De-Wipe Investigation report

Assessing the ability of De-Wipe hair and body wash to remove dioxins (PCDD/Fs) and polycyclic aromatic hydrocarbons (PAHs) from hair and skin. Report Number: R/DWS001/D2)

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Production History

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Executive Summary

Aim

The primary aim of this investigation was to undertake laboratory testing to assess the effectiveness of De-Wipe Hair and Body Wash to remove carcinogenic compounds found in industry and in fire debris (PAHs & dioxins) from hair and skin.

Approach

This investigation aims to compare the performance of the De-Wipe Hair and Body Wash against Milli-Q water in a controlled laboratory setting. Two classes of pollutants were investigated: dioxins (PCDD/Fs and polycyclic aromatic hydrocarbons (PAHs). Both are carcinogenic compounds that have been previously identified in fire debris and so pose a potential health risk to the UK fire and rescue services. Wash tests were performed on hair and skin, the wash was extracted and analysed by gas chromatography with tandem mass spectrometry.

Results

The results of this investigation indicate that De-Wipe is highly effective at removing dioxins from skin, and the surface of hair. It should be noted that these are lower bound conservative estimates of the effectiveness and the product may prove even more effective in real life scenarios.

Conclusions

The results of this investigation are highly encouraging and further studies should take place to assess the effectiveness of the De-Wipe Hair and Body Wash in field studies on both skin and hair.

(1) Introduction

Firefighters are exposed to various toxic chemicals, such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), (heavy) metals and various other combustion by-products, both during and while cleaning up after fires (Blomqvist et al., 2007; Baxter et al., 2014; Dobraca et al., 2015; Park et al., 2015). Although the nature and extent of exposure is variable, exposure to compounds such as PAHs and PCDD/Fs have been shown to cause adverse health effects in humans such as increased risk of cancer, reproductive developmental effects, immunosuppression, (ATSDR, 1995; Baxter et al., 2010; Rovira et al., 2010; Shaw et al., 2013; Slezakova et al., 2013; Daniels et al., 2014; Nadal et al., 2016; Oliveira et al., 2017).

Despite the use of protective clothing, firefighters are still exposed to different toxic chemicals that are deposited on their skin and hair. Chemicals, such as PCDD/Fs, deposited on human hair can be absorbed via the skin and can enter the blood stream (Miyabara et al., 2005; Li et al., 2020), therefore it is crucial that contaminants are removed from not only skin but also hair. De-Wipe has previously successfully developed wipes (De-Wipes) to remove harmful contaminants from the skin of firefighters and their PPE (De-Wipe Investigation report: R/DW001/F). In this study, De-Wipe Hair and Body Wash was tested on skin (substitute for human skin) and human hair (donated) to determine whether the effectivity of the Hair and Body Wash at removing PAHs and PCDD/Fs (**Table 1**).

Table 1. Materials and cleaning agents tested within this study, and the number of replicates (x3). Skin was wiped two times with a De-Wipe to remove product. A sample blank (vial) was also run with each set of extractions.

		Product	
		Analytical grade Water	De-Wipe Hair & Body Wash
Sample Type	Skin	x3	x3
	Hair	x3	x3

(2) Methods

Test protocol for skin:

(1) A test area of 5 cm^2 of skin was pre-cleaned with De-Wipe Hair and Body Wash and MilliQ H_20, air dried and subsequently cleaned with hexane.

(2) The surface was spiked with 20 µL of EPA-1613-STK (Wellington Laboratories Inc., Canada) containing 2,3,7,8-substituted chlorinated dibenzo-p-dioxins (PCDDs) and 2,3,7,8-substituted dibenzofurans (PCDFs) and EPA-PAH-STK (Wellington Laboratories Inc., Canada) containing 16 U.S. EPA priority PAHs.

(3) The spiking solutions were allowed to dry for 60 seconds, before applying 0.2 mL of De-Wipe Hair and Body Wash or water (dependant on the treatment). The skin was then washed with 20 mL of milli-Q water (blanks were excluded from the washes). This was repeated 3x.

(4) The surface of the skin was then wiped a 10 cm^2 De-Wipe. The wiping step consisted of wiping across the surface according to the ASTM standard wiping method for PCBs (**ASTM D6661 – 17:** *Standard Practice for field Collection of Organic Compounds from Surfaces Using Wipe Sampling*) and De-Wipe Investigation Report: R/DW001/F. Skin was wiped once with the De-Wipe, the wipe was then folded in half and wiped a second time and immediately transferred into 40 mL EPA certified clean VOA vials where they were spiked with 20 µl of isotope labelled PAHs and dioxins (EPA-1613-LCS and EPA-PAH-LC).

(5) Twenty millilitres of dichloromethane (DCM) and hexane (v/v – 1:1) was added to the glass vial (containing the spiked wipe) and placed in an ultrasonic bath (at 21°C) for 30 minutes.

(6) The solvent mixture was pipetted into a new clean 40 mL EPA certified glass vial using pre-cleaned glass Pasteur pipettes. Eight millilitres of DCM:hexane was added and vortexed for 30 seconds. This step was repeated twice and extracted and vortexed solvent solutions were combined to a final sample with a total volume of 36 mL.

(7) A RapidVap Vertex Dry Evaporator (Labconco, USA) and nitrogen (N_2) was used to concentrate ('blow down') to incipient dryness.

(8) Spiking of solutions with 10 µL internal standard (EPA-1613 and EPA-PAH) were added and topped up with which was topped with toluene to produce a final sample volume of 20 µL.
(9) Analysis of samples was performed by gas chromatography – tandem mass spectrometry (GC-APCI-qqqMS) (Waters Corporation, Massachusetts, USA); at Manchester Metropolitan University (MMU).
(10) QC procedural blanks were also processed to confirm that significant levels of dioxins were not present on the original samples prior to the addition of standards in step 2.

Test protocol for hair:

(1) Hair was pre-cleaned with De-Wipe Hair and Body Wash and MilliQ H_20 and then left to air dry for 24 hours.
(2) The hair was weighed into ~0.7 g sections and cut with steel scissors (pre-cleaned with Milli-Q H_20 and hexane). Hair samples were put into 40 mL EPA certified clean VOA glass vials.
(3) The surface of the hair was spiked with 20 µL of EPA-1613-STK (Wellington Laboratories Inc., Canada) containing 2,3,7,8-substituted chlorinated dibenzo-p-dioxins (PCDDs) and 2,3,7,8-substituted dibenzofurans (PCDFs) and EPA-PAH-STK (Wellington Laboratories Inc., Canada) containing 16 U.S. EPA priority PAHs.
(4) The spiking solutions were allowed to dry for 60 seconds, before applying 20 mL of De-Wipe Hair and Body Wash (1%) or water (dependant on the treatment). Extra care was taken to ensure that the hair was completely submerged in the De-Wipe Hair and Body Wash or water.
(5) The sample was vortexed for 60 seconds and subsequently the De-Wipe Hair and Body Wash and water mixture was discarded, and this step was repeated twice more but with only Milli-Q water (20 mL).
(6) The washed hair was were spiked with 20 µl of isotope labelled PAHs and dioxins (EPA-1613-LCS and EPA-PAH-LC).
(7) Twenty millilitres of dichloromethane (DCM) and hexane (v/v – 1:1) was added to the glass vial (containing the spiked hair) and placed in an ultrasonic bath (at 21°C) for 30 minutes.

(8) The solvent mixture was pipetted into a new clean 40 ml EPA certified glass vial using pre-cleaned glass Pasteur pipettes. The hair was discarded at this point. Eight millilitres of DCM:hexane was added and vortexed for 30 seconds. This step was repeated twice, and then the extracted and vortexed solvent solutions were combined to a final sample with a total volume of 36 mL.

(9) A RapidVap Vertex Dry Evaporator (Labconco, USA) and nitrogen (N_2) was used to concentrate (‘blow down’) to incipient dryness.

(10) Spiking of solutions with 10 μL internal standard (EPA-1613 and EPA-PAH) were added and topped up with 80 μL of toluene to produce a final sample volume of 100 μL

(11) Analysis of samples was performed by gas chromatography – tandem mass spectrometry (GC-APCI-qqqMS) (Waters Corporation, Massachusetts, USA); at MMU.

(12) Additionally, QC procedural blank samples were also processed to confirm that significant levels of dioxins were not present on the original samples prior to the addition of standards in step 3.

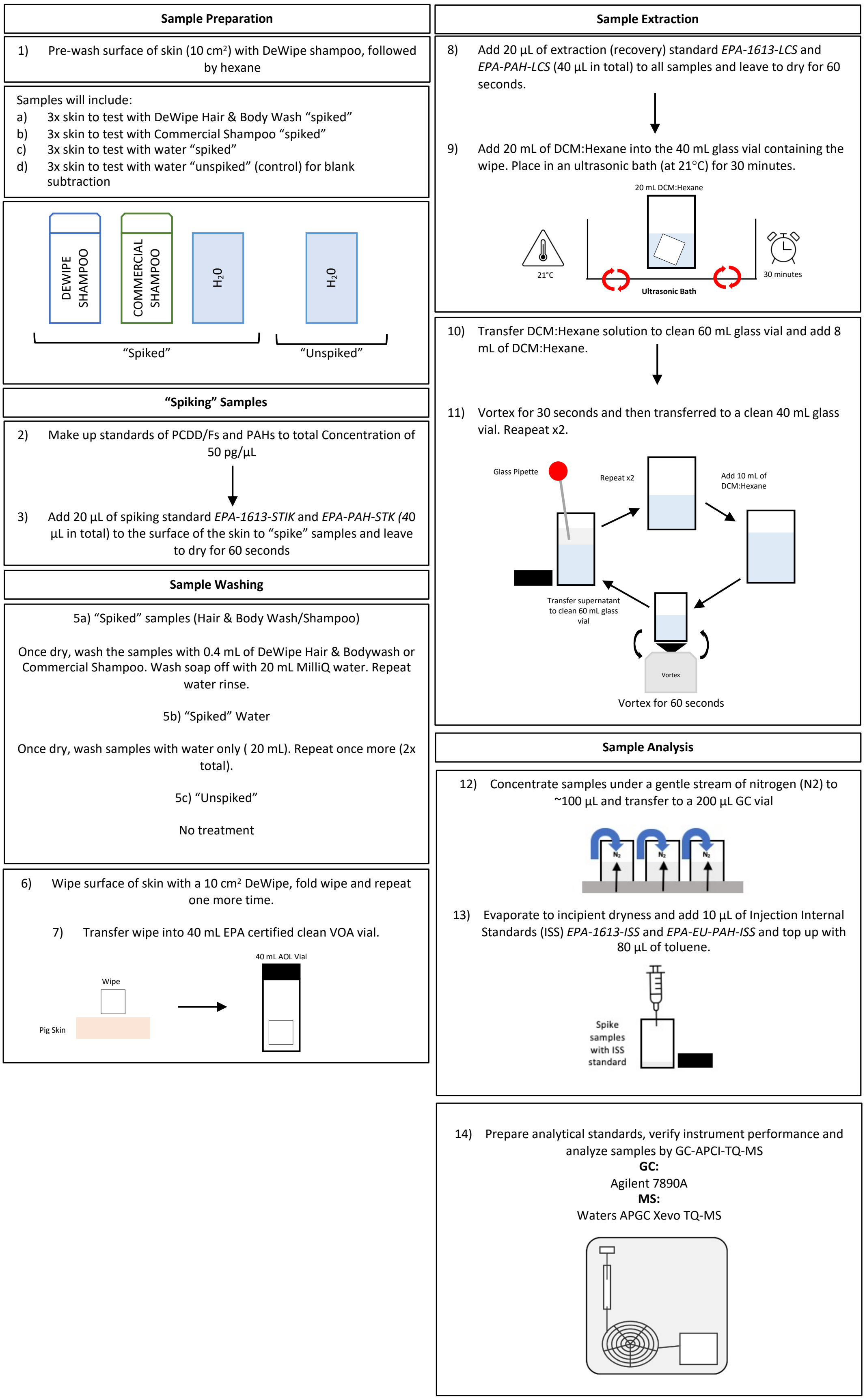

Figure 1. Schematic overview of extraction method for dioxins, furans and PAHs from skin, wiped with a De-Wipe.

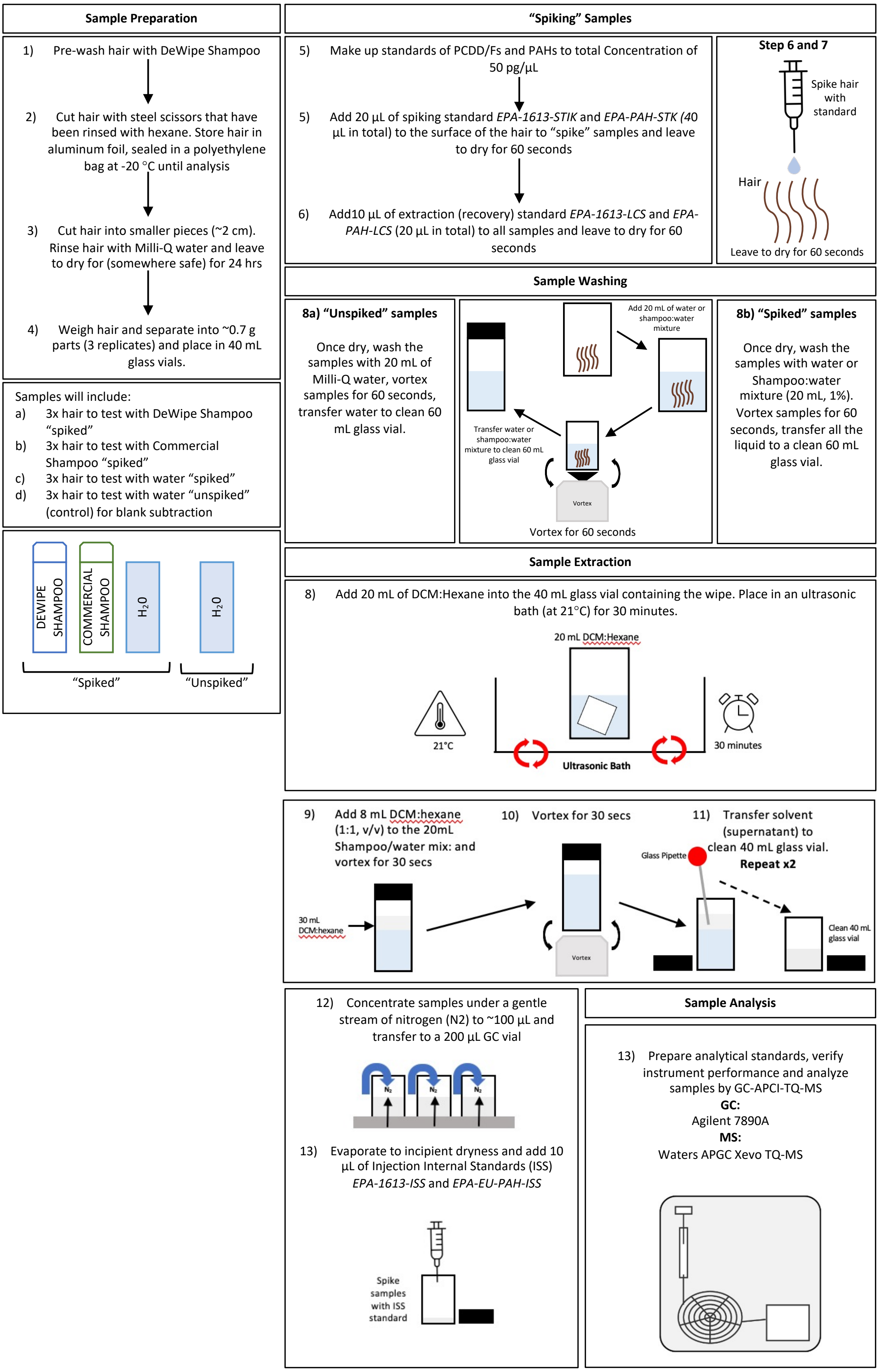

Figure 2. Schematic overview of extraction method for dioxins, furans and PAHs from hair.

(3) Results

Hair and skin extracts were analysed for 17 2378- substituted PCDD/Fs. Seventeen of the 210 PCDD/Fs were targetted as these were the 2378- chlorine subsituted congeners that pose the greatest health risks. Analytical accuracy and precision of measurement for PCDD/Fs was determined by repeated measurement (3 times) of a standard solution containing 87 pg/µL (sum of 17 2378-PCDD/F) resulting in 101% accuracy (± 1.13% SD). **Figure 3** show the concentration of PCDD/Fs determined for each treatment ("spiked", water and De-Wipe Hair and Body Wash) for skin and hair.

The results of this investigation indicate that De-Wipe Hair and Body Wash is effective at removing dioxins from skin. De-Wipe was also effective at removing over half of the dioxins from hair, with water being much less effective. It is important to note that this investigation was conducted on skin and human hair (loose). Therefore caution is advised when extrapolating these results to a real life scenario. It is anticipated that the De-Wipe Hair and Body Wash could be more effective under real life conditions as dioxins that are bound to particulate matter would be removed by the hair and body wash, rather than bound/sorbed directly to the surface of the hair. In addition, it is a challenge to replicate the process of washing hair in a laboratory and so these results represent a conservative lower bound estimate of removal. With constantly running warm/hot water and a more vigeorous washing technique (as would be expected when washing hair under a shower), the products are likely to prove more effective.

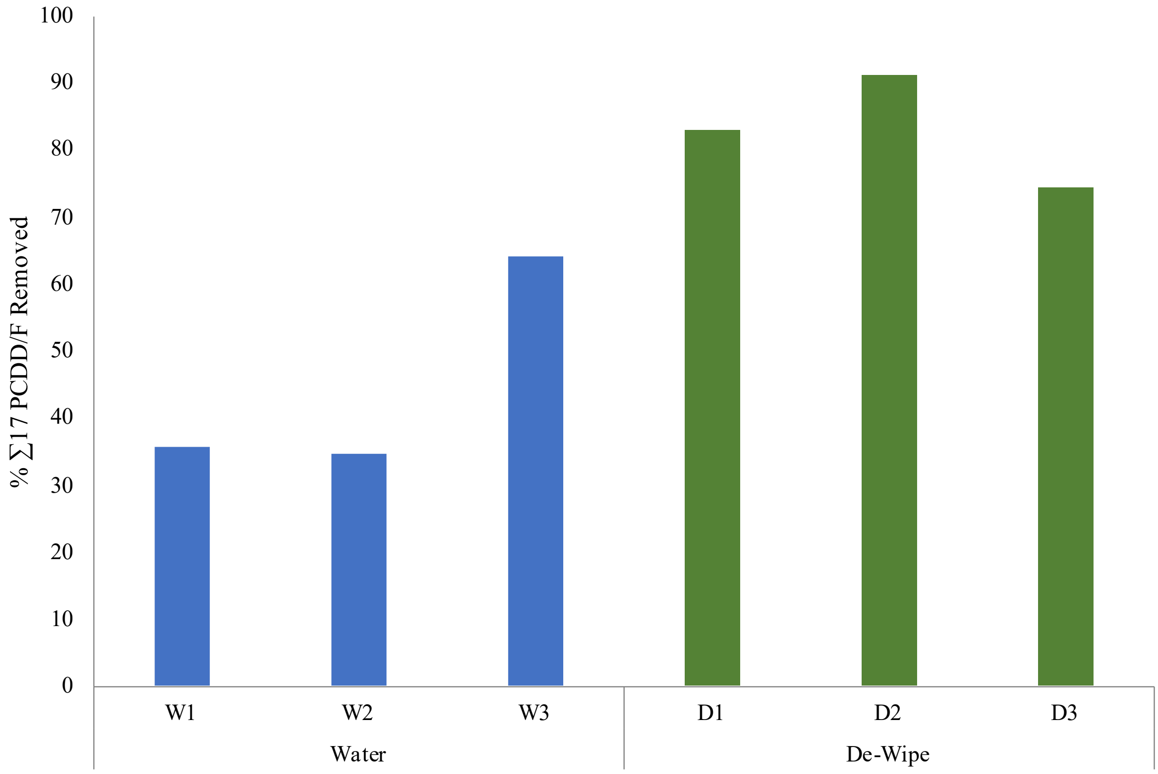

Figure 3. Percentage of PCDD/Fs (sum of 17) determined from skin. PCDD/Fs were removed using water and De-Wipe Hair and Body Wash. Sample blanks were not included in the figure.

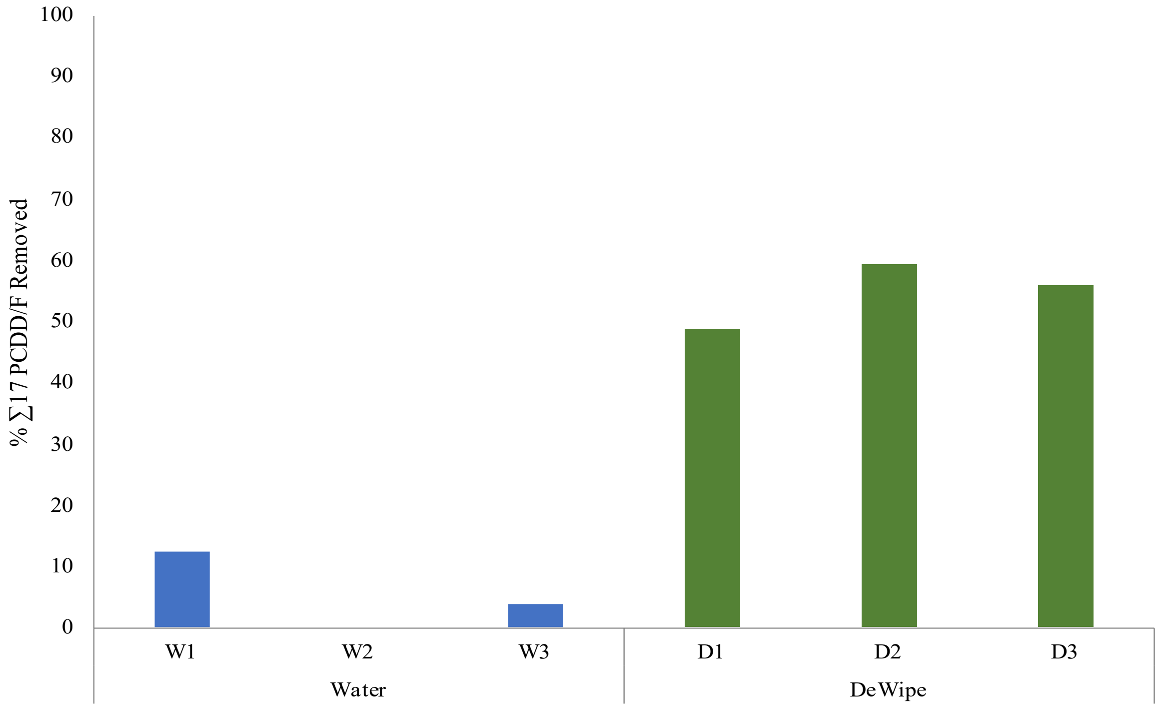

Figure 4. Percentage of PCDD/Fs (sum of 17) determined from skin. PCDD/Fs were removed using: water De-Wipe Hair and Body Wash. Sample blanks were not included in the figure. W2 indicates that no PCDD/Fs were removed from the hair.

(4) Conclusions and Recommendations

The results of this investigation are positive and indicate that De-Wipe Hair and Body Wash is able to remove over 80% of dioxins from skin and, a 1% solution can remove the majority of the dioxins from hair. It should be noted that these are lower bound conservative estimates of the effectiveness and the product may be expected to prove even more effective in real life scenarios. To validate this, further testing could include:

1. Using a more concentrated De-Wipe Hair and Body Wash solution to wash the hair, or use (e.g., 5%, 10%).
2. Testing the De-Wipe Hair and Body Wash under 'real-world' applications, i.e., washing the hair of first responders who have recently been exposed to fire debris.
3. Carry out testing of De-Wipe Hair and Body Wash on other pollutants and assessing the effectiveness at removing particulate matter, such as ash and soot that may contain dioxins and PAHs.

(5) References

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