contamination on the internal surfaces of the facepiece could be characterized. The four primary goals in selecting a sampling method were:

- to effectively collect contamination from the surfaces,
- to avoid introducing background levels of the chemicals of interest,
- to avoid damage to the firefighter facepieces
- to leave no residue behind after wiping, that could interfere with the safe and comfortable wearing of the equipment.

The manufacturer of the SCBA equipment wiped is MSA (Cranberry Township, PA). The manufacturer's website provides cleaning and disinfecting instructions for the equipment. Recommendations include cleaning the facemask after each use, using a proprietary cleaning solution available from the manufacturer. If the proprietary solution is not used, a mild detergent such as dish washing detergent may be used. Alcohol is specifically not recommended due to possible adverse effects on the rubber parts of the mask.(Mine Safety Appliances, 2012)

Tap water was initially selected to dampen the wipe materials. The contaminants of interest are not water-soluble, but water was selected because it was expected to be free of organic contaminants that might interfere with analyses, and because the surface tension of the water was expected to physically hold particulate contaminants from the facepieces more tightly than a dry wipe. Water is also not damaging to the materials of the facepieces, and leaves no residue behind.

Personnel at ALS Datachem, the analytical laboratory receiving the samples, were consulted on selecting sampling materials to avoid high background levels of the contaminants of interest. As a result of this consultation, white cotton gauze dampened with tap water was chosen for sampling.(Baxter, 2011) The samples were placed in specially-cleaned glass jars after collection. ALS Datachem supplied the cotton gauze, exam gloves and glass jars for wipe sample collection. (See Table 1.)

DEHP was the only contaminant of interest detected on the inside surfaces of the facepieces. The boiling point of DEHP is 384° C. Fires can reach temperatures as high as 1100°C.(Rossi, 2003) It is likely that DEHP volatilizes at the high temperatures encountered in a structure fire or vehicle fire, and then condenses as it cools. The condensed DEHP could form fine droplets or it could adsorb on the surface of fine ash or soot particles.

By visual observation, the facepieces seemed to be contaminated by fine particulate matter (See Figure 8.). No liquid smearing was observed as wipe samples were obtained. This contamination could have accumulated during use, during overhaul when the facepiece was not being worn, or from transfer from contamination on the firefighter's hands. There were large differences in the appearance of different facepiece wipes. Some gauze wipe samples looked much "grimier" than others. At the last location where samples were obtained ("Warehouse"), an effort was made to characterize the "griminess" of each wipe sample, to see if there was a correlation between the color of the wipe sample and the amount of DEHP detected.

The ANOVA procedure showed no significant association between the griminess of the wipe and the amount of DEHP measured. Several of the wipes characterized as "very grimy" held 2.5 µg of DEHP, while one of the wipes showing "barely visible dirt" held 3.3 µg of DEHP. It is possible that some of the particulate contamination was light in color and some was black, depending on the characteristics of the fire exposure that had occurred. Heavy contamination by light-colored particles may not have resulted in a "grimy-looking" wipe, while contamination was still present. This is consistent with the findings of Brandt-Rauf et al., who noted that the black appearance of smoke at structure fires did not correlate with the quantity of toxic substances present.(Brandt-Rauf et al., 1988)

The samples obtained from the first location (5th & Central) had significantly higher contamination levels than those from the other two locations. Many of these samples were

obtained from the Heavy Rescue Unit. One of the duties of the Heavy Rescue Unit is to respond to vehicle fires. There is a great deal of PVC in automobiles, due to the common use of vinyl for upholstery, supporting the possibility of high DEHP exposures. It is also possible that members of this unit respond to more fires than the average firefighter, or that they clean their facepieces less frequently. Their gear was all stored in close proximity on one wall of the same room. For this reason, the facepieces could also have been contaminated by fine ash or soot shaken loose from the other stored gear. They could also have been contaminated by material transferred from the hands of the firefighter.

Sample #24 was a re-wipe of the same facepiece that was wiped for Sample #10 (See Table 4), approximately 12 weeks later. Presumably, the 3 micrograms of DEHP found on that mask when wiped for a second time, were all accumulated during the 12 week period between the two wipe samples. It is unknown how many fires the owner of the mask responded to during that period.

The highest measured level of DEHP contamination on a firefighter SCBA facepiece was 17 micrograms. The US EPA has established a reference dose (RfD) for DEHP ingestion of 20 µg/kg-day. A 70-kg individual could safely consume 1400 µg of DEHP per day. Seventeen micrograms of DEHP on a facepiece may not seem like a large amount, but it is only one of many possible sources of exposure. The EPA has not established a reference concentration (RfC) for DEHP inhalation exposure, but when an RfC does exist, it is usually lower than the RfD.

Sample “2-clean” (See Table 5.) was obtained by wiping the same facepiece wiped for Sample 2 (See Table 4.), on the same day, after the facepiece was sprayed with MSA cleaning solution and wiped, according to department procedures. DEHP was non-detectable, making it unlikely

that DEHP contamination is coming from the cleaning solution or wiping cloths used. It also demonstrates the effectiveness of cleaning the facepiece.

Sample “3-outside” (See Table 5.) was obtained by wiping the exterior surface of the same facepiece wiped for Sample 3 (See Table 4.). The type of contamination (DEHP only) was similar between the inside and outside surfaces of the facepiece, but the level was lower on the outside than on the inside of the facepiece (4.8 micrograms outside vs. 8.1 micrograms inside). The reason for the difference in contamination level is unknown, but one possibility is that the interior contamination accumulated during overhaul, when the facepiece was not being worn.

One new, unused facepiece was wiped for comparison. The facepieces are constructed of nitrile rubber with a clear polycarbonate lens. A DEHP level of 1.1 micrograms, just above the 1 microgram limit of detection, was measured on the unused facepiece. This contamination could have been present on the facepiece when it was received, or it could have accumulated during storage, from deposition of resuspended fine particulate. The unused facepiece was kept in the same room where the personal protective gear from the Heavy Rescue unit was stored. It might also have come from transfer of contamination during handling.

C. Protective Clothing Samples

The protective clothing samples were contaminated with a far greater variety of chemicals, and at much higher levels than the facepieces. Contaminant levels found on the swatches of protective clothing have been reported as micrograms/swatch in Table 7. The weight of each sample is listed in the last row of the table, making it possible to calculate micrograms per gram of sample, for comparison.

All of the unused clothing samples were contaminated with a low level of DEHP, except for the hood, which showed no semivolatile contamination. This shows the ubiquitous nature of DEHP.

The outer layer of the unused glove, which was made of black kangaroo leather, had low levels of contamination from several other phthalates, as well.

Hood 1 and coat wristlet 1 had been recently worn in a structure fire when they were taken out of service due to excessive contamination. The hood was found to be contaminated with 10 different chemicals, including benzo(a)anthracene, and a large quantity of DEHP.

The wristlet from the coat worn by the same firefighter was contaminated with 12 chemicals, many of them different from the ones found on the hood. Contaminants on the wristlet included benzo(a)pyrene, along with a large amount of DEHP once again. Both are classified as probable human carcinogens by the US EPA. It is unknown what could account for the difference in contaminants between the wristlet and the hood. One possibility considered was that higher-boiling contaminants might be found preferentially on the wristlet, rather than the hood, as they might not have to volatilize in order to deposit on the wristlet. An ANOVA procedure, with the Tukey's studentized range test, was performed on the distribution of boiling points of the contaminants on the hood and the wristlet, and the distributions were not significantly different ($P < 0.05$).

The largest quantity of DEHP was found on the exterior layer of Glove 1. Surprisingly, the greatest number of different contaminants was found on the middle layer of this glove. Some of the contaminants found on the middle layer of the glove were not found on either the inner layer or the outer layer. These contaminants were PAHs, which are known to be light-sensitive. It is possible that the contaminants migrated through the outer layer of the glove, but were later degraded on the outer layer of glove due to light exposure, while the PAHs on the middle layer of the glove were protected from light exposure. The other possibility is that these PAHs were produced by degradation of the middle layer of the glove itself. The middle layer of the glove is

fabricated from the proprietary moisture barrier material, Pyrotect®. This is a potential area for further study.

It was observed that the inner layers of the two used gloves examined both appeared dirtier on the side facing the firefighter's hand than on the side facing the middle layer of the glove. Some of the discoloration found on the inside layer of the glove may come from transfer from debris on the firefighter's hand. However, as noted previously, the color may not indicate the level of contamination present.

DEHP contamination was found on every sample of used firefighter protective clothing that was examined. The levels of DEHP contamination (range: 50 to 7280 µg) were from 52 to 875 times higher than the highest level of any PAH (range: <LOD to 22.2 µg) found on the clothing. These results validate observations made by Stull et al. (Stull et al., 1996) and by Underwriters' Laboratories (Underwriters Laboratories Inc, 2010). Stull et al. found levels of DEHP on three used firefighter's coats that were from 15 to 33 times as high as the highest level of any PAH. (Stull et al., 1996) The Underwriters' Laboratories report provided only charts of their results, but DEHP levels were visually far higher than any other semivolatile contaminant, at least 2.6 times higher than the highest level of any PAH on 8 used firefighter gloves, and at least 4.5 times higher than the highest level of any PAH on 8 used firefighter hoods. (Underwriters Laboratories Inc, 2010)

VI. Conclusions and Further Study

A. Aim 1: Survey fire department personal protective equipment use and maintenance procedures.

Fire department policy for the use of respiratory protection follows the requirements of the OSHA standard for respiratory protection (Occupational Safety and Health Administration, 2011), even though government employees are not subject to OSHA regulations. Department policy calls for cleaning and disinfection of the SCBA facepiece with each use. In actual practice, this may not always happen.

Although levels of DEHP measured on the inside of firefighter facepieces and on samples of protective clothing are not directly comparable, levels found on facepiece wipes were much lower than levels measured on 2" x 4" swatches cut from other personal protective equipment. Despite the small quantities measured, because the facepiece is worn in intimate contact with the face, it would be wise to keep it as clean as possible. Particulate matter found on the inside of the facepiece could be blown into the eyes, nose or mouth when air is flowing and cause difficulty during emergency response. Regular cleaning, according to manufacturer's recommendations and the fire department's policy, is recommended. It is also recommended to store the facepiece in such a way that it does not become contaminated from other gear when not in use.

Gloves are removed first when exiting the fireground. As a result, contamination may be transferred from the helmet, hood, coat, pants and boots to the firefighter's hands when protective clothing is doffed, resulting in dermal exposure. The wearing of cotton undergloves or glove liners, as described by Laitinen et al., reduced PAH contamination on firefighters' hands by 80%. (Laitinen et al., 2010) Adopting this practice might reduce dermal exposure of firefighters.

One area of future research might be to vacuum and/or launder contaminated firefighter gear to see how much contamination can be removed by cleaning. If most of the contamination is found on fine ash or soot particles, vacuuming might be effective in removing much of it. If it is soaked into the fabric, laundering may be necessary.

B. Aim 2: Characterize contamination on inside surfaces of firefighter SCBA facepieces.

This is the first time that wipe samples from firefighter facepieces have been reported. Low levels of DEHP were consistently measured on the facepieces (range: <LOD to 17 micrograms; n=29). Wipes taken from facepieces used by the Heavy Rescue unit showed significantly higher levels of DEHP than those from two other locations. Further research is needed to identify the cause of the higher levels in gear from the Heavy Rescue unit. Some possible sources are vehicle fires or exposures during overhaul. If facepiece contamination is occurring during the overhaul phase of firefighting, when the facepiece is not being worn, firefighter inhalation exposures are also a possibility.

A sticky microscope slide, used to lift a sample of the contamination from the inside of a facepiece, revealed a mixture of irregularly-sized particulate and fiber contamination. Such particulate matter may also carry adsorbed chemical contamination, as shown in the study of soot from combustion of polyethylene and PVC by Stone et al., (Stone et al., 1973) and as observed by Bolstad-Johnson et al. (Bolstad-Johnson et al., 2000)

Due to the high boiling points of DEHP and PAHs, it is anticipated that they are deposited on firefighter gear either in the form of fine droplets or else adsorbed onto fine particulate matter. A direction of future research in this area might involve sampling aerosols produced during fire overhaul, and analyzing the contaminants present on the filter, as a measure of how much contamination is airborne during the overhaul phase of firefighting, when respiratory protection

is rarely worn. Contamination produced during different types of fires, such as vehicle fires, residential and commercial fires, might also be studied, to identify the sources of contaminants.

C. Aim 3: Characterize contamination on samples of used firefighter protective clothing.

Hoods are important protective gear to prevent dermal exposure because they are worn in close contact with the firefighter's skin. In particular, they are worn next to some of the most permeable skin in the human body. According to the work of Feldmann and Maibach on regional differences in skin permeability, only the skin of the scrotum is more permeable than that of the jaw angle, forehead and scalp.(Feldmann & Maibach, 1967) Hoods become contaminated during fire events, and, if not washed, continue to expose firefighters whenever they are worn, donned or doffed. Hoods should be laundered following fire response. Dermal absorption of DEHP is considered to be minimal, but it has never been studied under conditions such as those in which firefighters work. This is an area for further research.

The least-contaminated item of personal protective gear, the 2" x 4" sample of the inner layer of Glove 2, showed almost three times the level of DEHP as found on the most-contaminated facepiece (50.1 µg vs. 17 µg). Hood 1 was contaminated with 1111.8 µg of DEHP, or over 65 times as much DEHP. Based on this limited number of data points, contamination on personal protective gear may be a larger source of dermal exposure than that from facepiece contamination.

One cannot draw conclusions on levels of human exposure from measurements of contamination on personal protective gear. Many factors combine to convert contamination on clothing or skin to an effective dose to a target organ inside the human body. These include factors such as skin temperature, length of time that the gear is worn, heart rate, frequency of cleaning personal protective gear and frequency of washing the skin. Frequency of cleaning

personal protective gear and frequency of washing the skin are factors that can be controlled.

Frequent washing of gear and of the skin is recommended to reduce dermal exposures.

Biomonitoring studies in combination with exposure assessment could help to relate exposure to internal dose.

It was surprising to find contaminants on the middle layer of Glove 1 that were not found on the inner or outer layers. It may be worthwhile to investigate whether the material of the middle layer (Pyrotect®) decomposes when heated, as in a fire response.

Firefighter exposure to PAHs has been studied, but firefighter exposure to DEHP has not. The levels of DEHP found on used firefighter gear were far higher than levels of any PAH. DEHP exposure has been associated with several of the adverse health outcomes observed in firefighter populations, including cardiac and reproductive effects, prostate and testicular cancer.

Studies on the adverse health effects of DEHP have focused on ingestion. However, firefighter exposure to DEHP is most likely by the route of inhalation or dermal absorption. The action of DEHP in the human body may be different depending on the route of exposure. This area requires further investigation.

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Appendices

Appendix A – Respiratory Protection Program Checklist

Appendix B - List of Analytes by EPA Method 8270

Appendix A - Respiratory Protection Program Checklist

Fire Department _____ Date _____			
OSHA 29 CFR 1910.134			
Required Element	Yes	No	Comments
Trained program administrator	<input type="checkbox"/>	<input type="checkbox"/>	Name _____
-administers program	<input type="checkbox"/>	<input type="checkbox"/>	
-conducts evaluation of program effectiveness	<input type="checkbox"/>	<input type="checkbox"/>	
Procedure for selecting proper respirator	<input type="checkbox"/>	<input type="checkbox"/>	
Medical evaluation for employees	<input type="checkbox"/>	<input type="checkbox"/>	
Fit testing of respirators	<input type="checkbox"/>	<input type="checkbox"/>	
Procedures for proper respirator use in both routine and emergency situations	<input type="checkbox"/>	<input type="checkbox"/>	
Procedures and schedule for cleaning	<input type="checkbox"/>	<input type="checkbox"/>	
Procedures and schedule for disinfecting	<input type="checkbox"/>	<input type="checkbox"/>	
Procedures and schedule for storing	<input type="checkbox"/>	<input type="checkbox"/>	

Procedures and schedule for inspecting	<input type="checkbox"/>	<input type="checkbox"/>	
Procedures and schedule for repairing	<input type="checkbox"/>	<input type="checkbox"/>	
Procedures and schedule for discarding	<input type="checkbox"/>	<input type="checkbox"/>	
Procedures and schedule for otherwise maintaining	<input type="checkbox"/>	<input type="checkbox"/>	
Procedures to ensure adequate breathing air quality, quantity and flow rate	<input type="checkbox"/>	<input type="checkbox"/>	
Employee training in routine and emergency use of the respirator	<input type="checkbox"/>	<input type="checkbox"/>	
Employee training in proper use of the respirator, including putting on and removing, limitations on use and maintenance	<input type="checkbox"/>	<input type="checkbox"/>	
Procedures for regularly evaluating the effectiveness of the program	<input type="checkbox"/>	<input type="checkbox"/>	

Appendix B - List of Analytes by EPA Method 8270

Chemical	Report Limit
1-Methylnaphthalene	1.0 µg/sample
2-Methylnaphthalene	1.0 µg/sample
Acenaphthene	1.0 µg/sample
Acenaphthylene	1.0 µg/sample
Anthracene	1.0 µg/sample
Benzo(a)anthracene	1.0 µg/sample
Benzo(a)pyrene	1.0 µg/sample
Benzo(b)fluoranthene	1.0 µg/sample
Benzo(g,h,i)perylene	1.0 µg/sample
Benzo(k)fluoranthene	1.0 µg/sample
Bis(2-ethylhexyl)phthalate*	1.0 µg/sample
Butyl benzyl phthalate	1.0 µg/sample
Carbazole	1.0 µg/sample
Chrysene	1.0 µg/sample
Dibenzo(a,h)anthracene	1.0 µg/sample
Dibenzofuran	1.0 µg/sample
Diethyl phthalate	1.0 µg/sample
Dimethyl phthalate	1.0 µg/sample
Di-n-butyl phthalate	1.0 µg/sample
Di-n-octyl phthalate	1.0 µg/sample
Fluoranthene	1.0 µg/sample
Fluorene	1.0 µg/sample
Indeno(1,2,3-cd)pyrene	1.0 µg/sample
Naphthalene	1.0 µg/sample
Phenanthrene	1.0 µg/sample
Pyrene	1.0 µg/sample

*Di(2-ethylhexyl) Phthalate