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# Characteristics of Hazardous Substances Extracted from Laundry Water for Fire Protection Suit Exposed to Fire

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**Abstract:** (1) Background: It is well known that various toxic substances, including carcinogens, are generated at the fire scenes, so it is very important for firefighters to wear comprehensive personal protective equipment. The extent of the type and amount of harmful substances contained in the washing water of fire protection suits (FPS) exposed to fire scenes have not yet been confirmed. The purpose of this study is to evaluate the characteristics of harmful substances contained in wash water extracted from FPSs exposed to fire. (2) Methods: The study design was a simulation-based experimental study. To evaluate the degree of contamination exposure of FPSs, 10 sets of fire suits were classified into four groups as follows: newly supplied, field use, one fire exposure, and two consecutive fire exposures. In the experimental environment, after exposing three to four groups of FPSs to residential fire conditions. they were sealed in a plastic bag in the experimental space. The washing water for FPSs was extracted through manual washing in the order of Groups 1 to 4, and 24 items were analyzed according to the water pollution process test standards. (3) Results: According to the results of the FPS laundry analysis, the concentration of acrylonitrile in laundry was higher when exposed to fire twice than when exposed to fire once. Moreover, there was a dose–response relationship, and the risk of cumulative toxicity was shown. Naphthalene and diethylhexyl phthalate (DEHP) were detected to be high in the washing water of Group 3 FPSs exposed to incomplete combustion fire. Of the 24 items that were analyzed for in the water, four item exceeded the standard for sewage discharge facilities in accordance with the Water Environment Conservation Act. Copper and its compounds exceeded the standards by 3.4 times, antimony 4.8 times, acrylonitrile 26.0 times, and DEHP 4.1 times, respectively. (4) Conclusions: Therefore, when removing FPSs after firefighting activities, care should be taken to avoid contaminating the skin. In addition, facilities that wash FPS that have been exposed to a fire scene must have a sewage treatment and purification facility. However, if emergency decontamination of FPSs is conducted at the fire scene, the concentration of toxic substances contained in laundry can be reduced. In the case of large-scale fire, there is a risk of water pollution near the fire scene, so it is necessary to prepare a national countermeasure. The results of this study can be applied to the revision of regulations related to the building of the fire departments, reduction of water pollution, and water environment policy.

**Keywords:** fire; exposure; fire protection suit (FPS); contamination; laundry; sewage; water pollution; environmental, social, and governance (ESG)

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## 1. Introduction

A number of chemically hazardous substances, including gaseous substances and particulate substances, are generated at the fire scene, which is a type of social disaster [1].

Although it varies depending on the location, type, and aspect, 10 kinds of chemically toxic substances, such as carbon monoxide, carbon dioxide, acrolein, hydrogen cyanide, nitrogen oxide, hydrogen chloride, and formaldehyde, are generated at the fire scene [2,3]. Short or long-term exposure to these substances increases the risk of health problems due to various effects on the human body [2,4]. Therefore, in order to minimize exposure to harmful substances occurring at the fire scene, firefighters wear personal protective equipment to block harmful substances that can enter through the skin and respiratory tract [5,6]. For this reason, according to the International Agency for Research on Cancer (IARC), occupational exposure as a firefighter is classified as "carcinogenic to humans" (Group 1) based on "sufficient" evidence for cancer. At the same time, the occupation of firefighter, which corresponds to a shift worker with a risk of bio-disruption, was classified as a cancer risk of Group 2A [7]. Various toxic substances generated at the scene of a fire act as factors that increase the risk of various types of cancer for firefighters [8]. As for these risk factors, previous studies confirmed the relationship between fire exposure history and leukemia, as well as fire exposure time and lung cancer [9,10]. A recent meta-analysis showed that certain types of cancer, including melanoma, testicular cancer, bladder cancer, prostate cancer, and colorectal cancer, were reported as increased risks of firefighters [8,11,12]. In addition, the occupation of firefighters increases the risk of not only cancer, but also respiratory and cardiovascular diseases [13–17]. For this reason, it is very important to wear comprehensive personal protective equipment, including fire protection suits (FPSs), and self-contained breathing apparatus (SCBA) in places where flammable substances burn [18]. In addition, emergency decontamination of contaminated personal protective equipment at the end of field activities can reduce the risk of occupational exposure [19,20].

Contaminants on fire suits that were exposed to the fire scene can secondarily contaminate the surrounding environment. According to a previous study that evaluated the exposure of chemically hazardous substances in the fire department, the chemically hazardous substances and indoor air quality were simultaneously measured at the usual level and after the fire vehicle returned to the fire station after being dispatched to a fire [21,22]. As a result, it was confirmed that, out of 11 evaluation items, carbon dioxide, total volatile organic compounds, sulfuric acid, and formaldehyde 4 exceeded domestic and foreign standards [21]. In addition, the smoke reduction device installed in the garage of the fire department reduced various harmful substances, including elemental carbon and fine dust [23]. This means that chemically harmful factors generated at the fire scene are entering the fire department through the medium of firefighters and fire fighting vehicles that were active at the fire scene. In addition, diesel emissions from fire vehicles are Group 1 carcinogens that can affect the health of firefighters [7]. According to a survey of firefighters in a metropolitan area, the response that firefighters get at fire vehicles after taking off their fire-fighting suits at the scene of a fire was very low, at 9.1% [24]. More than 90% of firefighters board the fire truck without emergency decontamination [24]. At a fire scene, personal protective equipment, including the fire protection suits that firefighters wear to protect themselves, are also contaminated by exposure to various harmful substances. Secondarily, the protective suits come into contact with nonvolatile pollutants, such as polycyclic aromatic hydrocarbons (PAHs). According to previous studies, it was found that some contaminants have the potential to cause skin contamination of firefighters through penetration inside the fire suits [19]. This can be seen as a risk factor for the contaminated FPS at the fire scene. However, there are few published studies analyzing the water quality items to determine the heavy metals contained in the water when the fire protection suit exposed at the fire scene was washed [25]. Most of the research has been concerned with measuring the risk of gaseous and particulate matter occurring at the fire scene. However, in our study, we focused on evaluating water quality and the degree of environmental impact due to polluted heavy metals. Therefore, the purpose of this study is to evaluate the characteristics of the types and amounts of hazardous substances in FPSs exposed to fire.

## 2. Materials and Methods

### *2.1. Study Setting*

The number of fires occurring nationwide in Korea was 40,030 per year, and 284 deaths were reported in 2018. Of these, residential fires accounted for the largest share, with 7543 cases (18.8%) and 122 deaths (43.0%). According to the classification regarding fire location, as for the places where fires occurred in Korea, there were 12,002 cases (29.9%) at residential facilities, 5895 cases (14.7%) at industrial facilities, 5067 cases (12.6%) at automobiles and railroad cars, life service 4361 cases (10.8%), sales and business facilities 2599 cases (6.4%), and forestry 2258 cases (5.6%). Therefore, in this study, the residential fire location, one of the most common types of fires in Korea, was set as the research environment [26].

### *2.2. Experimental Setting*

In this experimental study, a 3.0 m × 3.0 m × 2.8 m temporary building site was constructed, and a simulation-based fire experiment was conducted at the Seoul Metropolitan Fire Service Academy. This experimental study was conducted by dividing the fire protection suits into 4 groups. The study was conducted from 8 a.m. to 7 p.m. on Thursday, 16 May 2019. The weather on the day of the experiment was clear, and the temperature at the beginning of the experiment was 16.0 °C, and at the end, it was 29.0 °C. An experimental set, similar to a studio, was created by modeling the internal environment of a temporary building with furniture and items used in real houses. The interior of the private house was set to reflect the characteristics of the bedroom and living room, and the interior of the temporary building, which is the environment for conducting the experiment, was also constructed very similar to the environment of the actual house. The schematic diagram of the interior projected vertically from the ceiling is shown (Figure 1). The fire protection suit was reproduced to simulate the situation where a firefighter actually extinguishes a fire inside the fire scene by dividing the top and bottom of the suit on a stand-type hanger inside the simulation set. In addition, when the inside of a temporary building is actually ignited to simulate a residential fire, not only the internal structure, but also the fire protection suit, can all be consumed. Therefore, a certain amount of the combustion products that actually existed in the experimental area were put into a furnace inside the temporary building, and the door was closed after igniting. Incomplete combustion and complete combustion were carried out by controlling the amount of oxygen injected through the window of the temporary building to create fire conditions.

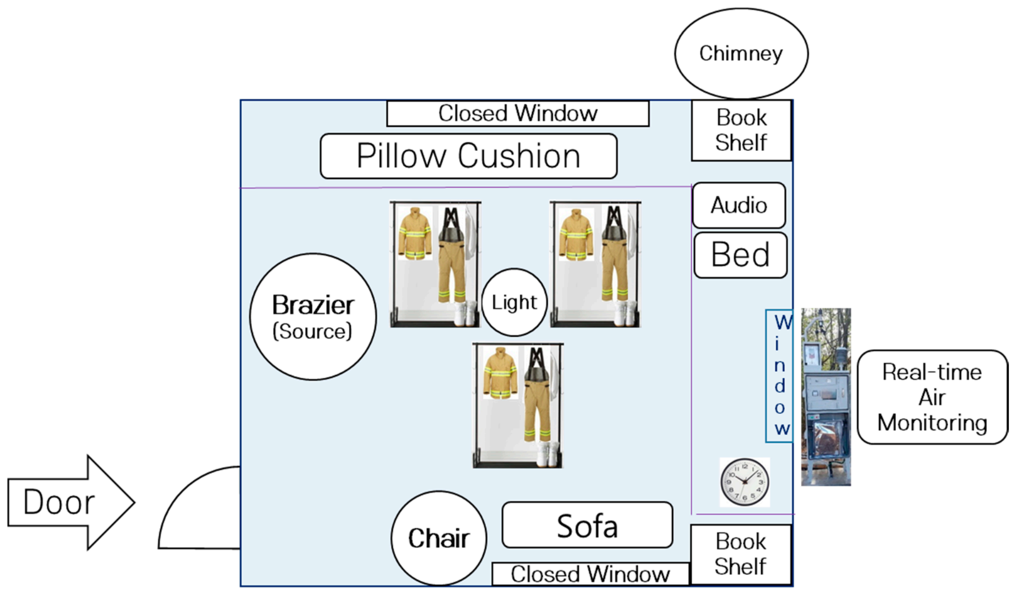


**Figure 1.** Schematic diagram of experimental scene.

### 2.3. Study Design and Subject

This study design is a simulation-based experimental study. FPSs were classified into four groups to evaluate the degree of contamination of FPSs caused by harmful chemical substances generated at residential fire scenes. The 10 sets of fire protection suit used in this study consisted of FPS with the same year of manufacture, manufacturing bureau, size, and fabric composition to ensure the same experimental conditions. Consequently, the bias that may occur in the experimental results was removed in advance.

The fire protection suits were classified into a total of four experimental groups. From Group 2 to Group 4, three fire protection suits were configured for each group in order to minimize the occurrence of errors in the measured values during the experiment. Group 1 is newly supplied fire protection suit that has never been used, Group 2 is fire protection suit that is in use at the fire scene, Group 3 is a suit exposed to one fire, and Group 4 is a suit which has been exposed twice in a row. The reason for classifying Group 4 into another group that was exposed to two consecutive fires is that the fire protection suit worn after the fire was dispatched may be used continuously without washing; therefore, this group confirms the magnitude and extent of the actual additional contamination (Table 1).

**Table 1.** Demographic characteristics of simulated fire protection suits by group distribution.

| | **Group 1** | **Group 2** | **Group 3** | **Group 4** |
|---|---|---|---|---|
| Classification of fire protection suit | Newly supplied | Washed firefighter protection suit in use | One fire exposure | Fire exposure twice in a row |
| Quantity | 1 set | 3 sets | 3 sets | 3 sets |
| Year of manufacture | 2013 | 2013 | 2013 | 2013 |
| Manufacturer | Philippines Sancheong | Philippines Sancheong | Philippines Sancheong | Philippines Sancheong |
| Size | No. 6 | No. 6 | No. 6 | No. 6 |
| Fire exposure | None | None | Incomplete combustion | Complete combustion |
| | Characteristics of the tops and bottoms of the fire protection suits | | | |
| Tops and bottoms of the fire protection suits (common to Groups 1~4) |  | |  | |
| | ■ Outer and inner material, felt: 100% aramid fibers<br>■ Breathable and waterproof cloth: 100% aramid fiber, PTFE film<br>■ Reflective tape: 100% aramid fiber, reflective coating (width 75 mm) | | | |

PTFE: polytetrafluoroethylene.

At this time, chemically hazardous substances generated at the fire scene may accumulate in the fire protection suit and remain there; therefore, we evaluate the risk and the amount of hazardous substances remaining in the fire protection suit. Both Groups 3 and 4 were placed in the simulation set, and incomplete combustion was performed. In order to equalize the experimental conditions for the fire protection suits, the same year of manufacture, country of manufacture, size, and fabric composition were selected to remove any bias that may occur in the experimental results (Table 1).

### 2.4. Experimental Scenario and Sampling Strategy

The experimental scenario for measuring exposure to hazardous substances in fire scenes and FPSs was as follows:

1. Inside the temporary building, 6 sets of FPSs for Groups 3 and 4 were hung on internal hangers to create an environment similar to that in which firefighters extinguish fires indoors.

2. Various combustibles that could come out of the house were put in the fire pot inside the temporary building and burned for 60 min. At this time, the type and amount of the combustible material included polyurethane, a sofa, plastic bags, plastic bottles, paper, newspapers, blankets, etc., and were evenly cut into certain sizes. The amount of oxygen flowing into the interior was controlled through an open window, a structure of a temporary building. In addition, the situation of fire investigation after the fire was reproduced in the same way.
3. After 60 min from the start of the measurement in the situation of an incomplete combustion fire, two firefighters wore full-body personal protective equipment and entered the temporary building to bring out the FPSs included in the Group 3. Hazardous substances at the fire scene are characterized by volatile characteristics, so 3 sets of FPSs were put in a container, sealed, and returned.
4. After 20 min, the second complete combustion flame fire experiment was started.
5. A total of 60 min after the start of the flame fire measurement, two firefighters again entered the test measurement site. The FPS included in Group 4 was put in a container, sealed, and brought back.

### 2.5. Extraction of FPS Laundry

In order to find out the degree of secondary cross-contamination regarding the contaminants of FPS, laundry water analysis was performed on 10 fire protection suits classified into Groups 1 through 4. At this time, the suits were washed using a manual washing method. The laundry water of FPS was extracted from 8:30 p.m. on May 19 (Sun) to 3:40 a.m. on May 20 (Mon) at a designated location within the Seoul Metropolitan Fire Service Academy. At this time, the extracted laundry water was not subjected to separate chemical treatment and proceeded to the analysis step. The manual washing method and procedure were as follows.

The washing machine was not used, and tap water was received in a circular aluminum basin by a manual method, and the top and bottom of the FPS were completely immersed in water. At this time, all 10 sets of FPSs suit were folded in the same way, placed at the same location in the basin, and received the same amount of water. Laundry water was extracted using the following method: one person stepped on the suit and washed it, and the water was extracted by stepping on it for 20 min per FPS. In addition, in the intermediate step between the washing of one suit and the washing of the next suit, the aluminum basin was cleaned and rinsed several times to remove harmful substances from the circular basin. This was done to eliminate the factors affecting the next laundry composition and to increase the accuracy of water analysis. When water is extracted using a washing machine, it may be affected by scale and residual detergent remaining in the existing washing machine. Therefore, the manual method was selected for laundry water extraction. In this study, washing and extracting the water from the laundry was performed in the order of Group 1 to 4.

### 2.6. Measurement and Analysis for Laundry of FPS

In this study, items such as heavy metals on fire protective suits were extracted and analyzed. The measurement and analysis of heavy metals (Pb/Cd/Cu/Fe/Mn/Al/Ni/Co/As) were performed by referring to the method of the US National Institute for Occupational Health and Safety (NIOSH) 7300 (ELEMENTS by ICP). The sample was collected by attaching a 37 mm cellulose ester membrane filter to a 3-piece cassette and connecting it to a high flow pump (CASELLA, TUFF I.S. ENGLAND) at approximately 2 L/min. Furthermore, the sample collection pump performed flow rate correction using a flow rate corrector (DEFENDER, 510-M, Denver, CO, USA) before and after sample collection. The MCE filter from which the sample was collected was injected with 5 mL of $HNO_3$ as a pretreatment solution, incubated on a hot plate, topped off with 10 mL of distilled water, and then analyzed with an inductively coupled plasma emission spectrometer (ICP/OES) (AVIO500DV, PerkinElmer, American Fork, UT, USA). The quality of the sample was confirmed by selecting the wavelength of the heavy metal to be analyzed, such as Pb and Cd, in the device. For quantification, a standard solution was prepared by diluting each substance step by step, and a calibration curve was prepared from this (Appendix A).

The washing water for FPS was analyzed according to the water pollution process test standard. For the analysis of heavy metals such as arsenic (ES 04400.3c), metals inductively coupled plasma atomic emission spectroscopy was applied mutatis mutandis. The analysis method for volatile organic compounds was based on ES 04602.1b. Vinyl chloride, acrylonitrile, and bromoform were based on ES 04603.2b, using the headspace/gas chromatograph mass spectrometry method. Finally, for volatile organic compounds, headspace/gas, chromatographic mass spectrometry was applied mutatis mutandis.

The analysis of heavy metals was performed by adding nitric acid (5 mL) to the sample (45 mL) according to the micro acid decomposition method (ES 04150. 1b), a pretreatment method suggested in the water pollution process test method, and decomposing organic substances and interfering substances by irradiating microwaves under high temperature and high pressure conditions. Analysis was performed using ICP-OES (Agilent-5100). For the analysis of volatile organic compounds, QP-2010Ultra from Shimadzu (Kyoto, Japan) was used.

For analysis, 10 mL of a sample was transferred into a 40 mL vial, and 20 µL of an internal standard solution (10 ng/µL) was added to the sample before analysis using gas chromatography-mass spectrometry (GC-MS) after pretreatment of the headspace by sealing it with a silicone stopper coated with the material. The appendix shows the analysis method for laundry water of the FPSs. As a result of the analysis, the coefficient of determination ($R^2$) value was more than 0.999 for heavy metals and 0.99 or more for volatile organic compounds (Appendices B and C).

The quantification range of volatile organic compounds was set to 1–100 µg/L, and the method detection limit (MDL) of volatile organic compounds was quantified by adding a standard substance at a concentration level of 10 µg/L per item. As a result, all items were measured to be less than 5 µg/L, and all were in line with the goal of performing their quality control.

## 3. Results

### *3.1. Demographic Findings of Detecting and Analyzing Harzadous Substances in FPSs*

In order to further analyze the degree of heavy metal contamination of fire protection suits exposed to the fire scene, fire protection suit laundry water analysis was performed. Of the total 24 analyzed agents, 8 agents were contaminants detected in the laundry water of the fire protection suits.

Barium (Ba) was detected in all four 4 groups of fire protection suits, and the largest amount was detected in Group 3. Copper (Cu) was detected in all 4 groups of fire protection suit, and the largest amount was detected in Group 3. Nickel (Ni) was detected in Groups 2-4, and the largest amount was detected in Group 3. Antimony (Sb) was detected in Groups 3-4, and the largest amount was detected in Group 3. Zinc (Zn) was identified as a heavy metal detected in all four groups of fire protection suits. Acrylonitrile was detected in Groups 3 to 4, and a larger amount was detected in Group 4 than in Group 3. This is a result of a clear dose–response relationship between exposure and outcome (Table 2).

Naphthalene was detected in Groups 3 to 4 of FPSs, and a larger amount was detected in the incomplete combustion fire exposure for Group 3 than for Group 4. Diethylhexylphthalate (DEHP) was detected in all groups of FPSs, and the largest amount was detected in Group 3. The laundry water of FPSs exposed to the fire was classified as wastewater according to the Water Environment Conservation Act (Table 2).

The analysis of the laundry water of FPSs, which was conducted to assess the contamination of these fire protection suits, confirmed that four agents exceeded the standards for wastewater discharge facilities for specific water quality hazardous substances. The four agents that fall under the application criteria for wastewater discharge facilities were identified as Cu, Sb, acrylonitrile, and DEHP (Table 2).

**Table 2.** Results of laundry water analysis on fire protection suits by group distribution.

| No | Type of Pollutant (Unit: mg/L) | G1 | G 2-1 | G 2-2 | G 2-3 | G 3-1 | G 3-2 | G 3-3 | G 4-1 | G 4-2 | G 4-3 | DW | SBR |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Arsenic (As) | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.026 |
| 2 | Barium (Ba) | 0.019 | 0.018 | 0.059 | 0.062 | 0.049 | 0.09 | 0.094 | 0.108 | 0.019 | 0.019 | 0.121 | 0.019 |
| 3 | Cadmium (Cd) | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| 4 | Chrome (Cr) | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.762 |
| 5 | Copper (Cu) | 0.032 | 0.03 | 0.128 | 0.091 | 0.132 | 0.32 | 0.339 | 0.219 | N.D. | N.D. | 0.033 | N.D. |
| 6 | Nickel (Ni) | N.D. | N.D. | 0.024 | 0.028 | 0.024 | 0.086 | 0.133 | 0.066 | N.D. | N.D. | 0.031 | 0.018 |
| 7 | Lead (Pb) | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| 8 | Antimony (Sb) | N.D. | N.D. | N.D. | N.D. | N.D. | 0.087 | 0.096 | 0.052 | N.D. | N.D. | 0.037 | 0.026 |
| 9 | Selenium (Se) | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| 10 | Zinc (Zn) | 0.063 | 0.06 | 0.851 | 0.723 | 0.586 | 2.419 | 3.01 | 2.758 | 0.061 | 0.052 | 0.482 | 0.003 |
| 11 | Vinyl chloride | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| 12 | Dichloroethylene-1.1 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| 13 | Dichloromethane ($CH_2Cl_2$) | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| 14 | Acrylonitrile | N.D. | N.D. | N.D. | N.D. | 0.052 | 0.054 | 0.066 | 0.124 | 0.13 | 0.105 | N.D. | N.D. |
| 15 | Chloroform ($CHCl_3$) | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | 0.014 | 0.008 |
| 16 | Trichloroethene-1.1 | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| 17 | Carbon tetrachloride ($CCl_4$) | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| 18 | 1,2-Dichloroethene | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| 19 | TCE | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| 20 | PCE | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| 21 | Styrene | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| 22 | Bromoform | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. | N.D. |
| 23 | Naphthalene | N.D. | N.D. | N.D. | N.D. | 0.028 | 0.031 | 0.022 | 0.007 | 0.007 | 0.006 | N.D. | N.D. |
| 24 | DEHP | 0.024 | 0.029 | 0.014 | 0.011 | 0.033 | 0.022 | 0.034 | 0.012 | N.D. | 0.01 | N.D. | 0.003 |

G—group; DW—default water; SBR—stainless basin water; N.D.—none detected; TCE—trichloroethylene; PCE—perchloroethylene; DEHP—diethylhexylphthalate.

### *3.2. Results of QA/QC FPS Analysis*

As a result of the analysis, the coefficient of determination ($R^2$) value was 0.999 or higher for heavy metals and 0.99 or higher for volatile organic compounds. The quantification range of volatile organic compounds was set to 1–100 μg/L, and the method detection limit (MDL) of volatile organic compounds was quantified by adding a standard substance at a concentration level of 10 μg/L per item. As a result, all of the items were measured to be less than 5 μg/L, and all of them were in line with the goal of performing their own quality control. The QA/QC results for each analysis item are shown in Table 3.

**Table 3.** QA/QC result of FPS laundry water quality analysis.

| No | Item | LOD (mg/L) | MDL (mg/L) | Accuracy, % | Precision, CV |
|---|---|---|---|---|---|
| 1 | Arsenic (As) | 0.05 | 0.007 | 98.6 | 0.3 |
| 2 | Barium (Ba) | 0.003 | 0.002 | 105.5 | 0.2 |
| 3 | Cadmium (Cd) | 0.004 | 0.001 | 96.7 | 0.3 |
| 4 | Chrome (Cr) | 0.007 | 0.002 | 99.7 | 0.1 |
| 5 | Copper (Cu) | 0.006 | 0.001 | 98.2 | 0.4 |
| 6 | Nickel (Ni) | 0.015 | 0.003 | 98.5 | 0.0 |
| 7 | Lead (Pb) | 0.04 | 0.008 | 95.9 | 0.1 |
| 8 | Antimony (Sb) | 0.02 | 0.010 | 105.6 | 0.4 |
| 9 | Selenium (Se) | 0.03 | 0.005 | 96.5 | 0.6 |
| 10 | Zinc (Zn) | 0.002 | 0.001 | 98.1 | 0.8 |
| 11 | Vinyl chloride | 0.005 | 0.003 | 89.6 | 9.7 |
| 12 | 1,1-Dichloroethene | 0.005 | 0.003 | 89.7 | 8.9 |
| 13 | Dichloromethane | 0.005 | 0.005 | 91.8 | 8.2 |
| 14 | Acrylonitrile | 0.005 | 0.005 | 108.4 | 9.0 |
| 15 | Chloroform | 0.005 | 0.002 | 92.4 | 4.5 |
| 16 | Carbon tetrachloride | 0.005 | 0.004 | 94.5 | 7.0 |
| 17 | Benzene | 0.005 | 0.002 | 90.3 | 4.7 |
| 18 | 1,2-Dichloroethane | 0.005 | 0.003 | 99.9 | 4.1 |
| 19 | Trichloroethene | 0.005 | 0.001 | 92.5 | 5.0 |
| 20 | Tetrachloroethylene | 0.005 | 0.002 | 95.8 | 5.9 |

**Table 3.** *Cont.*

| No | Item | LOD (mg/L) | MDL (mg/L) | Accuracy, % | Precision, CV |
|---|---|---|---|---|---|
| 21 | Styrene | 0.005 | 0.0005 | 100.0 | 3.0 |
| 22 | Bromoform | 0.005 | 0.002 | 102.8 | 4.4 |
| 23 | Naphthalene | 0.003 | 0.0007 | 100.0 | 5.0 |
| 24 | DEHP | 0.0025 | 0.0003 | 111.1 | 0.23 |

LOD—limit of detection; MDL—method detection limit; QA—quality assurance; QC—quality control; CV—coefficient of variation; DEHP—di-(2-Ethylhexyl)phthalate.

### *3.3. Results of Comparison of Items Exceeding the Standards of the Act*

FPS laundry exposed to fire is classified as "wastewater" according to the standards of the Water Environment Conservation Act. In our study, we analyzed the FPS laundry to investigate the contamination status of the FPS exposed to fire. As a result, it was confirmed that four measurement items exceeded the application standards for specific hazardous substances regarding wastewater discharge facilities stipulated in the Enforcement Regulations of the Water Environment Conservation Act. The four detected items corresponding to the criteria for the application of wastewater discharge facilities were as follows: copper and its compounds, antimony, acrylonitrile, and DEHP. Among the four measurement items, acrylonitrile was detected to be 26 times higher than the legal standard concentration. This is the experimental result of continuously exposing the fire protective suit to incomplete (smoke) and complete (smoke) fires. Sb, DEHP, and Cu were measured to be 4.8 times, 4.1 times, and 3.4 times higher, respectively, than the reference concentration in the FPS exposed only to incomplete fires (Table 4, Figure 2).

**Table 4.** Criteria for the application of wastewater discharge facilities for specific toxic substances in water and the maximum concentration in FPS laundry water.

| No | Items | Reference Concentration (A) (mg/L) | FPS Laundry Measured Concentration (B) (mg/L) | B/A (Ratio) | Others |
|---|---|---|---|---|---|
| 1 | Cu | 0.100 | 0.339 | 3.4 times | Group 3-3 |
| 2 | Sb | 0.020 | 0.096 | 4.8 times | Group 3-3 |
| 3 | Acrylonitrile | 0.005 | 0.130 | 26.0 times | Group 4-2 |
| 4 | DEHP | 0.008 | 0.033 | 4.1 times | Group 3-1 |

Cu—copper; Sb—antimony; DEHP—di-(2-Ethylhexyl)phthalate.

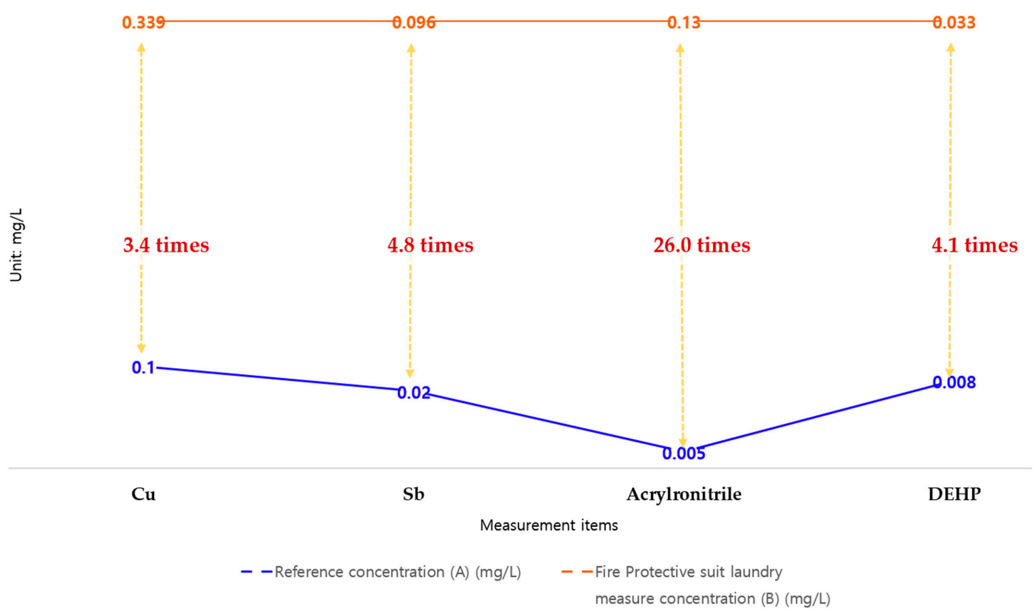


**Figure 2.** Comparison of measurement result and act standard. Cu—copper; Sb—antimony; DEHP—di-(2-Ethylhexyl)phthalate.

## 4. Discussions

### 4.1. Implications for Analysis of Water Extracted from FPS Laundry

There have been few prior studies analyzing the laundry of fire protection clothing exposed to fire. This study has important meaning, since heavy metals (harmful substances) were analyzed by extracting the washing water of FPSs exposed to the fire scene. In addition, it is also meaningful that water analysis was performed on the new fire suits and the fire suits in use, respectively, without exposure to fire. At the time of the experimental design of this study, there were no prior studies. However, according to a recently published study, benzene, toluene, and naphthalene were detected in the washing water of fire suits in smoke-filled fire exposure simulations [25]. In our study, naphthalene was detected in the FPSs from an incomplete combustible fire, among the 24 items for which the washing water was analyzed. In a previous study, due to the exposure to a smoke fire similar to the conditions used in our study, the results of the water analysis are similar to those obtained in our study [25]. Through comparison with a recently published preceding study, we were able to find the commonality that naphthalene, a Group 1 carcinogen, was detected in incomplete combustion fires. It was confirmed that barium, copper, zinc, and DEHP were detected in the new fire suits. In these results, except for DEHP, three identical components were detected using basic substance analysis. In addition, five components of barium, copper, nickel, zinc, and DEHP were detected in the laundry analysis of the fire protection clothing in use.

As a result of the washing water analysis in our study, there were two extraction items that corresponded to the IARC carcinogenic level. One was naphthalene, a Group 2B carcinogen, which was detected to be 11.6 times higher in incomplete combustion smoke fires than in complete flame fires [27]. The other is DEHP, which belongs to carcinogenic Group 2B [28]. It is a liquid component that can cause tears, cough, and throat irritation, if inhaled as vapor. According to the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), DEHP is classified as a substance with a risk of reproductive toxicity, and it is suspected of disrupting sex hormones or damaging the fetus or fertility [28–30]. DEHP was also detected to be 4.1 times higher in Group 3 than Group 4, which was exposed to a smoking fire alone. In addition, in the case of the remaining detection components, except for acrylonitrile, most of them were detected to be higher in the group exposed to only the fuming fire. However, acrylonitrile was detected to be 2.1 times higher in the 4 groups exposed to both smoke and flame fires. In summary, it was confirmed that there were differences in the types and amounts of harmful substances generated according to the type of fire.

### 4.2. Review of Wastewater Generated by Fire Departments

The fire department, the emergency response team, and the 119 safety center wash clothes using a washing machine dedicated to FPS. At this time, it is estimated that the amount of wastewater generated when washing one set of FPS (one top and bottom) is about 70 L. In the results of a survey conducted on firefighters, it was found that on average, they were dispatched to a burning fire 2–3 times per week. Therefore, FPS, other personal protective equipment, and fire water hoses were calculated to receive combustion fire contaminants twice a week, and fire vehicles were cleaned once a week, according to standard procedure. At the time of the experiment, the Seoul Fire Department had 24 fire department emergency response teams and 119 safety centers.

In addition, wastewater from each fire department dispatching department is generated when washing: (1) FPS, (2) other personal protective equipment (SCBA masks, helmets, boots, etc.), (3) water hoses, and (4) fire vehicles. Therefore, for the calculation of the amount of wastewater, if the amount of wastewater generated by the above four routes is calculated, the amount of wastewater generated by each fire department dispatch department can be estimated. First, the amount of wastewater generated through the four routes was calculated by dividing it into the following two types. First, the daily amount of wastewater generated by the emergency response team of about 30 people is calculated to be about 497 L, based on the minimum generation. Second, the daily amount of wastewater generated at the 119 safety center, with about 10 employees, can be calculated to be approximately 179 L.

Korea's regulations on the site and building standards for fire-fighting buildings [31] stipulates the site selection for fire-fighting buildings and the arrangement of government facilities for construction. Only the area for each essential facility is presented, and there are no installation regulations for wastewater purification facilities, so it is proposed that revision is necessary in the future. In contrast, in the NFPA Code, the fire department is constructed by dividing the dispatch route and equipment storage room according to the presence or absence of contamination [32].

Fire experiments and fire suppression training are repeatedly conducted for education and research in each fire department, by means such as the fire service academy. In this case, the water used for experiments and training may also flow into nearby rivers and affect water quality, so it is necessary to prepare for this in the future.

### *4.3. Implications for Reducing Environmental Pollution around Medium to Large Scale Fire Scenes*

Recently, large-scale fires that have to be extinguished for several days, such as the forest fires in Uljin, Gangwon province, and the Coupang Distribution Center in Gyeonggi province, continue to re-ignite. At this time, a huge amount of hazardous substances will not only be generated at the fire scene, but will also contaminate fire protection suits and personal protective equipment. In the case of fires that have occurred in the past, there have been claims that an emergency response system for water pollution is necessary. In the event of a fire of a medium or larger scale near a river, the water used for extinguishing the fire may flow directly into the nearby river. In this case, this is problematic because it can rapidly affect the ecosystem of nearby rivers. However, there are currently no emergency standards for the treatment of fire extinguishing water from fire scenes. It is necessary to follow-up on this issue with future research for the establishment of relevant standards.

Assuming that less than 2000 $m^3$ of wastewater per day is applied, based on the results from a fire that occurred at a solid fuel manufacturing plant in Cheongju, the results measured at one point exceeded the recommended standards in amounts that were 21.7 times higher for COD, 28 times higher for TOC, 1.8 times higher for SS, 5.9 times higher for T-P, and, among the heavy metals, 2.3 times higher for lead. It is determined that the polluted water is considerably diluted by the time it passes through the fishing grounds, but it is a fact that it pollutes and disturbs the ecosystem, and secondarily, it causes harmful substances to be absorbed and accumulated in the soil. In such a case, it will be necessary to prevent the consumption of crops grown in the soil for a specific period of time in order to minimize the human impact. Therefore, it is necessary to establish an emergency response monitoring system at the national or city/province level to minimize secondary damage. It is necessary to prepare standards regarding fires that occur in specific locations near rivers, or regarding fires of a specific scale or larger. It will also be necessary to prepare measures, such as prohibiting eating and drinking potentially contaminated items grown near a fire site, for a certain period by issuing emergency response monitoring and taking administrative measures.

### *4.4. Implications for Environmental Protection and Social Responbility*

Environment, social, governance (ESG) is a non-financial element emerging as the standard for corporate and national management and investment regarding environmental protection, social responsibility, and governance. Environmental protection includes climate change and risks, resource depletion, waste, pollution, and deforestation. The components of social responsibility include human rights (gender, age, work, and family), working conditions (health and safety), employment relationships (union relationships), labor exploitation, and responsible production [33].

Among the three elements of ESG, environmental and social responsibility are concepts that can be applied to the analysis of the FPSs laundry, which is the result of our research.

First, based on the research results, it is necessary to make an active effort to reduce wastewater discharge at the level of the fire agency to protect the water environment. Second, it will be necessary to implement a system, such as emergency response monitoring, to reduce the impact of air and water pollution predicted in the event of a large-scale fire at the national or municipal level. This constitutes protection for the environment, and it should be approached regarding the implications for social responsibility.

### *4.5. Prospects for the Texture of Future Smart High-Tech Fire Protection Suits*

It is common for fire protection suits to be designed according to protective or practical functions rather than aesthetics. In the past, fire protection suit worn by firefighters also use aramid-based materials to reduce the occupational exposure of firefighters to toxic substances at fire scenes. The research published in the Republic of Korea regarding the materials of fire protection suits is all based on the degree of thermal protection performance, and there are few studies on the material of fire protection clothing abroad. In some previous studies on CBRN protective clothing, there was a discussion on the principle and characteristics of the material of the protective clothing and its breathability. However, it is difficult to find a study on the texture of fire protection suits worn at fire scenes. In order to protect the human body, the texture of the fire protection suit should adsorb harmful substances well, but it should have no effect on the wearer's skin. Finally, the development of smart high-tech materials for firefighting and firefighting suits will be necessary in the future to prevent cross-contamination or indirect contamination of fire protection suits exposed to harmful substances generated at the fire scene.

### *4.6. Strengths, Limitations and Further Study*

In this study, it is very encouraging that the washing water for FPSs was analyzed to be only 3.4 to 26 times higher than the standard concentration for 4 items that were classified as specific water quality hazardous substances. Above all, since this study was the result of burning a hypothetical building of less than one pyeong, it is highly likely that it was under-estimated. Therefore, based on the results of this study, the types and quantities of contaminants that can be measured in a fire protection suit exposed to actual fires could be significantly greater. Moreover, our study is the result of an experiment limited to residential fires. In case of fire in places where highly toxic substances exist, such as forest fires, factory fires, hospital fires, and laboratory fires, more types and higher concentrations of hazardous substances would be detected, and this is a topic for future study.

Our study could not evaluate the direct effect of the specific substances detected in the FPS wash water exposed to the fire scene on the actual water quality. However, it was possible to confirm the effect through the fact that the four specific water quality substances exceeded the standard concentrations.

Finally, it can be seen as another limitation that the factors that can affect the contamination of FPS at the fire scene, such as water supply at the fire scene and the type and amount of combustibles, were not taken into account when a temporary building of less than 3.0 m $\times$ 3.0 m $\times$ 2.8 m was burned. However, the current study data will be meaningful for follow-up research based on the analysis of wash water from FPSs exposed to fire. In the case of fire, environmental impact research regarding water and air should be conducted for environmental preservation.

## 5. Conclusions

In a residential fire simulation-based experimental study using a temporary building, we classified pollutants on FPSs exposed to fire into four groups, extracted the wash water from each group, and conducted a water quality analysis. As a result, acrylonitrile showed a higher dose–response tendency after two consecutive exposures than after a single exposure, showing a risk of causing cumulative toxicity in the human body. Naphthalene, one of the Group 1 carcinogens designated by the IARC, was detected at a higher level in the FPSs exposed to incomplete combustion fires. In addition, DEHP, one of the sex hormone-disrupting substances, was also detected to be higher in the fire protective suits exposed to incomplete combustion fires. Due to this exposure effect, it was confirmed that firefighters need to decontaminate at the scene and conduct a thorough body washing after returning from a fire. In addition, as a result of this study, it was confirmed that four items exceeded the application standards for wastewater discharge facilities for specific hazardous substances. It could be estimated that the water quality in Seoul is likely to be affected by repeated spills from several fire departments. Therefore, fire organizations must realize that not only harmful gas filtration and emission purification facilities, but also facilities capable of purifying wastewater are needed. In addition, in the case of a fire where waste water flows into a river from the fire scene, it is likely to have an effect on water pollution in the short and long term, and secondary pollution is to be expected. This study can be utilized to establish countermeasures to reduce the effects on water quality and water pollution caused by water used for fire suppression and FPS laundry. Finally, this study can be used indirectly to establish a monitoring system for environmental and ecosystem (including water quality and soil) conservation measures to prevent secondary contamination and negative health effects for nearby residents in the event of a large-scale fire.

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## Appendix A. Extraction Items and Analysis Method of Washing Water for Fire Protection Suits Exposed to Fire

| No | Agent | LOD (mg/L) | Analysis Method |
|---|---|---|---|
| 1 | As | 0.05 | ES 04406.3a Arsenic-inductively coupled plasma-atomic emission spectroscopy |
| 2 | Ba | 0.003 | ES 04405.2a Barium-inductively coupled plasma-atomic emission spectroscopy |
| 3 | Cd | 0.004 | ES 04413.3a Cadmium-inductively coupled plasma-atomic emission spectroscopy |
| 4 | Cr | 0.007 | ES 04414.3a Chromium-inductively coupled plasma-atomic emission spectroscopy |
| 5 | Cu | 0.006 | ES 04401.3a Copper-inductively coupled plasma-atomic emission spectroscopy |
| 6 | Ni | 0.015 | ES 04403.3a Nickel-inductively coupled plasma-atomic emission spectroscopy |
| 7 | Pb | 0.04 | ES 04402.3a Lead-inductively coupled plasma-atomic emission spectroscopy |
| 8 | Sb | 0.02 | ES 04410.1a Antimony-inductively coupled plasma-atomic emission spectroscopy |
| 9 | Se | 0.03 | ES 04407.2a Selenium-inductively coupled plasma-mass spectrometry |
| 10 | Zn | 0.002 | ES 04409.3a Zinc-inductively coupled plasma-atomic spectroscopy |
| 11 | Vinyl Chloride (VC) | 0.005 | ES 04602.1b Vinyl chloride, acrylonitrile, bromoform-headspace/gas chromatography-mass spectrometry |
| 12 | 1.1-Dichloroethylene | 0.005 | ES 04603.2b Volatile organic compounds-headspace/gas chromatography-mass spectrometry |
| 13 | Dichloromethan | 0.005 | ES 04603.2b Volatile organic compounds-headspace/gas chromatography-mass spectrometry |
| 14 | Aacrylonitrile | 0.005 | ES 04602.1b vinyl chloride, acrylonitrile, bromoform-headspace/gas chromatography-mass spectrometry |
| 15 | Chloroform | 0.005 | ES 04603.2b volatile organic compounds-headspace/gas chromatography-mass spectrometry |
| 16 | 1.1-trichloroethane | 0.005 | ES 04603.2b Volatile organic compounds-headspace/gas chromatography-mass spectrometry |

| No | Agent | LOD (mg/L) | Analysis Method |
|---|---|---|---|
| 17 | Tetrachloromethane | 0.005 | ES 04603.2b Volatile organic compounds-headspace/gas chromatography-mass spectrometry |
| 18 | 1.2-Ethylene dichloride | 0.005 | ES 04603.2b Volatile organic compounds-headspace/gas chromatography-mass spectrometry |
| 19 | Trichloroethylene (TCE) | 0.005 | ES 04603.2b Volatile organic compounds-headspace/gas chromatography-mass spectrometry |
| 20 | Perchloroethylene (PCE) | 0.005 | ES 04603.2b Volatile organic compounds-headspace/gas chromatography-mass spectrometry |
| 21 | Styrene | 0.006 | ES 04610.1 Styrene-headspace, gas chromatography-mass spectrometry |
| 22 | Bromoform | 0.005 | ES 04602.1b Vinyl chloride, acrylonitrile, bromoform-headspace/gas chromatography-mass spectrometry |
| 23 | Naphthalene | 0.003 | ES 04607.1 Naphthalene-headspace/gas chromatography-mass spectrometry |
| 24 | Di-(2-Ethylhexyl)phthalate (DEHP) | 0.0025 | ES 04501.3b Diethylhexylphthalate-gas chromatography-mass spectrometry |

## Appendix B. ICP-OES Analysis Conditions for Heavy Metals

| Type | Condition |
|---|---|
| RF power | 1.2 kW |
| Plasma flow | 15.0 L/min |
| Auxiliary flow | 1.50 L/min |
| Nebulizer flow | 0.75 L/min |
| Pump rate | 15 rpm |

ICP-OES—inductively coupled plasma optical emission spectrometry.

## Appendix C. GC/MS Analysis Conditions for Volatile Organic Compounds

| GC | Condition |
|---|---|
| Capillary column | Rtx-624 (60 m × 0.32 mm × 1.8 um) |
| Oven temp. | 40 °C (7 min), 5 °C/min to 140 °C (5 min), 25 °C/min to 240 °C (3 min) |
| Carrier gas | He, 1.45 mL/min |
| Intel temp. | 250 °C |
| Injection mode | Split (Split ratio: 20) |
| **MS** | **Condition** |
| Ionization | EI mode |
| Measuring | SIM mode |
| Ion source temp. | 200 °C |
| Interface temp. | 260 °C |
| Solvent cut time | 3.5 min |
| Detector voltage | 0.3 kV |

GC—gas chromatography; MS—mass spectrometry; Temp.—temperature; EI—electron ionization; SIM—selective ion monitoring.

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