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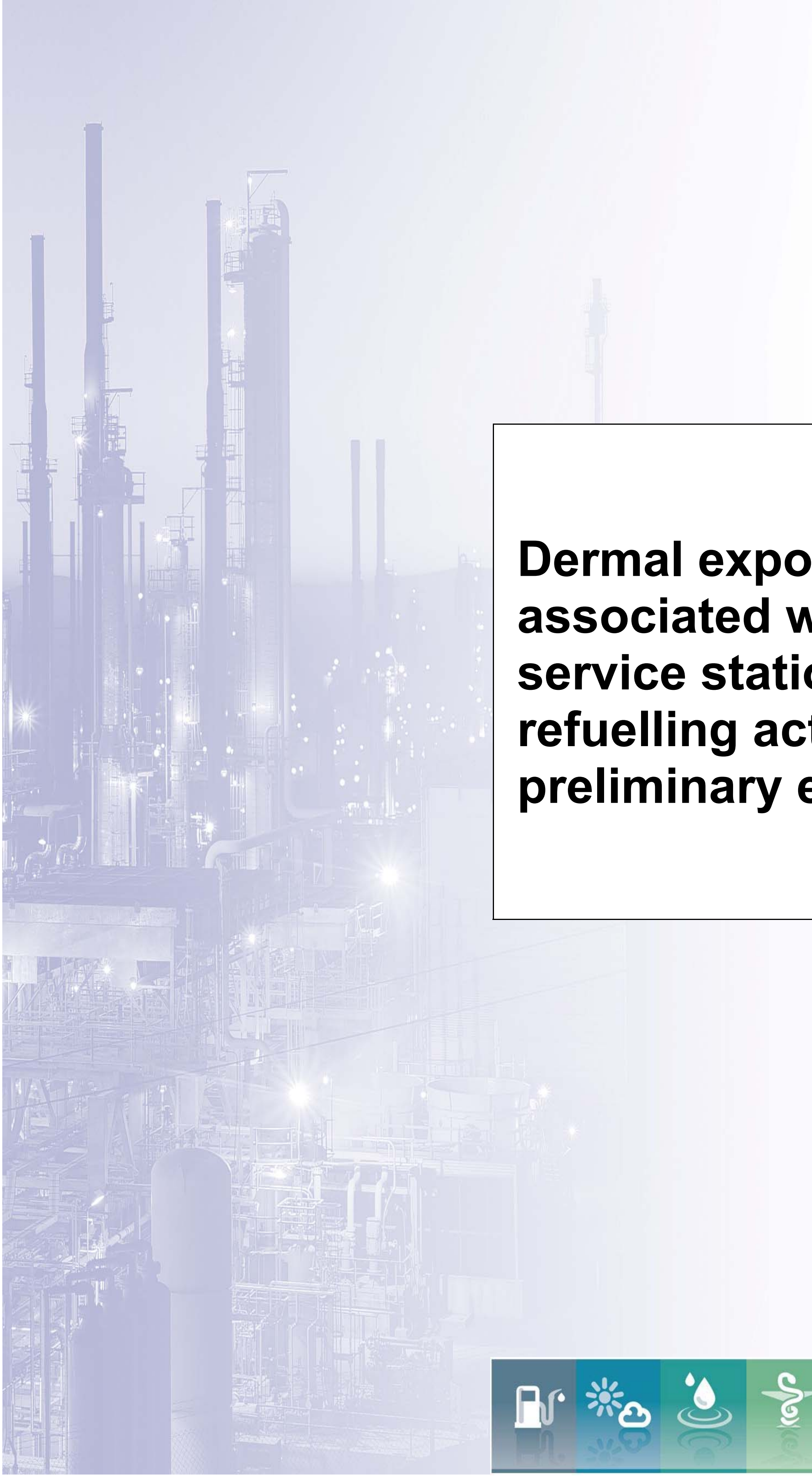

Dermal exposures associated with service station refuelling activities: preliminary evaluation

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Dermal exposures associated with service station refuelling activities: preliminary evaluation

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ABSTRACT

This study investigates dermal exposure to petrol and diesel fuel in service station attendants responsible for the refuelling of automobiles. In phase 1 of the study, six attendants from three service stations wore a carbon patch sample inside and outside their clothing to assess dermal exposure and to evaluate the potential clothing penetration. Hand washing samples were also obtained to assess fuel hydrocarbons on the skin as a result of routine contact with equipment surfaces such as the dispenser nozzle grip, button panel, and dispenser hoses. Dermal exposure to petrol and diesel fuel was also quantified as the amount of individual hydrocarbon congeners ranging from C_6-C_{28}. These determinations were supplemented with benzene, toluene, ethylbenzene, *m*+*p*-xylene, *o*-xylene, methyl *t*-butyl ether, *n*-hexane, and *n*-heptane measurements using gas chromatography with mass selective detection.

The hand wash measurements used to assess skin exposure to the hands form diesel fuel dispensing activities at service stations showed a considerable variability, the concentrations ranged 3,4 - 78 ng for hydrocarbons in the diesel fuel range. Hydrocarbon levels on the hands were compared against the corresponding levels on the dispensing equipment to identify components that could serve as tracers or markers of exposure. The highest correlation coefficient ($r^2 = 0.958$) was observed for the C_{21} hydrocarbon congener which was strongly related to the diesel fuel levels on the hands. Reduced variability was observed when the diesel fuel results were normalised for fuel volumes dispensed by operators during each work shift. Hydrocarbon concentration across the different equipment surfaces was not significantly correlated, except for the button panel and the nozzle grip of the diesel dispenser. The highest correlation coefficient found was for toluene associated with petrol fuel activities for patch samples placed inside or outside the clothing. Due to the small number of samples collected findings are limited and may represent under or over estimates.

Phase 2 of the study assessed the dermal transfer coefficient for C_{14}-C_{28} hydrocarbons from equipment surfaces to the hands. For this study, hand wipe samples were taken at hourly intervals from attendants and separately from equipment surfaces for a period of 4 hours on each of three work days. The dermal transfer coefficient was calculated as the ratio of the hand wipes expressed as ng/hr to the levels on nozzle grips and button panels expressed ng/cm^2. The median value for the twelve measurements was 25 cm^2/hr. This number provides a means of calculating the hydrocarbon load to the hands after measuring C_{14}-C_{28} hydrocarbon levels on an equipment surface.

KEYWORDS

Dermal exposure, fuel stations, hydrocarbons, uptake, equipment surface levels, refuelling, diesel, petrol, dermal transfer coefficient, attendants, patch samples

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SUMMARY

This study contained six specific goals that were satisfied as summarized below.

1. Characterization of the petroleum hydrocarbons present on petrol and diesel dispenser nozzle grip, button panel, and dispenser hoses:
   Results showed all surface wipe samples examined contained petroleum hydrocarbons in the diesel range C_{14}-C_{28}; however, the levels of selected tracers constituents differed depending on the surface. The diesel dispenser nozzle grip results showed the highest values based on the sum value for the tracers and were approximately 20 times higher than results for the button panel. Hydrocarbons on these two surfaces were significantly related, possibly due to the transfer of hydrocarbons from the nozzle grip to the button panel via the hands of the attendants. Hydrocarbons on other surfaces, although significant, did not seem to be attributable to a defined mechanism of transfer.

2. Quantification of hydrocarbon levels on the hands of attendants at the end of the work shift:
   The results showed that diesel fuel and specific hydrocarbon tracers were present on the attendants' hands. Transfer to the hands was dependant on the amount of fuel dispensed during the work shift. The mechanism of transfer was related to hydrocarbons on the equipment surfaces that were subsequently deposited onto the skin. This conclusion was reached after finding a high correlation between the levels on the equipment surface (nozzle grip and button panel) and the levels on the attendants' hands.

3. Assessment to exposure levels to skin surface areas other than the hands:
   This evaluation was performed using sampling patches placed on the forearm and chest. Subsequent analysis showed presence of primarily light hydrocarbon congeners less than C_{12} that were representative of airborne vapour. Heavy hydrocarbon loading of the skin only occurred after contact with equipment surfaces or the direct deposition of liquid aerosols. Sampling patch results indicated that the amount of petrol fuel dispensed during the work shift affected the presence of hydrocarbon measured by the sampling patches for areas other than the hands.

4. Measurement of hydrocarbon levels inside and outside the clothing at the same body location to assess the protective capacity of the clothing worn.
   Based on median values it appears cotton work clothing may reduce hydrocarbon vapor concentrations at skin surface from fifteen to sixty four percent. Results however from two attendants measured higher concentrations under clothing for charcoal chest patch, which suggests that accidental contact with hydrocarbons could have occurred from a localized splash to clothing or from contact with wetted hands or equipment surfaces.

5. Evaluation of the dermal transfer coefficient from equipment surfaces to the skin:
   The dermal transfer coefficient was calculated as the ratio of the hydrocarbon measured by the hand wipe samples to measurements from *surfaces* (nozzle grips and button panels) collected concurrently. A median value of 25 cm^2/hr was determined for the sum of the C_{14}-C_{28} tracers. The dermal transfer coefficient appeared affected by the frequency of contact with the equipment surfaces examined. The dermal transfer coefficient enables potential skin exposures of hydrocarbons to be assessed based on surface sampling results under comparable circumstances.

6. Assessment of the impact that work practices have on dermal exposure levels: None of the attendants wore gloves during the work shift so all measurements were conducted under the same circumstances. Questionnaires administered and observations made during the study indicated that attendants practised good hygiene however hand and clothing wash frequency was found to be highly variable.

1. INTRODUCTION

This study was aimed at (i) characterizing the nature of skin exposures in service station attendants and (ii) identifying measures for managing dermal exposures in this work environment. The measurement of surface residues on workplace equipment allows the identification of potential sources of dermal exposure in service station attendants who regularly dispense petrol or diesel fuel. Similarly, assessing hand deposition is of particular importance since this is the site that would most frequently come into contact with equipment residues when a worker avoids the use of gloves. Since the hydrocarbons present in petrol and diesel fuel may also penetrate protective clothing, it is also important to evaluate the deposition of fuel tracers inside and outside of the clothing. This provides some measure of the protection afforded by use of protective garments under actual work conditions.

The specific goals of the present research are summarized below:

1. to characterize the levels of petroleum hydrocarbons potentially present on surfaces (i.e., petrol and diesel dispenser nozzle grip, dispenser hoses, and button panels);
2. to quantify the hydrocarbon on hands at the end of an attendant's work shift;
3. to assess the hydrocarbon exposures to skin surface for areas of the body other than an attendant's hands;
4. to measure the hydrocarbon levels inside and outside of the clothing in order to evaluate the protective capacity of the clothing being worn;
5. to estimate the dermal transfer coefficient from equipment surfaces to the skin; and,
6. to assess whether different work habits or practices impact dermal exposure levels.

Human exposure via skin contact may occur through a number of different pathways including direct immersion and aerosol deposition. Immersion is the process whereby a skin surface comes into direct contact with a liquid or a gas; it can occur when an attendant wears clothing which have been exposed to a chemical or when the clothing being worn does not provide suitable protection against the chemicals being handled.

Direct skin deposition can be caused by contact with an equipment surface that has been in contact with the fuel. The transfer of a chemical from an equipment surface to unprotected skin is a complex mechanical process that is influenced by factors such as contact pressure, substance affinity for the skin, work practices, and hygienic conditions. Direct dermal transfer is of particular interest with diesel fuels since they contain "heavy" petroleum hydrocarbons that do not readily evaporate and can remain on equipment surfaces. The most affected skin areas are those of the hands and forearms, which often come into direct contact with equipment surfaces; however, transfer to other areas of the skin cannot be entirely ruled out depending on an attendants particular work habits. In addition, it is also important to investigate the potential for dermal exposures due to vapour or liquid penetration through work clothing.

Dermal contact may also contribute to uptake via other routes of exposure. Residual petroleum fractions present on the hands or on the clothing can be unintentionally transferred to eyes, nose, and mouth. To evaluate the relationship between the extent of dermal contact and the degree of surface concentrations of hydrocarbons, it is important to identify the sources of exposure and the mechanisms responsible for the transfer to the equipment surfaces (exposure characterization). The efficacy of any strategies aimed at eliminating or reducing dermal exposure through the use of personal protective equipment should be verified using measurements taken under real working conditions. Actually, the degree of effectiveness for specific chemical or mixture will be influenced by work practices, the hygiene standards that are in force, and by any deterioration that has taken place over time.

In the present study, the techniques used to evaluate dermal exposure to petroleum hydrocarbons from service station operations are based on three sampling approaches. The first technique intercepted the mass transport of the hydrocarbon by collecting the sample onto a medium (cutaneous surrogate) placed on the skin surface or on the clothing for a particular length of time. The second technique used a two-step process involving (i) washing or wiping which removed hydrocarbons from the skin by applying an external force equal to or greater than the force holding the hydrocarbon on the skin surface, and (ii) subsequent analytical measurement of the hydrocarbons collected from the skin surface at the time of sampling. The third technique is only valid for hydrocarbon transfers resulting from direct contact with an equipment surface and uses inferential information measurements of residual hydrocarbon on an equipment surface to make some judgements regarding the dermal load. The ratio between skin deposition rate (ng/hr) and hydrocarbons removed from the surface (ng/cm^2) allows a determination of the dermal transfer coefficient (DTC). The DTC, measured in cm^2/hr, may be affected by the frequency of contact between the skin and a surface. As a result; its usefulness is dependent upon the dermal loading estimate that is derived from the level of surface concentrations of hydrocarbons. Determining a DTC is difficult in service station attendants for the following reasons:

1. attendants may dispense different types of fuels or petroleum products during the same shift;
2. hand loading is the result of direct hydrocarbon transfer from the equipment surfaces as well as ancillary contact with vapours and splashed liquids from all the products being handled;
3. surfaces may contain residual levels of principally with high molecular weight hydrocarbons because the lighter components will evaporate;
4. a single attendant may come into contact with multiple equipment surfaces that possess different surface concentrations.

For these reasons use of this measure in future studies at service stations may be reconsidered.

2. MATERIALS AND METHODS

This study was performed in two separate phases and relied on information collected in two pre-administered questionnaires. The questionnaires were given to either the service station managers or the attendants. The first questionnaire concerned company operations (**Table A1.2**) and the second concerned the attendant's personal characteristics (**Table A1.3**). The questions are shown in Forms 1 and 2 in **Appendix 1**. The weight and height data of each attendant was collected from the personal information requests in Form 2 and subsequently used to estimate the total skin surface area of each attendant.

2.1. TEST SUBJECTS

2.1.1. Phase 1

The first phase of the project identified three different service stations operating in the city of Siena, Italy. Two different attendants were sampled in each service station. The measurements described below were taken at each service station on three different days. The service station and the attendant identification code are shown in **Table 1** together with the shift that was monitored and the volume of petrol or diesel dispensed during the work shift.

At service station number 1, a single attendant was present for each shift, so the same attendant was monitored for the morning shift and the afternoon shift but they were labelled separately. In the other two service stations, only the afternoon shift was monitored since two attendants were always present. All attendants on each sampling day wore clothing that was considered to be clean at the beginning of the work shift.

Table 1 Sampling information for the three service stations examined in this study

Service Station No.	Attendant	Date	Shift	Petrol dispensed (L)	Diesel dispensed (L)
1	1	29.05.2012	13:00-19:00	320	915
	2		7:00-13:00	320	1050
	1	5.6.2012	7:00-13:00	400	1100
	2		13:00-19:00	300	1300
	1	7.6.2012	13:00-19:00	400	1200
	2		7:00-13:00	370	900
2	3	29.05.2012	15:00-19:00	680	1563
	4		15:00-19:00	680	1563
	3	5.6.2012	15:00-19:00	680	1563
	4		15:00-19:00	680	1563
	3	7.6.2012	15:00-19:00	859	1921
	4		15:00-19:00	859	1921
3	5	29.05.2012	1.1.1 15:00-19:00	1.1.2 786	1.1.3 509
	6		15:00-19:00	786	509
	5	5.6.2012	15:00-19:00	760	480
	6		15:00-19:00	760	480
	5	7.6.2012	15:00-19:00	795	658
	6		15:00-19:00	795	659

2.1.2. Phase 2

Only one of the service stations from phase 1 was monitored in phase 2 and only one attendant participated, but the attendant was not the same individual who was examined in phase 1. The sampling was performed as described below in section 2.2.2 during an afternoon shift on three different days: 12 September 2012, 18 September 2012, and 24 September 2012.

2.2. HYDROCARBON SAMPLING

2.2.1. Patch samples – phase 1

To assess dermal exposure to areas of the body other than the hands, activated carbon cloth patches were prepared that could be later analysed in the laboratory. The patches were placed in contact with the skin on the right forearm of right-handed attendants. For left-handed attendants, the patches were placed on the left forearm. If the attendants wore a long-sleeve shirt, another patch was placed over the garment. The patch on the garment was slightly offset from the patch on the skin surface to avoid occlusion; thereby allowing the protective efficiency of the clothing to be measured. If the attendant wore a short-sleeved shirt, one patch was placed on the forearm and two patches were placed on the chest. One of the chest patches was in contact with the skin and the other on top of the clothing. Each attendant therefore received a minimum of 2 or a maximum of 3 patches.

The patches had an exposed surface diameter of 37 mm and were composed of three layers of carbon cloth cut into a circular shape. They were supported by an aluminium sheet mounted on a piece of polyethylene. At the end of an exposure period lasting an entire work shift, the patch composed of three layers of carbon cloth was analysed. The sequence of operations used to prepare the patches is shown in **Figure 1**, whereas the handling of the patches after the exposure period is shown in **Figure 2**.

Figure 1 Laboratory assembly of the patch samples

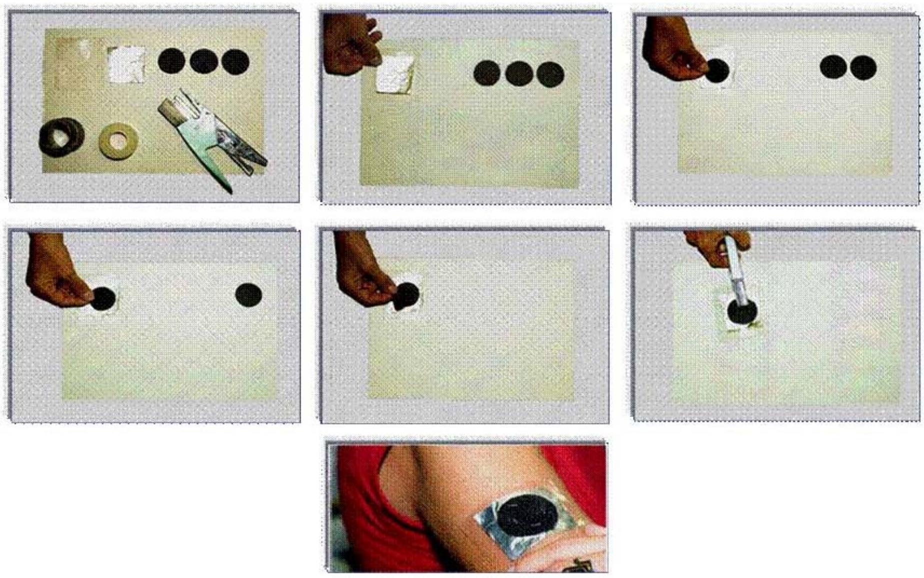
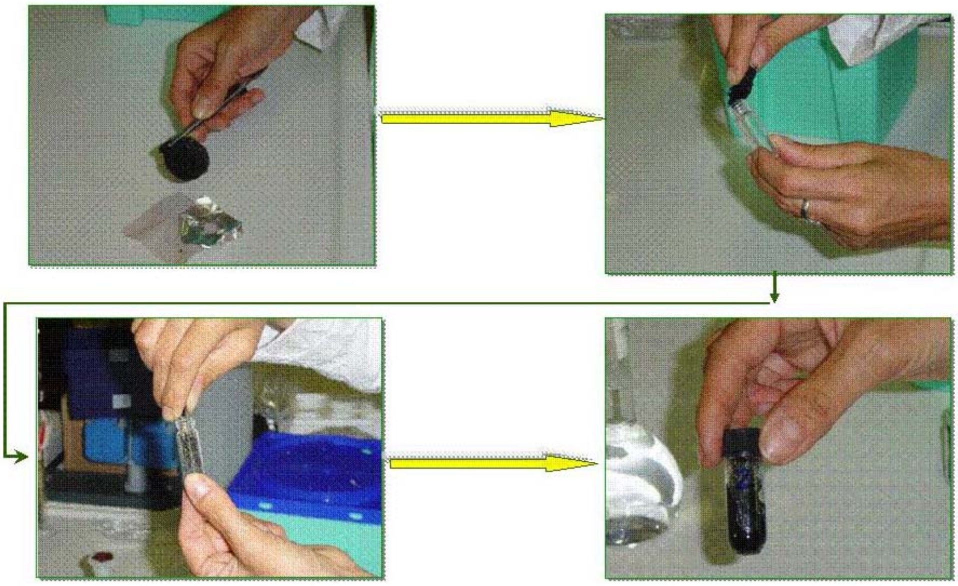


Figure 2 Laboratory handling of the patch samples following exposure



The load of hydrocarbons on the hands was measured by a thorough washing with 150 ml of ethanol over both hands at the end of the shift or prior to breaks when the attendants routinely washed their hands (e.g. before going to the bathroom or before lunch). The ethanol washings from each attendant were collected into a single container whose hydrocarbon content was subsequently measured. Since light hydrocarbons evaporate from the skin surface, the results may be biased toward the heavier hydrocarbons Hand-washing was the preferred approach and it was impractical to place patch samples on the hand surface given the tasks required to be performed.

2.2.2. Surface wipe samples – phase 1

A surface wipe method removal scheme was used to evaluate the attendant's potential skin exposure from equipment surfaces. The surfaces sampled were the petrol hose, diesel hose, nozzle grip of petrol dispenser, nozzle grip of diesel dispenser, and button panel. Sampling was performed at the end of the shift using two 10 x 10 cm non-woven TNT gauze sponges impregnated with dichloromethane. The surface area that needed to be sampled was estimated so as to provide detectable results in the ng/cm^2 concentration range. For the button panels, an area of 400 cm^2 was sampled, for petrol and diesel nozzle grips 600 cm^2, and for diesel and petrol hoses 535 cm^2, which was equivalent to a 50 cm length of hose that was about 5 cm in diameter. To estimate the surface sampled from the nozzle grips we took as a reference the area for the palms of the hands. Assuming that an average total skin surface area is about 19,000 cm^2 and that two hands represent 5.6% of the total skin surface (1064 cm^2), we estimated that the grip of a nozzle is about 60% of the surface of the two palms or about 600 cm^2.

2.2.3. Hand wipe samples - phase 2

To assess presence of hydrocarbons on the hands, a wipe test was used. Samples were collected every 60 minutes to the end of the work shift using two 10 x 10 cm non-woven TNT sponges impregnated with ethanol. At the same time as the two hands were wiped, the equipment surfaces (petrol hose, diesel hose, nozzle grip of gasoline dispenser, nozzle grip of diesel dispenser and button panels) were also wipe sampled using same technique described for Phase 1. At regular intervals of time, the total number of litres of petrol and diesel dispensed by the fuel pumps was recorded. The volume reported was that dispensed by the attendants sampled. Volume dispensed by customer self service was not included.

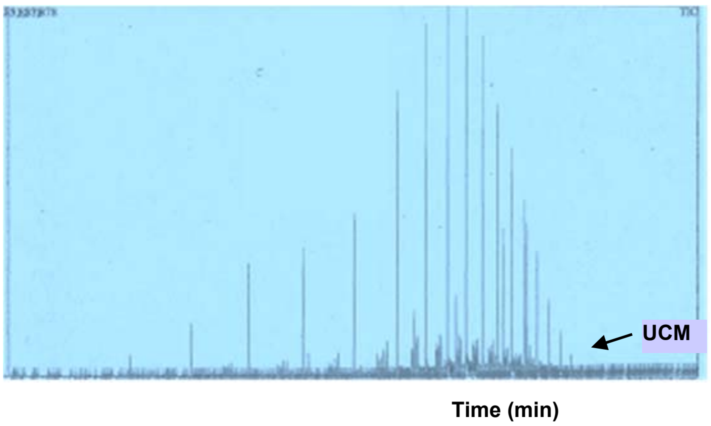
In this phase of the study the recovery efficiency associating the surface wiping method, and the fuel evaporation rate after a 4 hour time interval were also evaluated.

2.3. SPECIMEN ANALYSIS AND EXPRESSION OF RESULTS

Sample analysis was performed by means of gas chromatography using a mass selective detector operated in full scan mode (m/z 40 to 400), using deuterated *o*-xylene as an internal standard. There is no standard method for analysis of gasoline and gas oil range hydrocarbons from the same sample. The choice of xylene was derived from the need of having a peak that would be detected later than n-hexane (the standard used in gasoline analysis). Test samples were analysed for benzene, toluene, ethylbenzene, *m,p*-xylene, *o*-xylene, MTBE, and straight chain hydrocarbons ranging from C_6 to C_{28}. Quantitation of these individual tracers was accomplished using calibration curves prepared using known amounts of each chemical.

Results expressed as diesel and petrol fuel levels were based on calibrations curves prepared with differing amounts of bulk fuel samples from the service stations sampled which were compared to the internal laboratory stock fuel that served as standard. These differing calibration techniques yielded different sets of information that are comparable by applying a linear regression analysis. A total ion chromatogram (TIC) such as the one depicted in **Figure 3** was generated for all samples. This type of chromatogram is capable of resolving the individual hydrocarbons as distinct peaks that lie upon many unresolved peaks that will not be quantified individually but will contribute to the total diesel fuel level.

Figure 3 Example of a tracer chromatogram showing hydrocarbons up to C28 and the total ion chromatograph for a diesel fuel showing the typical diesel profile and the unresolved peaks



In the following study, the hydrocarbon results were reported as were the sum of specific tracers (benzene, toluene, ethylbenzene, m,p,o-xylene, MTBE and straight chain hydrocarbons ranging from C6 to C28) and the sum of the same hydrocarbons up to than C_{12} benzene, toluene, ethylbenzene, m,p,o-xylene, MTBE and straight chain hydrocarbons ranging from C6 to C28) . **Table 2** defines and explains these measurement terms in greater detail and provides a basis for understanding their relevance. Unlike the vapour samples used for individual tracer analysis, the TIC for samples that have contacted a liquid or aerosol will display a UCM (Unresolved Complex Mixture) hump. The contribution of the hydrocarbons in the UCM hump are excluded the total hydrocarbon tracer measurements and included in the diesel and petrol measurements.

Table 2 Types of measurements performed and their underlying characteristics

Measurement	**Type of sample (physical form)**	**Calibration standard**	**Ion chromatograph appearance**		**Peaks examined**
			Resolved peaks	**Unresolved peaks**	
individual tracers, sum of all determined tracers, sum of all determined tracers up to C12	All sampled (vapour, liquid and aerosol)	pure aromatics and alkanes C_6-C_{28}	found	not found	individual tracer peaks
diesel fuel	Hand washing samples (liquid and aerosol)	diesel fuel	found	found (included)	sum all resolved and unresolved peaks (C_8-C_{28})
petrol fuel	Patch samples (vapour, liquid and aerosol)	petrol fuel	found	found (included)	sum all resolved and unresolved peaks (C_6-C_{14})

Since diesel fuel contains a higher percentage of non-volatile or semi-volatile tracers (C_8-C_{28}) than petrol, the diesel fuel calibration curve was used to examine the hydrocarbon content in the ethanol hand washing samples, which reflect contact with a liquid fuel. In contrast, the petrol fuel calibration curve was used for the patch samples that had adsorbed the volatilized hydrocarbon vapours (C_6-C_{14}) released into the air.

2.3.1. Patch sample analysis

Immediately after sampling, the patch samples were extracted with 2 ml of carbon disulfide containing the internal standard. The samples were then stored at a temperature of -20°C until the chromatographic analysis was performed. Quantitative determination of the individual hydrocarbon tracers was performed by preparing a calibration curve that involved the use of blank patch samples containing known mass amounts of each hydrocarbon ranging from about 3 to 80 µg/sample. The limit of quantification (LOQ) was 0.5 µg/sample for all hydrocarbon tracers. The results from the patch samples were also expressed as petrol fuel by preparing a separate calibration curve using blank patches containing known volumes of a petroleum fuel whose density had previously been determined. The resulting LOQ using the petrol calibration curve was 10 µg/sample. The calibration curve used to analyse the test samples depended on the amount of light hydrocarbons present on patches. The final hydrocarbon determination was performed after subtracting the values for field blanks collected on the same day. The results for the patches were expressed in µg/cm^2

using a value of 10.75 cm^2 for the patch surface area (37 mm diameter circular patches).

2.3.2. Wipe test analysis

Immediately after sampling, the moist specimens were placed in a capped glass container and maintained at a temperature of -20 °C until the beginning of the analysis. At that time, the samples were extracted twice with 20 ml portions of dichloromethane by placing the sample in an ultrasonic bath for 20 minutes. The recovered dichloromethane was evaporated down to approximately 1 ml and the internal standard was added before analysis by gas chromatography. The quantification was carried out by preparing a calibration curve using scalar amounts of each hydrocarbon at levels ranging from about 3 to 100 µg/sample. The final results were adjusted for both extraction efficiency and wiping efficiency. In addition, a blank correction was performed by subtracting the hydrocarbon levels found on field blanks collected on the same day as the samples. The LOQ was 2 µg/sample for the C_9, C_{10}, C_{11}, and C_{12} congeners, 1 µg/sample C_{13} and C_{14}, and 0.5 µg/sample for all of the remaining congeners. All results were expressed as µg/cm^2 which took into consideration the equipment surface area that was examined.

2.3.3. Hand washing analysis

Immediately after sampling, the ethanol wash was collected in a glass container with a screw cap and kept at a temperature of -20 °C until the analysis was performed. Quantitative determination of individual hydrocarbons was done by preparing a calibration curve in ethanol using known amounts of each hydrocarbon at levels ranging from about 3 to 100 µg/sample. The LOQ for the individual congeners was the same as the values for the wipe test samples. Measurements were also expressed as the diesel fuel level based on a calibration curve prepared using known quantities of a fuel with a known density. These results were expressed as diesel fuel because the heavier and less volatile hydrocarbon tracers were found to prevail on the hand samples. The LOQ for this method was 10 µg/sample. The results from the hand washing samples were expressed as µg/hands and took into account the total volume of liquid recovered per single wash. Samples were diluted if they showed concentrations higher than the maximum value of the calibration curve.

2.4. DATA ANALYSIS

2.4.1. Wiping efficiency

To evaluate the efficiency of surface wiping technique, six 100 cm^2 flat aluminium trays were employed. After thorough cleaning using dichloromethane, 50 µl of diesel fuel was deposited onto the surface. The trays were then immediately wipe tested with a gauze sponge as described above. The test samples were the analysed for hydrocarbon content in the same manner as the phase 2 samples from the attendants and equipment surfaces.

Wiping efficiency may be affected by the type of surface sampled, the properties of the chemical on the sampled surface, the matrix in which the sampled mixture is dissolved, and the type of sampling method. Since an evaluation could not be performed on every type of equipment surface due to cost considerations, a standardized approach was adopted for all surface types. The wiping efficiency was evaluated using diesel fuel because of the rapid volatilization that occurs when petrol is present on an equipment surface. The results of the wiping efficiency measurements are shown in **Table 3**. The values shown have been used as correction factors to adjust the individual tracer measurements. In addition, the wiping efficiency values were also used to correct the hand washing measurements from Phase 2 since it was not practical or reasonable to deliberately expose the hands of the attendants to obtain a more direct determination. Overall, the surface removal efficiencies were generally very high with values ranging from about 75-85% for most hydrocarbons with a carbon number greater than C_{12}.

Table 3 Wiping efficiency of individual hydrocarbons present in diesel fuel

Hydrocarbon	Wiping efficiency expressed as a percentage
MTBE	Not present in diesel fuel
benzene	Not present in diesel fuel
toluene	32.4
ethylbenzene	35.7
m+*p*-xylene	40.9
o-xylene	47.4
C_6	Not present in diesel fuel
C_7	Not present in diesel fuel
C_8	19.1
C_9	19.7
C_{10}	43.0
C_{11}	60.6
C_{12}	73.7
C_{13}	80.6
C_{14}	84.6
C_{15}	85.1
C_{16}	81.9
C_{17}	80.8
C_{18}	78.3
C_{19}	77.9
C_{20}	77.9
C_{21}	76.8
C_{22}	76.5
C_{23}	75.5
C_{24}	77.7
C_{25}	75.6
C_{26}	75.4
C_{27}	83.1
C_{28}	65.1

2.4.2. Hydrocarbon evaporation rates

To assess the extent of evaporation, twelve flat aluminium trays were utilized. After cleaning the surfaces using dichloromethane, 50 µl of diesel or petrol fuel were deposited onto the surface. After 4 hours, the remaining liquid hydrocarbons were collected using the wipe test procedure described above. The test samples were subjected to the same analytical method used with the attendant and equipment samples.

The results shown in **Table 4** confirm that the lightweight hydrocarbons readily evaporate. The values have not been used to develop an adjustment factor since the length of time between surface concentration and wipe testing cannot be accurately determined for the test samples. However, the results show that the C_{16}-C_{28} hydrocarbons evaporated by 20% or less over the 4 hr period, which confirmed that they were suitable for use as non-volatile tracers.

Table 4 Percent evaporation of individual hydrocarbons present in petrol and in diesel after a 4-hour length of time

Hydrocarbon	Diesel matrix (%)	Petrol matrix (%)	Average (%)
MTBE	-	100.0	100.00
benzene	-	100.0	100.00
toluene	53.5	99.6	76.55
ethylbenzene	100.0	100.0	100.00
m+*p*-xylene	100.0	100.0	99.98
o-xylene	100.0	100.0	99.99
C_6	100.0	-	100.00
C_7	100.0	100.0	100.00
C_8	100.0	100.0	100.00
C_9	93.1	99.3	96.19
C_{10}	100.0	93.6	96.79
C_{11}	99.4	99.0	99.17
C_{12}	95.1	88.8	91.95
C_{13}	78.6	85.1	81.88
C_{14}	53.3	46.5	49.88
C_{15}	31.7	43.0	37.35
C_{16}	23.7	-	23.67
C_{17}	18.4	-	18.44
C_{18}	11.5	-	11.54
C_{19}	9.5	-	9.49
C_{20}	11.0	-	11.02
C_{21}	7.4	-	7.44
C_{22}	7.4	-	7.38
C_{23}	9.4	-	9.40
C_{24}	7.4	-	7.37
C_{25}	9.9	-	9.91
C_{26}	8.2	-	8.22
C_{27}	26.6	-	26.63
C_{28}	0.0	-	0.00

2.4.3. Body surface area

For each attendant, the dermal contact on areas other than the hands was determined using a variety of metrics for both the individual tracers, diesel and petrol fuel measurements and total petroleum hydrocarbon levels found on the patches samples. Details regarding these calculations are provided in **Appendix 1**.

2.5. STATISTICAL ANALYSIS

Values below the LOQ level were entered as zero. Parametric linear regression and Student's t-test for paired and unpaired samples were used to evaluate the data. The significance level was set at $\alpha=0.05$.

3. RESULTS

3.1. CHARACTERISTICS OF MONITORED SERVICE STATIONS

The operating characteristics of the three service stations are described below in **Table 5**, **6**, and **7** as determined by the responses to the first questionnaire described in **Table A1.2** of **Appendix 1**.

Table 5 Description of the operating characteristics for service station number one

Station 1				
Types of fuels dispensed	Unleaded petrol YES	Diesel YES	LPG NO	Other (specify) --
Number of pumps dispensers per fuel type	Unleaded petrol 4	Diesel 2	LPG --	Other (specify) --
Work shifts with service	2			
Number of employees per shift	1			
Self-Service	YES			
Average daily activity	number of petrol vehicles 30-40	number of diesel vehicles 60-80	number of LPG vehicles --	large lorries and heavy vehicles Data not available
Fuel dispensed on average per day	Unleaded petrol 300-400 litres	Diesel 900-1000	LPG --	Other (specify) --
Other activities besides fuel sales	Bar/Restaurant Bar	Sale of car accessories YES	Car Wash NO	Other (specify) Tire and oil level inspection

Table 6 Description of the operating characteristics for service station number two

Station 2				
Types of fuels dispensed	Unleaded petrol YES	Diesel YES	LPG NO	Other (specify) --
Number of pumps dispensers per fuel type	Unleaded petrol 2	Diesel 2	LPG --	Other (specify) --
Work shifts with service	2			
Number of employees per shift	2			
Self-Service	YES			
Average daily activity	number of petrol vehicles Data not available	number of diesel vehicles Data not available	number of LPG vehicles --	large lorries and heavy vehicles Data not available
Fuel dispensed on average per day	Unleaded petrol 1500-1600 litres	Diesel 1000-1100 litres	LPG --	Other (specify) --
Other activities besides fuel sales	Bar/Restaurant NO	Sale of car accessories NO	Car wash NO	Other (specify) Tire and oil level inspection

Table 7 Description of the operating characteristics for service station number three

Station 3				
Types of fuels dispensed	Unleaded petrol YES	Diesel YES	LPG NO	Other (specify) --
Number of pumps dispensers per fuel type	Unleaded petrol 8	Diesel 8	LPG --	Other (specify) --
Work shifts with service	2			
Number of employees per shift	2			
Self-Service	YES			
Average daily activity	number of petrol vehicles 150	number of diesel vehicles 300	number of LPG vehicles --	large lorries and heavy vehicles Data not available
Fuel dispensed on average per day	Unleaded petrol 2500-3000 litres	Diesel 6000-6500 litres	LPG --	Other (specify) --
Other activities besides fuel sales	Bar/Restaurant Bar	Sale of car accessories YES	Car wash YES	Other (specify) Tire and oil level inspection

The average age of the attendants examined in this study was 27.8 ± 5.8 years. None of the attendants used gloves during the work shift and two the six attendants sampled reported to be non-smokers. The number of times that the attendants reported to wash their hands during the shift was extremely variable and ranged from 1 to 10. Only one attendant reported to have experienced work-related skin irritation on the hands in the past. Two attendants reported hand cream use especially after a work shift in the winter season. Hand cream was not applied during hand wash or wipe sample intervals Questionnaire response indicated that clothing was removed daily and taken home after the work shift. Work clothes were washed at least once a week but in some cases they were washed daily.

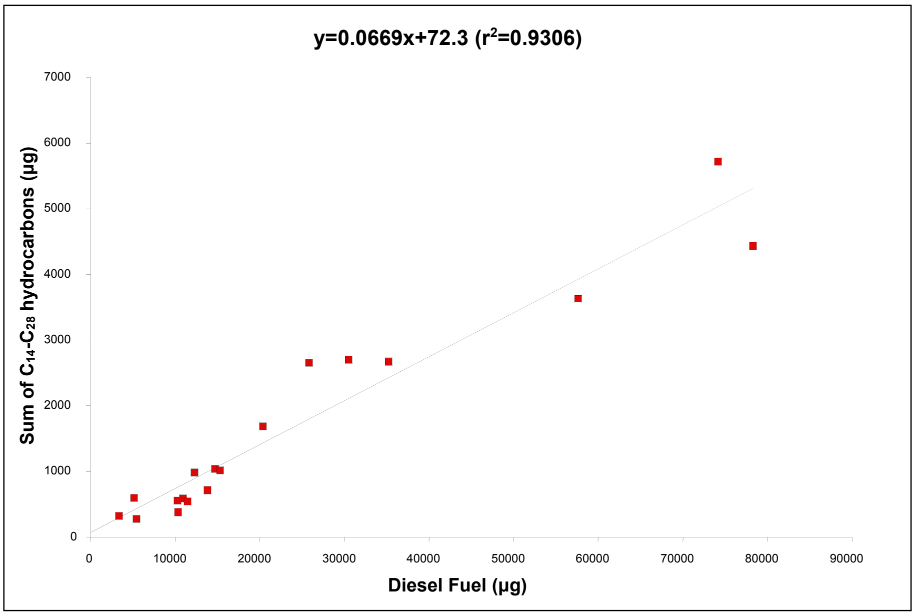
3.2. IDENTIFICATION OF SIGNIFICANT TRACERS

Specific standardized petroleum tracers are not available as exposure markers for service station attendants. As such, it was not possible to define a standard mixture of petroleum components that could be used as a reference for examining surface concentration and dermal contact. Consequently, a methodology was needed that expressed the results from patch and hand washing samples as a single petroleum fraction that was suitable for both petrol and diesel and capable of accounting for the simultaneous exposure to both petroleum products. A search of the scientific literature revealed an identification scheme that could be applied to complex mixtures that could not be fully characterized. It included the selection of a number of representative hydrocarbon tracers that were characteristic of the entire mixture.

Since attendants mainly handled petrol and diesel fuel in the present study, we identified the following tracers for patches and for hand washing samples: benzene, toluene, ethylbenzene, *m,p*-xylene, *o*-xylene, methyl *t*–butyl ether (MTBE), and all of the straight chain hydrocarbons from C_6 to C_{28}. These tracers are present in the fuels dispensed at the three workplaces examined.

The feasibility of using these tracers for hand washing samples was evaluated by examining the association between these tracer measurements and diesel fuel levels using a linear regression analysis. The results, depicted in **Figure 4**, show that the levels in diesel fuel are related to the amounts in hand washing samples when the results are expressed as the sum of tracers from C_{14}-C_{28}. The results of the regression analysis indicate that using the sum of tracer levels is highly representative of diesel fuel since a coefficient of determination (r^2) of 93% was obtained. The slope of the regression equation (y=0.0669x+72.3) indicates that the sum of the C_{14}-C_{28} tracers was about 7% of the diesel fuel levels on average. Each individual fuel tracer was subsequently examined to determine if the strength of the relationship was higher for some tracers than for others.

Figure 4 A linear regression analysis comparing diesel fuel levels with the sum of C_{14}-C_{28} hydrocarbon tracers in hand washing samples



As shown in **Table 8**, the highest correlations were obtained with hydrocarbons C_{17} through C_{21} along with hydrocarbon C_{23}. Among these, the best marker in terms of reliability is C_{21} because it showed the highest correlation coefficient and accounted for 0.9% of the diesel fuel level based on the slope of the regression equation. The heavier hydrocarbons were present in higher quantities in hand samples than diesel fuel samples which may and may have due to the handling of other petroleum products such as engine oils and lubricants and may have introduced some bias to the results.

Table 8 A linear regression analysis comparing diesel fuel levels with individual hydrocarbons tracers in hand washing samples

Hydrocarbon	Equation	r^2	Statistical significance (p)
C_{14}	-	-	Non significant
C_{15}	y=0.00097x+0.966	0.459	Significant ($p<0.002$)
C_{16}	y=0.0019x+7.46	0.761	Significant ($p<0.0001$)
C_{17}	y=0.0055x-12.98	0.929	Significant ($p<0.0001$)
C_{18}	y=0.0089x-20.62	0.946	Significant ($p<0.0001$)
C_{19}	y=0.0087x-20.62	0.930	Significant ($p<0.0001$)
C_{20}	y=0.0079x+23.64	0.951	Significant ($p<0.0001$)
C_{21}	y=0.0091x-18.87	0.958	Significant ($p<0.0001$)
C_{22}	y=0.0074x+41.80	0.709	Significant ($p<0.0001$)
C_{23}	y=0.0053x+16.45	0.915	Significant ($p<0.0001$)
C_{24}	y=0.0042x+18.89	0.764	Significant ($p<0.0001$)
C_{25}	y=0.0029x+7.24	0.733	Significant ($p<0.0001$)
C_{26}	y=0.0015x+18.90	0.501	Significant ($p<0.001$)
C_{27}	y=0.0012x+11.40	0.477	Significant ($p<0.001$)
C_{28}	y=0.00093x+19.10	0.352	Significant ($p<0.009$)

A similar regression analysis was performed with the patch samples to determine the feasibility of using the assayed hydrocarbons as tracers. In this instance, the results were expressed µg/cm^2 for both the sum of hydrocarbons up to C_{12} which was indicative of vapour exposures, and the total hydrocarbon levels which were indicative of liquid splashes and exposure to aerosols. The results from these analyses are shown in **Figures 6** and **7** for patch samples worn above and below the clothing. The results show that both types of hydrocarbon measurements were representative of petrol fuel levels, even though the r^2 value for the patch sample model was less than that observed for hand washing samples. A comparison of the two regressions shows that the contribution of heavy hydrocarbons ($>C_{12}$) is negligible at about 0.2% as measured by the difference in slope value for the sum of hydrocarbons less than C_{12} and the value for total hydrocarbons. These data indicate that the measurements using patch samples is mainly attributable to the lightweight petrol tracers.

The regressions shown in **Figures 5** and **6** improved considerably when the analysis was restricted to those patch samples placed outside clothing. When the sample type was restricted in this way, the regression of petrol fuel levels versus the sum of hydrocarbons less than C_{12} yielded the following regression equation: $y=0.090x-0.002$ ($r^2=0.506$; $p<0.0001$). Similarly, the regression of petrol fuel levels against the total hydrocarbons produced the equation $y=0.091x+0.764$ ($r^2=0.469$; $p<0.0001$). The improved relationships were expected since the patch samples placed inside clothing were not as numerous and these samples were protected from any direct liquid contact with the petrol fuel being dispensed.

Figure 5 A linear regression analysis comparing petrol levels with the sum of hydrocarbon tracers up to C12 for patch samples placed inside and outside clothing

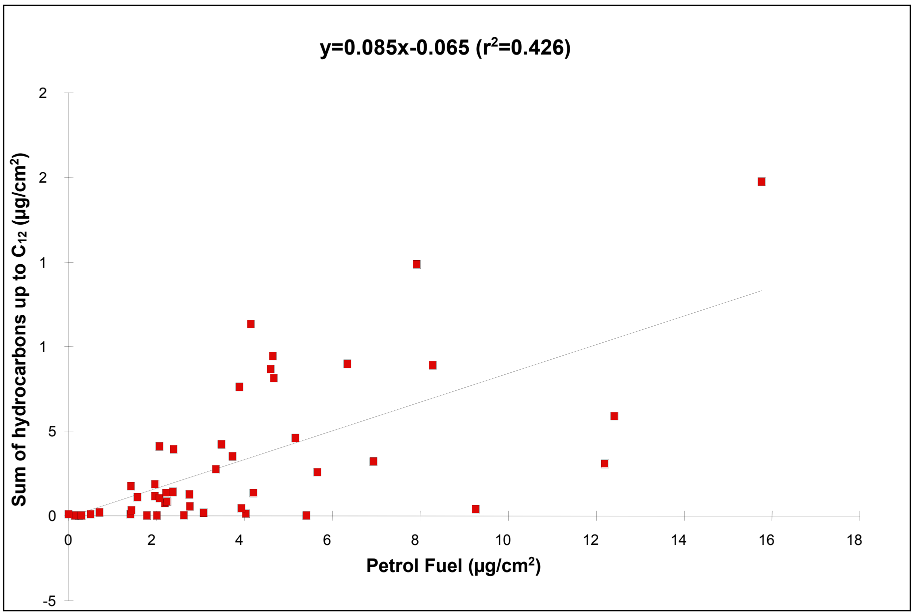
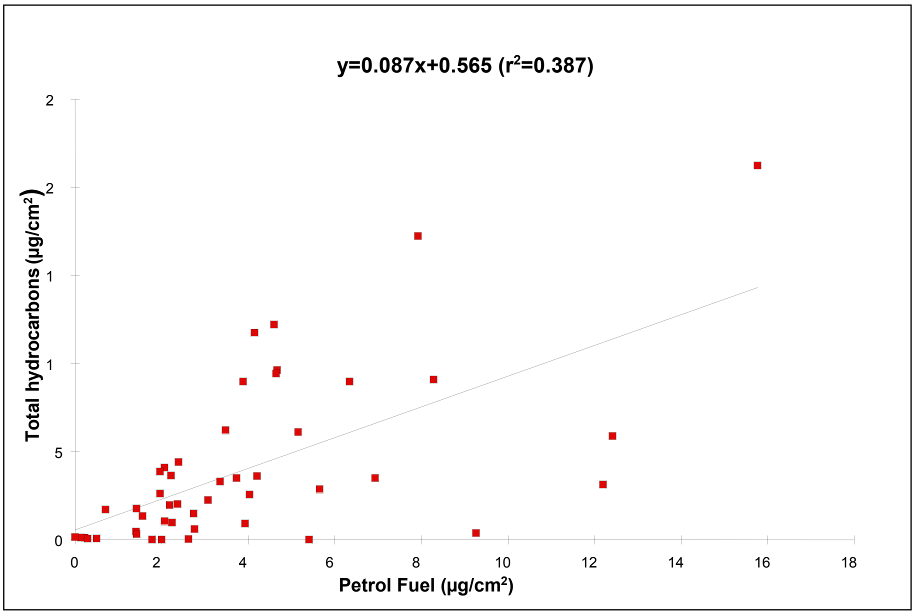


Figure 6 A linear regression analysis comparing petrol levels with the sum of total hydrocarbon for patch samples placed inside and outside clothing



The individual hydrocarbon tracers were also examined to determine if some congeners were more highly related to petrol fuel levels than others. The results are shown in **Table 9** for those samples that did not show a high level of background concentration that would have skewed the regression results. The best tracers in this comparison were the light aromatic hydrocarbons. Toluene shows the highest r^2 and slope value. Heavier hydrocarbons, as mentioned above, showed little tendency to evaporate and were only found sporadically on clothing patch samples that came into contact with liquid hydrocarbons from the hands or equipment surfaces.

Table 9 A linear regression analysis comparing petrol levels with individual hydrocarbons tracers in patch samples placed inside and outside clothing

Hydrocarbon	Equation	r^2	Statistical significance (p)
MTBE	y=0.019x-0.0080	0.392	Significant (p<0.0001)
benzene	y=0.0077x-0.096	0.391	Significant (p<0.0001)
toluene	y=0.030x-0.227	0.408	Significant (p<0.0001)
ethylbenzene	y=0.0021x-0.0029	0.307	Significant (p<0.0001)
m+*p*-xylene	y=0.0079x-0.015	0.347	Significant (p<0.0001)
o-xylene	y=0.0028x+0.004	0.326	Significant (p<0.0001)
C_6	-	-	Non significant
C_7	y=0.0059x-0,045	0.354	Significant (p<0.0001)
C_8	-	-	Non significant
C_9	-	-	Non significant
C_{10}	-	-	Non significant
C_{11}	-	-	Non significant
C_{12}	-	-	Non significant
C_{13}	-	-	Non significant
C_{14}	-	-	Non significant
C_{15}	-	-	Non significant
C_{16}	-	-	Non significant
C_{17}	-	-	Non significant
C_{18}	-	-	Non significant
C_{19}	-	-	Non significant
C_{20}	-	-	Non significant
C_{21}	-	-	Non significant
C_{22}	-	-	Non significant
C_{23}	-	-	Non significant
C_{24}	-	-	Non significant
C_{25}	-	-	Non significant
C_{26}	-	-	Non significant
C_{27}	-	-	Non significant
C_{28}	-	-	Non significant

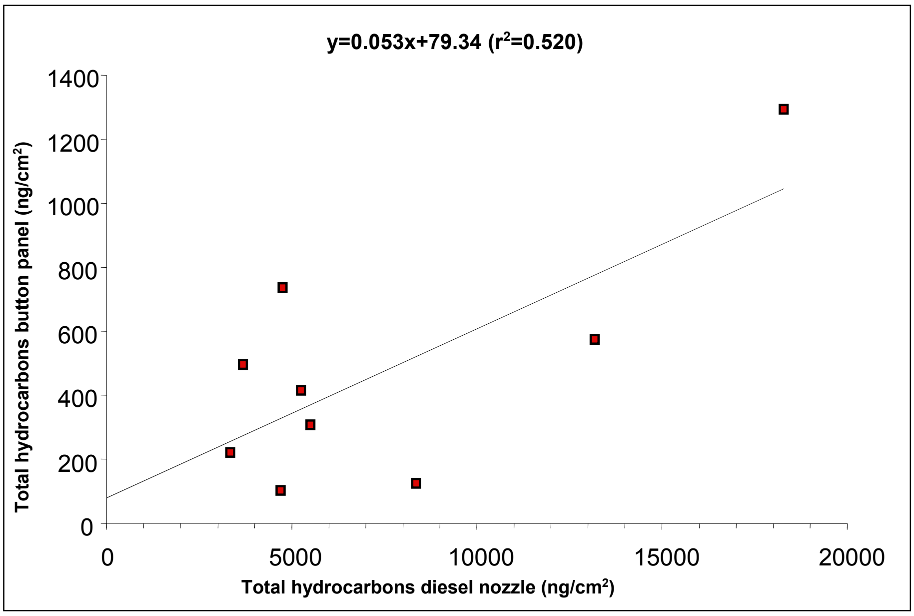
3.3. EQUIPMENT SURFACE CONCENTRATIONS (PHASE I)

The level of hydrocarbons on each type of equipment surface was individually examined. The results provided in **Appendix 2** give the mean (±SD), median, minimum, and maximum along with the 25th and 75th percentile values for the C_{14}-C_{28} congeners as well as the total hydrocarbon measurements. Each table contains a breakdown of the results for the button panel, petrol dispenser hose, diesel dispenser hose, petrol nozzle grip, and diesel nozzle grip. A comparison of the values in **Tables A2.1-A2.5** shows that a very limited number of equipment samples reported concentrations of hydrocarbons with C_{14} except for the diesel nozzle grip, which was routinely showed concentrations of all of the hydrocarbons examined. The percentage of positive detections (levels above the LOQ) and the magnitude of the concentrations should be interpreted with the help of **Table 4**, which shows the percent evaporation for the individual hydrocarbons present in petrol and diesel after a 4-hour exposure period. Since C_{14} shows 50% evaporation after 4 hours, the levels of hydrocarbons will be related to the time interval between the transfer and the sample collection. These factors likely explain the systematic concentrations detected on the nozzle grip of the diesel dispensers and the low concentrations of the other equipment surfaces. Similar reasoning can be applied to C_{15} which shows a 4-hr evaporation of approximately 37%, and to C_{16} which shows a 4-hr evaporation of about 24%. The occasional levels observed for heavy hydrocarbons $>C_{22}$ is associated with the small percentage of these hydrocarbons in diesel fuel, which limits their presence to those surfaces such as the nozzle grip.

Comparing the equipment surface data using a Student's t-test for paired data ($\alpha=0.05$), the concentrations on the button panel was significantly less than the other equipment surfaces when the results were expressed as total hydrocarbons. In addition, the nozzle grip of the diesel dispenser was found to have the highest concentrations and the difference between the petrol hose and the diesel hose surface levels was not statistically significant.

No statistically significant relationships were observed except for the total hydrocarbon levels on the button panel and nozzle grip of the diesel dispenser, which is depicted in **Figure 7**. This relationship was likely due to the direct transfer of hydrocarbons from the nozzle grip of the diesel dispenser to the button panel, whereas the levels of hydrocarbons on other equipment surfaces does not seem to be associated with a common transfer mechanism.

Figure 7 Linear regression analysis comparing the total hydrocarbon tracer concentration on the nozzle grip of the diesel dispenser with the concentration of the button panel



3.4. HAND CONTACT (PHASE I)

Because of body heat, air movement, vapour pressure, and skin penetration, the hands behave as a dynamic system and the exposure estimated from surface wiping samples gives an instantaneous picture of the amount left on the skin at the time of sampling. Consequently, the value is an underestimate of true dermal contact because surface wiping does not measure all of the hydrocarbons that have come into contact with this skin surface over time. Gloves, if used, serve a dual function. In one respect, they can reduce surface evaporation and their use may result in a higher estimate of dermal exposure compared relative to bare skin. In another respect, the hand loading from surface contact and direct deposition may be reduced by the semi-protective barrier that gloves provide. Importantly, however, the attendants examined in this study did not wear gloves during their fuel dispensing activities.

Table 10 shows the results for hand contact expressed either as diesel fuel mass, or diesel mass per litre of fuel dispensed and as individual hydrocarbon tracers. It should be noted that the determination of hand loading using the litres of diesel dispensed considered the total amount of fuel metered during the entire work shift so the dispensed volume was equally divided between the two attendants at stations 2 and 3. This was not necessary at station 1 since a single attendant worked the entire shift (see **Table 1**).

The hand measurements showed considerable variability, which was consistent with all of different surfaces types and concentration levels that an attendant comes into contact with during a work shift. The general quantity of fuel dispensed somewhat affected the hydrocarbon loading on each attendant's hands. Because of the high standard deviations, the results were expressed as the percent coefficient of variation (CV% = SD/mean x 100), which decreased from 95% when expressed as diesel fuel mass to 86% when expressed per litre of dispensed diesel fuel. Expressing the results per litres of dispensed diesel fuel eliminated that portion of the variability that was associated with the amount of fuel that was handled during the shift.

The analyses also showed that a very limited number of samples contained the C_{14} tracer. The percentage of results above the LOQ increased with C_{15} and C_{16}, and reached 100% for hydrocarbons with a carbon content of C_{17} or higher. These results are consistent with the observations for equipment surface concentration where the C_{14} tracer showed a variable percentage of positive detections that ranged from 0 to 22% for most surfaces other than the nozzle grip. By comparison, C_{14} loading of the hands yielded positive detections with 28% of the measurements. Likewise, C_{15} was positively detected in 22 to 100% of the equipment surfaces samples versus 67% of the hand samples.

Table 10 Hydrocarbon tracer and total diesel fuel hand loading[†]

Hydrocarbon*	% data >LOQ	Min-Max	25th percentile	Median	75th percentile	Mean ± SD
C_{14}	28	0-33.4	0.0	0.0	6.4	5.7±11.1
C_{15}	67	0-117.8	0.0	9.6	45.7	24.4±32.9
C_{16}	94	0-159.4	19.9	28.2	82.0	54.5±51.3
C_{17}	100	4.4-466.9	39.9	68.1	145.2	122.2±133.3
C_{18}	100	18.7-761.1	49.2	114.7	239.0	194.8±210.6
C_{19}	100	15-755.8	35.4	78.7	188.1	168.2±207.8
C_{20}	100	62.6-718.5	88.1	143.6	255.1	214.5±186.1
C_{21}	100	16.8-765	64.0	125.8	263.9	202.9±215.4
C_{22}	100	20.8-662.8	55.2	123	362.0	220±201.2
C_{23}	100	32-488	57.6	96.7	194.6	145±127.8
C_{24}	100	14.4-335	23.9	88.4	195.6	121.5±111.6
C_{25}	100	5.7-230.4	15.7	35.5	141.9	77.7±78.3
C_{26}	100	6.3-168.2	20.8	27.5	96.7	56.3±50.3
C_{27}	100	6.5-140.3	12.2	18.9	65.5	42.8±43.3
C_{28}	100	4.6-130.5	15.7	23.9	61.2	41.6±36.1
diesel fuel	100	3.4-78.3	10.5	14.3	29.4	24.2±23
diesel dispensed (µg/L)	100	2.2-71.2	6.2	19.3	47.7	28±24.1

[†] 18 measurements
* hydrocarbon tracer levels in µg and diesel fuel levels in mg

Figure 8 shows the individual diesel fuel results for those attendants examined throughout the duration of the study. The results are expressed as µg of diesel fuel per litre of fuel dispensed. Attendants 1 and 2 were employed at station 1, attendants 3 and 4 at station 2, and attendants 5 and 6 at station 3. It is readily apparent that hand contact with diesel fuel was lowest for those attendants who served at station 2 when the results were expressed relative to the amount of fuel dispensed. These two attendants seemed to have developed similar work habits over the course of the study period. Likewise, attendants 5 and 6 were not appreciably different either individually or across time. Separate conclusions apply to attendants 1 and 2, who showed substantial individual and time-dependant differences during the course of the study. Tobacco smoking did not seem to affect hand loading with hydrocarbons since dermal contact was not noticeably lower in attendants 1 and 5, who were non-smokers.

Figure 8 Daily diesel fuel hand loading of each attendant (AT) participating in the study

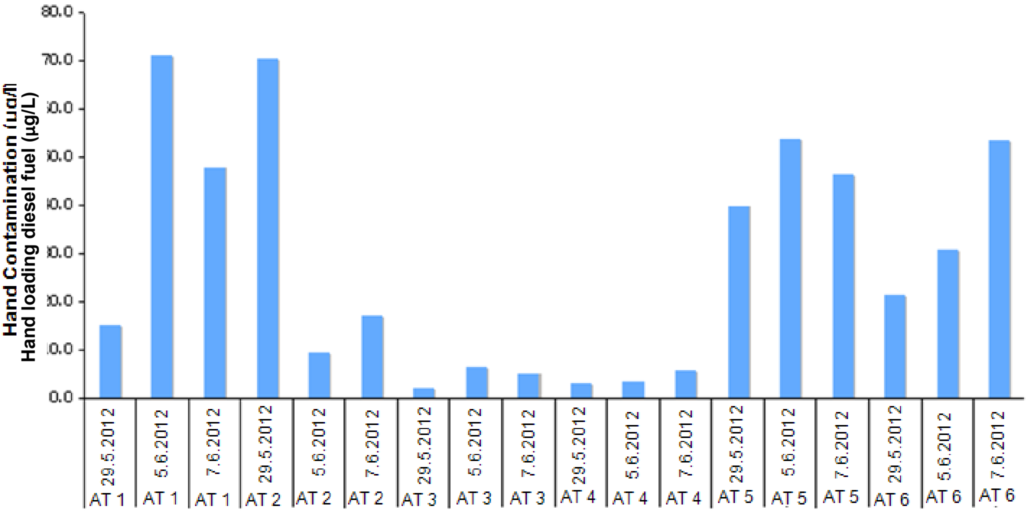
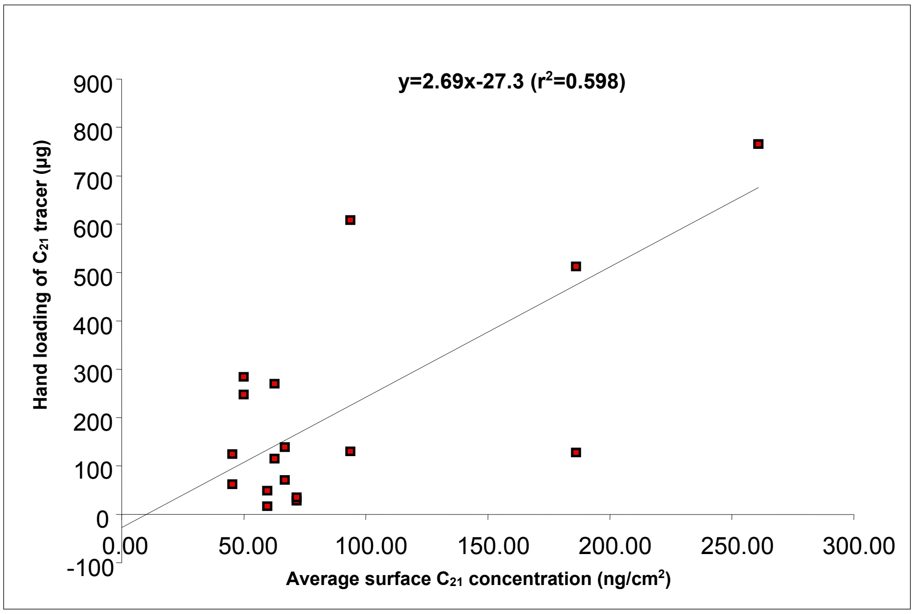


Table 11 shows the results of a regression analysis that compares individual hydrocarbon tracers and the sum of the C_{14}-C_{28} hydrocarbons on the equipment surfaces with comparable levels on the hands. The analysis assumed that hand loading was mainly attributable to contact and transfer from equipment surfaces. The results for the C_{21} congener are depicted separately in **Figure 9** since the results from **Table 8** revealed that this tracer was the strongest marker for the hand loading of diesel fuel. This finding was further confirmed for the equipment surfaces since the r^2 value showed that 60% of the variance could be explained by the C_{21} levels. By comparison, the regression for C_{24} was not statistically significant because the hand concentration levels was likely associated with other hydrocarbon sources such as engine oil and lubricants.

Table 11 Linear regression analysis of the tracers found in the hand washing samples (µg) and the average found on equipment surfaces (ng/cm2)

Hydrocarbon	Equation	r^2	Statistical significance (p)
C_{14}	-	-	Non significant
C_{15}	-	-	Non significant
C_{16}	y=0.225x+29.47	0.394	Significant (p<0.01)
C_{17}	y=0.631x+40.89	0.590	Significant (p<0.0001)
C_{18}	y=1.065x+38.84	0.619	Significant (p<0.0001)
C_{19}	y=1.589x-16.84	0.608	Significant (p<0.0001)
C_{20}	y=1.856x+41.81	0.566	Significant (p<0.0001)
C_{22}	y=2.669x+46.05	0.429	Significant (p<0.0001)
C_{23}	y=3.047x-1.44	0.561	Significant (p<0.0001)
C_{24}	-	-	Non significant
C_{25}	y=2.501x+10.28		Significant (p<0.013)
C_{26}	-	-	Non significant
C_{27}	-	-	Non significant
C_{28}	-	-	Non significant
sum of C_{14} to C_{28}	y=1.239x-973.3	0.471	Significant (p<0.01)

Figure 9 Linear regression analysis comparing C21 concentrations on surfaces (average of all surfaces) with hand loading



A more detailed analysis was also performed that examined the relationship between C_{21} and the comparable tracer levels on individual equipment surfaces. **Figures A3.1-A3.5** in **Appendix 3** show the relationship between the C_{21} hand loading and the amount on (i) the nozzle grip for the diesel dispenser, (ii) the nozzle grip of the petrol dispenser, (iii) the button panel, (iv) the diesel hose, and (v) the button panel and nozzle grips combined. The regression results comparing hand concentration levels with petrol hose levels has not been provided since the results were not statistically significant. The highest correlation was observed between C_{21} hand loading levels and the C_{21} tracers on the nozzle grips and the button panel, which are the surfaces that an attendant routinely makes contact with during fuel dispensing. **Figure A3.5** shows that a good correlation was observed between C_{21} hand loading and the average levels on both the nozzle grips and button panels; confirming the importance of these equipment surfaces for determining an attendant's hand exposure.

3.5. PATCH MEASUREMENTS (PHASE I)

A variety of measurements were performed on the patch samples placed inside and outside the clothing. **Tables 12** and **13** provide the results for hydrocarbon measurements with samples placed (i) in contact with the skin under a cotton T-shirt and (ii) on the bare forearm and over the clothing at the forearm level. The measurements are shown for individual hydrocarbon tracers, petrol fuel, petrol per litre of fuel dispensed, total hydrocarbon content, and as the sum of hydrocarbons up to C_{12}. As was seen for the hand washing samples, the data was highly variable and the amount of petrol dispensed greatly impacted the amount of hydrocarbon on the patches. In fact, the variability expressed as a coefficient of variation declined from 67% when expressed as petrol to 41% when expressed as petrol per litre of fuel dispensed for patches inside the t-shirt. A similar decline from 83% to 67% was observed for patches placed outside the clothing or on skin not covered by clothing. Normalizing the results for the volume of dispensed petrol eliminated fuel handling as a confounding factor that affected the variability.

The results reveal that the percentage of positive analytical detections was appreciably higher for the lighter hydrocarbons less than C_{10} than for those that were heavier, however, increased detection were observed in the C_{14}-C_{21} range. As noted earlier, carbon cloth patches are capable of readily adsorbing airborne volatile hydrocarbons. The patches used in this study act as passive samplers. The value obtained is representative of the vapour reaching that skin area during the work shift. The measurement do not take into account evaporative process from the skin because, once captured, the hydrocarbons are not released from the patch until extraction in the laboratory. The non-volatile heavy hydrocarbons need to be adsorbed by the charcoal patch from a direct contact with liquid or on an exposed equipment surface. The presence of both light and heavy hydrocarbon tracers on the patches confirms that the sampling medium and the placement technique were suitable for the purposes of this study.

Comparing the data for patches placed inside and outside of the clothing using a Student's t-test for paired data ($\alpha=0.05$) revealed significantly increased hydrocarbon levels on the patches placed outside clothing for specific tracers including benzene, toluene, ethylbenzene, xylenes and MTBE. A statistically significant difference was not observed for the individual hydrocarbon tracers, total hydrocarbon values, the sum of hydrocarbons up to C_{12}, or petrol fuel amounts.

Table 12 Measurements (µg/cm^2) of hydrocarbon tracers and petrol fuel on patches placed in contact with skin under a cotton t-shirt[†,]

Hydrocarbon	% data >LOQ	Min-Max	25th percentile	Median	75th percentile	Mean ± SD
MTBE	67	0-1.00	0.00	0.20	0.38	0.3±0.2
Benzene	22	0-0.4	0.00	0.00	0.00	0±0
Toluene	61	0-1.7	0.00	0.10	0.24	0.3±0.1
Ethylbenzene	28	0-0.2	0.00	0.00	0.03	0±0
m,p-xylenes	72	0-0.6	0.00	0.03	0.11	0.1±0
o-xylene	44	0-0.2	0.00	0.00	0.06	0±0
C_6	28	0-11.1	0.00	0.00	0.01	1±0.5
C_7	39	0-0.4	0.00	0.00	0.07	0.1±0
C_8	28	0-0.1	0.00	0.00	0.03	0±0
C_9	28	0-0.1	0.00	0.00	0.04	0±0
C_{10}	11	0-0.1	0.00	0.00	0.00	0±0
C_{11}	0	0-0	0.00	0.00	0.00	0±0
C_{12}	11	0-0.1	0.00	0.00	0.00	0±0
C_{13}	6	0-0.2	0.00	0.00	0.00	0±0
C_{14}	28	0-0.4	0.00	0.00	0.07	0.1±0
C_{15}	17	0-0.4	0.00	0.00	0.00	0±0
C_{16}	28	0-0.8	0.00	0.00	0.08	0.1±0
C_{17}	44	0-0.6	0.00	0.00	0.12	0.1±0.1
C_{18}	56	0-0.7	0.00	0.06	0.19	0.1±0.1
C_{19}	44	0-0.3	0.00	0.00	0.08	0.1±0
C_{20}	61	0-0.2	0.00	0.06	0.12	0.1±0.1
C_{21}	6	0-0.1	0.00	0.00	0.00	0±0
C_{22}	0	0-0	0.00	0.00	0.00	0±0
C_{23}	0	0-0	0.00	0.00	0.00	0±0
C_{24}	6	0-0	0.00	0.00	0.00	0±0
C_{25}	6	0-0.1	0.00	0.00	0.00	0±0
C_{26}	17	0-0.1	0.00	0.00	0.00	0±0
C_{27}	28	0-0.1	0.00	0.00	0.03	0±0
C_{28}	6	0-0.1	0.00	0.00	0.00	0±0
sum of hydrocarbon tracers	100	0-12.2	0.20	1.01	2.01	2.5±1.2
sum of hydrocarbon tracers <C_{12}	78	0-11.3	0.10	0.66	1.32	1.9±0.8
petrol fuel	94	1.4-92.6	16.20	23.07	40.95	29±19.5
petrol dispensed (µg/L)	94	0.00-0.13	0.02	0.05	0.07	0.05±0.02

[†] 18 measurements

* hydrocarbon tracer levels in µg and diesel fuel levels in mg

Table 13 Measurements (µg/cm2) of hydrocarbon tracers and petrol fuel on patches placed over clothing or on the forearm skin not covered by clothing†

Hydrocarbon	% data >LOQ	Min-Max	25th percentile	Median	75th percentile	Mean ± SD
MTBE	87	0-5.1	0.10	0.50	1.00	0.9±2
benzene	60	0-2.3	0.00	0.10	0.30	0.4±0.1
toluene	77	0-13.9	0.10	0.80	1.40	1.8±0.5
ethylbenzene	67	0-1.6	0.00	0.10	0.20	0.2±0
m,p-xylenes	90	0-6.2	0.00	0.20	0.60	0.6±0.2
o-xylene	67	0-2.3	0.00	0.10	0.30	0.2±0.1
C_6	37	0-5.3	0.00	0.00	0.80	0.6±0.6
C_7	70	0-1.8	0.00	0.10	0.30	0.3±0.1
C_8	30	0-0.4	0.00	0.00	0.07	0±0
C_9	30	0-0.3	0.00	0.00	0.03	0±0
C_{10}	17	0-0.3	0.00	0.00	0.00	0±0
C_{11}	3	0-0.1	0.00	0.00	0.00	0±0
C_{12}	7	0-0.1	0.00	0.00	0.00	0±0
C_{13}	13	0-0.1	0.00	0.00	0.00	0±0
C_{14}	30	0-0.8	0.00	0.00	0.20	0.1±0
C_{15}	30	0-0.1	0.00	0.00	0.00	0±0
C_{16}	37	0-1.0	0.00	0.00	0.20	0.1±0
C_{17}	47	0-0.6	0.00	0.00	0.20	0.1±0
C_{18}	60	0-1.3	0.00	0.10	0.30	0.2±0
C_{19}	50	0-0.5	0.00	0.00	0.20	0.1±0.1
C_{20}	47	0-0.7	0.00	0.00	0.20	0.1±0
C_{21}	23	0-0.1	0.00	0.00	0.00	0±0
C_{22}	20	0-0.1	0.00	0.00	0.00	0±0
C_{23}	7	0-0.2	0.00	0.00	0.00	0±0
C_{24}	7	0-0.2	0.00	0.00	0.00	0±0
C_{25}	7	0-0.1	0.00	0.00	0.00	0±0
C_{26}	20	0-0.2	0.00	0.00	0.00	0±0
C_{27}	20	0-0.2	0.00	0.00	0.00	0±0
C_{28}	20	0-0.2	0.00	0.00	0.00	0±0
sum of hydrocarbon tracers	97	0-37.7	1.90	3.50	8.30	6±1.9
sum of hydrocarbon tracers <C_{12}	97	0-33.1	0.50	2.80	7.20	5±1.9
petrol fuel	97	0-554.8	20.20	36.00	61.70	61.8±51
petrol dispensed (µg/L)	97	0.00-0.71	0.03	0.06	0.10	0.10±0.06

† 30 measurements

* hydrocarbon tracer levels in µg and diesel fuel levels in mg

A percent difference for hydrocarbons measured above and under work clothing is given in **Table 14**. Cotton work clothing is a relatively permeable fabric and not expected to prevent vapour diffusion. Cotton work clothing is often preferred to enhance comfort by contributing to evaporation of perspiration from the skin through a “wicking” action controlling skin humidity by removing water vapour off the skin. Physical hand and body motions associated with refuelling tasks also enhance ventilation within clothing. Based on median values it appears cotton work clothing may reduce hydrocarbon vapour concentrations from fifteen to sixty four percent**.** This is probably due to the fact that fabric reduces the penetration of the heavier component, that are in the physical form of aerosol and remain on the clothes. However as shown in **Figure 11**, results from two attendants measured higher under clothing for the charcoal chest patch, which suggests that accidental contact with hydrocarbons are possible due to localized splash to clothing or from contact with wetted hands or equipment surfaces.

Table 14 Penetration through clothing expressed as a percentage (skin sample/external sample x 100)

Statistic	**petrol fuel**	**sum of hydrocarbons <C12**	**sum of C_6-C_{28} hydrocarbons**
All samples (18 measurements)			
Minimum	7	0	0
25th percentile	33	3	12
Median	62	21	29
75th percentile	>100	31	36
Maximum	>100	>100	>100
Chest samples (12 measurements)			
Minimum	7	0	0
25th percentile	16	0	2
Median	48	15	25
75th percentile	>100	33	48
Maximum	>100	>100	>100
Forearm samples (6 measurements)			
Minimum	33	12	12
25th percentile	46	20	31
Median	64	26	33
75th percentile	65	30	35
Maximum	>100	31	36

A separate analysis was performed to highlight the differences observed for individual sampling days, attendants, and service stations. **Figures 10** and **11** show the results for clothing penetration on individual attendants who wore patches on the forearm (station 1) or the chest (stations 2 and 3).

Figure 10 Hydrocarbon penetrations through forearm clothing expressed as the sum of hydrocarbons up to C_{12} and the sum of all C_6-C_{28} tracers

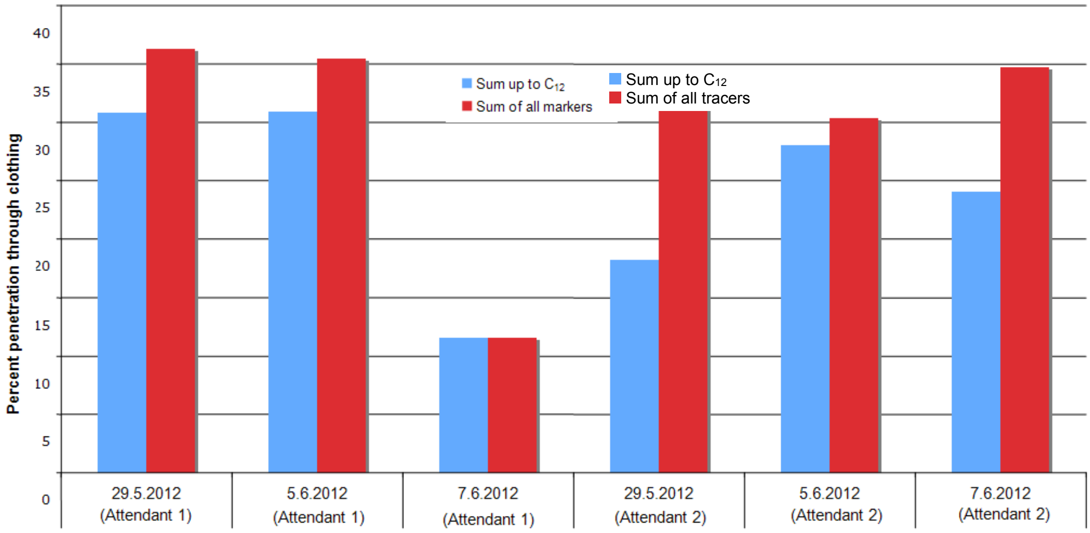
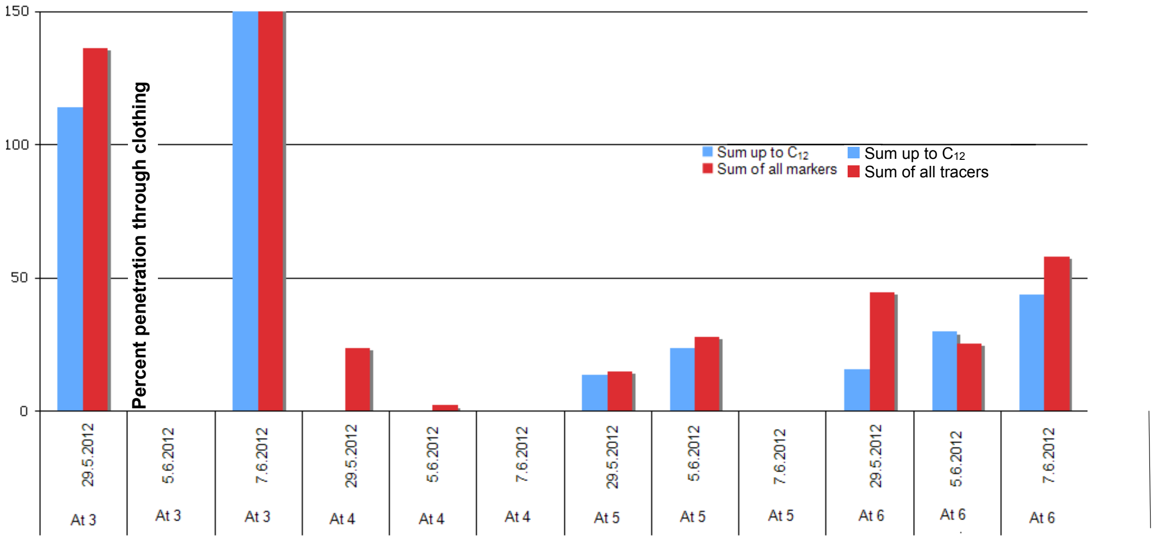


Figure 11 Hydrocarbon penetrations through the clothing on the chest expressed as the sum of hydrocarbons up to C_{12} and the sum of all C_6-C_{28} tracers



Clothing penetration at the forearms was reasonably consistent for attendants 1 and 2; however there was substantial variability amongst attendants for samples placed on the chest beneath clothing. Variability exceeded 100% on some sampling days.

3.6. DERMAL TRANSFER COEFFICIENT (PHASE II)

The concentration of the sum of the C_{14}-C_{28} hydrocarbon tracers on equipment surfaces was measured in individual samples collected every hour during 3 afternoon shifts at service station 1. The results are shown in **Figure 12** for each of the equipment surfaces examined. **Figure 13** shows the daily average for the sum of the C_{14}-C_{28} hydrocarbon tracers in the four samples collected from each of the six equipment surfaces examined. As noted for the data in the Phase 1 analysis, the highest concentration of hydrocarbons was observed for the nozzle grip of the diesel dispenser, whereas less concentration was found on the button panel and the petrol hose. Intermediate concentration levels were observed for the diesel hose and for the nozzle grip of the petrol dispenser. **Figure 14** shows the daily hand loading with the sum of the C_{14}-C_{28} hydrocarbon tracers in the individual samples collected over the duration of the study.

Figure 12 Levels of surface concentration with sum of C_{14}-C_{28} hydrocarbon tracers in separate samples collected over the three study days (ng/cm^2)

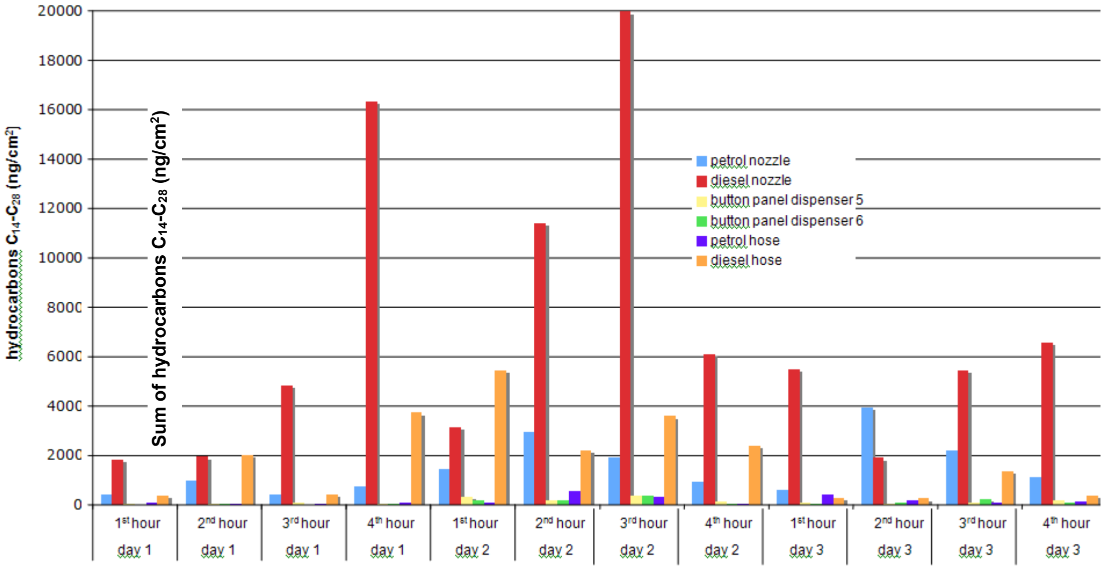


Figure 13 Average concentration of surfaces with sum of hydrocarbons C14-C28 on each of the three study days (ng/cm2)

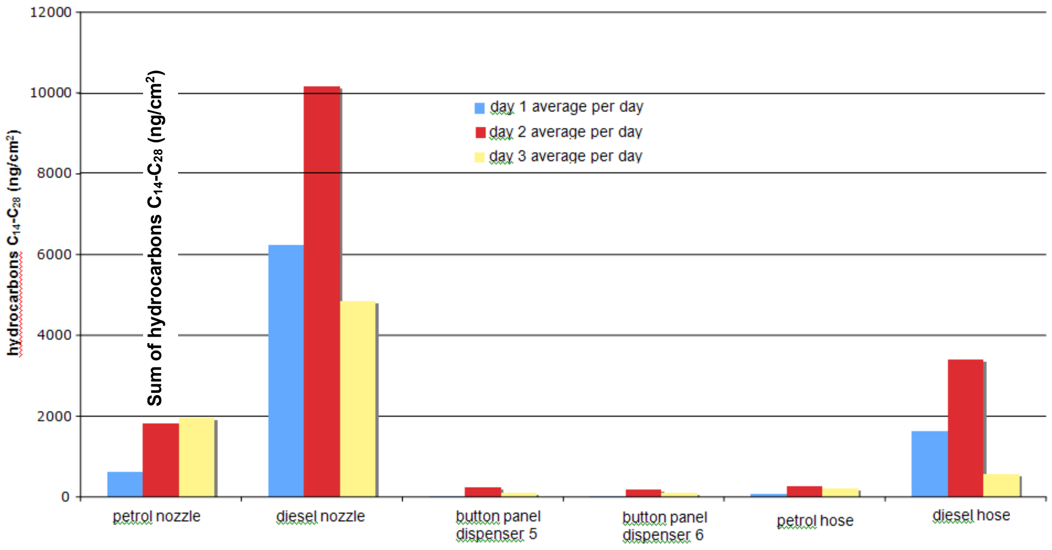
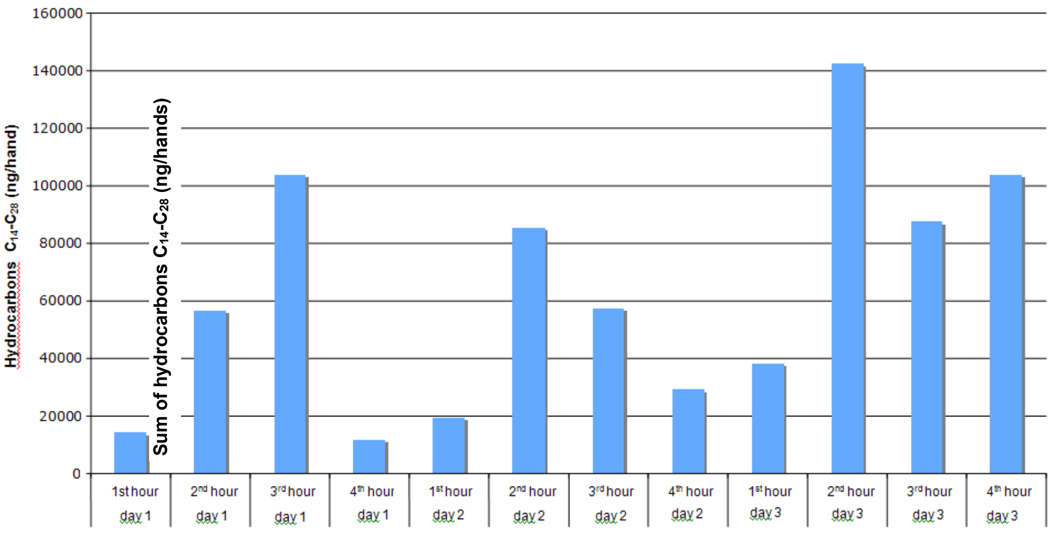


Figure 14 Hand load for sum of hydrocarbon tracers C_{14}-C_{28} individual samples collected over the three study days (ng/hands)



The data from phase 2 allowed a dermal transfer coefficient (DTC) to be calculated, although there are uncertainties as noted earlier in the introduction. The DTC is equal to the ratio between the hydrocarbon load to the hands (expressed in ng/hr), and the average concentration on the equipment surfaces (expressed in ng/cm²). The DTC values were calculated using the individual hourly measurements of hand loading. By virtue of the linear regression analyses results provided in **Figures A3.1**, **A3.2**, **A3.3**, and **A3.4** of **Appendix 3**, the most applicable surfaces for the DTC calculation were the petrol and diesel nozzle grips and the button panels. The results of this analysis are shown in **Table 15**.

Table 15 Dermal transfer coefficient (cm^2/hr) for the sum of C_{14}-C_{28} hydrocarbon tracers calculated on the basis of the hand loading and the surface concentration on button panels and nozzle grips

Statistic	Transfer coefficient (cm^2/hr)
mean ± S D	38.7±30.5
minimum	2.8
maximum	95.8
10th percentile	10.7
25th percentile	16.0
median	24.9
75th percentile	58.2
90th percentile	78.2
95th percentile	86.2
CV%	79

The DTC is affected by the contact frequency with the surfaces being considered. By knowing the level of hydrocarbons on the equipment surfaces, the DTC provides a means for estimating the C_{14}-C_{28} hydrocarbon hand loading. Since the C_{14}-C_{28} hydrocarbon tracers represent approximately 7% of the diesel fuel levels, it is possible to determine total hand loading from diesel fuel. The DTC values calculated for each individual hydrocarbon tracer are shown in **Table 16**.

Table 16 Dermal transfer coefficient (cm^2/hr) for individual hydrocarbon tracers calculated on the basis simultaneous hand loading and button panel and nozzle grip concentration measurements

Hydrocarbon	Min-Max	25th percentile	Median	75th percentile	Mean ± SD
C_{14}	0-21.5	0.0	0.0	0.0	1.8±6.2
C_{15}	0-111.5	0.0	0.0	5.5	12.4±32
C_{16}	0-157.4	11.4	13.7	33.9	28.9±42.6
C_{17}	2.6-213.8	15.3	23.2	56.5	47.1±59.3
C_{18}	3.5-239.9	17.6	31.6	71.3	55±64.2
C_{19}	4.8-296.1	17.6	48.7	79.8	65.5±78
C_{20}	4.6-258.4	22.4	48.9	100.5	74.3±71.4
C_{21}	6.9-281.3	28.1	65.9	104.9	81.6±77.4
C_{22}	5.5-325.1	20.1	44.8	109.9	81.1±88.4
C_{23}	0-348	35.9	58.6	143.8	100.9±103.1
C_{24}	6.4-100	11.3	19.0	25.8	25.1±25.2
C_{25}	0-326	0.0	25.3	110.0	67.1±96
C_{26}	0-271.8	0.0	0.0	96.2	54.7±84.9
C_{27}	0-876.2	0.0	0.0	87.6	132.4±271.6
C_{28}	0-1233.5	25.3	46.6	381.6	261.3±389.6

4. DISCUSSION

This study was designed to evaluate dermal exposures associated with fuel dispensing activities. To date, this topic has not been extensively investigated as noted by the lack of historical data and scientific publications. Dermal effects and skin absorption of petroleum-derived hydrocarbons was the subject of a recent report published by Concawe [8]. In addition, the systemic health effects caused by dermal exposure to chemicals have been technically assessed by ECETOC [10].

Schneider developed a conceptual model for dermal exposure that used a schematic approach applicable to fuel dispensing activities [15]. The model assumes that fuel dispensing represents the primary transfer operation, which can be defined as the process or activity whereby a substance is introduced into one of the compartments in the model. Other transfer sources such as the fuel tanks that are opened during the refuelling process cannot be ruled out. The remaining compartments of the model can be identified as air, equipment surfaces, the outer layer of clothing, the inner layer of clothing, and the skin. The mass transport processes connecting these compartments are described below.

1. Emission is the transport of the fuels from the primary source to one of the identified compartments.
2. Deposition is the transport from the air to any of the surfaces.
3. Re-suspension or evaporation is the transport from the surfaces to the air.
4. Transfer is the transport by direct contact between a surface and the skin, the outer layer of clothing or the inner layer of clothing.
5. Removal is the opposite of transfer and describes transport way from the skin;
6. Re-distribution is the partitioning of the agent or chemical across different areas of the body or from one skin surface to another.
7. Decontamination is the removal through surface cleaning and the washing of clothes and skin.
8. Penetration and permeation involve the transport of substances through one of two barriers: the stratum corneum or the clothing fabric.

In the service station exposure scenario, transport from the source to the air may occur by evaporation or aerosol emission, while transport to the skin or clothing surfaces can take place by splashing, pouring, dipping or deposition. All skin loading processes and mechanisms have been investigated in this study in order to develop appropriate control strategies.

The investigation was carried out at three service stations with different characteristics from the point of view of the number of attendants performing the petrol and diesel dispensing activities and the quantity of fuel dispensed during the work shift. Diesel and petrol fuel specifications issued by the European Union under EN 590 (diesel) and EN 228 (unleaded petrol) requires that each Member State reformulate locally sold petrol and diesel according to local climatic conditions [5]. As such there are both spatial and temporal differences in fuel composition across different countries. Although the differences between winter and summer blends are generally restricted to fuel vapour pressure and density, refineries are given some latitude in how they accomplish the seasonal change. Petrol and diesel fuels used during the summer period in Italy may be compositionally different from those used during the winter in more northern countries. Since these differences cannot be easily classified, the relevance of these dermal exposure measurements for other regions of Europe cannot be reliably determined; however, it is assumed that the results provide a reasonable approximation of worst case contact from petrol and diesel fuels since both vapour and liquid contact are taken into consideration.

The six attendants monitored (two for each service station) were highly uniform in terms of age and the work clothing. None of the attendants used gloves and they all wore cotton clothes washed at home; only two of the attendants used a long-sleeved undershirt. Some of the differences found among the service stations and their attendants were used to identify critical factors that impacted the measurements. In particular, the amount of petrol and diesel dispensed were used to normalize the exposure data to reduce variability and improve comparability between studies.

The present study was performed in two different phases. The purpose of the first phase was to determine dermal exposure under typical use conditions, whereby the levels of hydrocarbons resulting from an attendant touching the nozzle grip for the petrol and diesel dispensers, the button panels, and the petrol and diesel dispenser hoses were focused upon since hydrocarbons may be transferred from the equipment to the skin during their use. The second phase was carried out specifically to calculate dermal transfer coefficients. Dermal coefficients have previously been determined for a number of agricultural operations [1,3,4].

Surface sampling techniques were used in both phases of the study; allowing important information to be collected on hydrocarbon transfer to the skin. These data provided information on the skin transfer processes in the first phase of the study and estimates of the dermal transfer coefficients in the second phase. OSHA (Occupational Safety Health Administration) has published evaluation guidelines for surface sampling methods that take into account the sampling and analytical methods employed as well as factors such as removal and extraction efficiency, chemical interference, and sample storage [13].

The dermal exposure evaluations in the present study used direct measurement methods based on the principles of interception and removal [6,7,12]. Biological monitoring measurements were not used to obtain an indirect measure of dermal exposure because of economic considerations and the limited number of hydrocarbon markers possessing validated biological exposure indicators (i.e. *n*-hexane, benzene, toluene, ethylbenzene, xylenes). In addition, biological monitoring would also have measured the body burden resulting from inhalation exposures, which was not a goal of this study.

The collection methods utilized in this study measured the amount of substance that could be removed from the skin at the time of sampling. The principles for using these methods for hydrocarbon removal are based on the application of an external force greater than or equal to the force adhering the chemical to the skin. This external force can include mechanical energy, hydrodynamic drag, or chemical wetting. These techniques generally underestimate exposure potential because a substance can (i) be absorbed by the skin, (ii) evaporate from the skin, and (iii) be partially removed from the skin as a function of the removal efficiency [7,12].

In this study, surface removal techniques were specifically applied to the hands. These samples may have underestimated the dermal exposure. As hands behave as a dynamic system, and the estimated dermal loading represents what is left on the skin at the time of removal. Gloves, had they been worn, would have had a double function. In one respect, they would have reduced evaporation from the skin by increasing the persistence of hydrocarbons in contact with the skin surface; but in another respect, glove use would have reduced the transfer to the skin by decreasing deposition and the time of contact with hydrocarbons present on equipment surfaces.

If non-disposable gloves had been worn, consideration would need to be given to the hydrocarbon loading that may have arisen from glove penetration which could have provided another pathway for hand transfer to occur [11].

Two different removal techniques were used on the hands in phase 1 and phase 2 of this study. In phase 1, hand washing was employed, whereas surface wipe testing was utilized in phase 2. The reason for using a wipe test in phase 2 concerned the need for a method that allowed for the hourly calculation of a dermal transfer coefficient. Hand washing would have diluted the recovered hydrocarbons in a high volume of ethanol and measurable levels of some hydrocarbons may not have been attained. We cannot compare the efficiency of the two removal techniques using data from the present study. If the hourly data collected in phase 2 on the same attendant for the three day examination period were summed up and compared to the results from phase 1 for a 4-hr exposure, there would only be three data points and the statistical comparison between phase 1 and phase 2 would not be sufficiently strong.

The sampling method employed in this study involved intercepting the mass transport of the petroleum hydrocarbons using a sampling medium placed on the skin or on the clothing for a defined period of time. The sampling patches were then analysed in the laboratory to determine the amount of hydrocarbons per unit area. This technique was used to evaluate the skin loading at different areas of the body including the hands and inside or outside the clothing at the forearm and chest level. The patches only covering a small part of the exposed skin area that was of interest, and they behaved as passive samplers that adsorbed the hydrocarbons by vapour diffusion. The mass of material collected represented all of the hydrocarbons that reached the skin area during the work shift and did not take into account the evaporative losses from the skin surface because, once captured on the patch, the adsorbed hydrocarbons will not be liberated except by solvent extraction in the laboratory.

Since they act as passive samplers, the activated carbon fabric patches only absorb the hydrocarbon components that are present as a vapour. This was confirmed by the high percentage of samples where the more volatile light hydrocarbons were detected at levels above the limit of detection. Patch absorption of heavy hydrocarbons can only occur after direct skin contact or via the deposition of liquid aerosols in those specific areas where the patch has been located. Since both light and heavy hydrocarbon fractions were detected on the patches, the results suggest that the sampling medium and analytical technique can be a viable method for assessing the skin exposure to hydrocarbons during refuelling operations.

Patch measurements inside and outside the clothing at the same regions of the body (chest and forearm) has shed light on the protective capacity of the cotton undershirts worn by the attendants. A rough estimate of skin loading at the end of the work shifts could be derived for petrol and diesel fuels using standard techniques [2]. An estimate of the applied dermal dose can be defined as the amount of hydrocarbons that reaches the bare skin and is available for absorption has been calculated. The applied dose represents the sum of the hydrocarbons that reach the bare skin. The derived potential dermal dose also factored into consideration the hydrocarbon fraction that was transferred to the skin after permeation through the clothing. Permeation was measured by placing a patch at various anatomical regions that were considered to be representative for the transfer of hydrocarbons to specific anatomical regions of the body.

An intrinsic limitation of this approach was that the reliability of the patch sample measurements depended on the uniformity of skin deposition in the region of interest. A non-uniform transfer to the skin may lead to an overestimation or an underestimation of the skin loading at this site. If, for example, a liquid splash made contact with a patch, the measurement will be biased high since the anomalous results would be extrapolated to other regions of the body that may not have been affected. The resulting potential dose determinations would result in an exposure overestimation that could, in some instances, be very high. If the splash did not make contact with the patch, the opposite would occur and the measurements would lead to an underestimate of the dermal exposure. In this study, the intrinsic limitations of the diffusive patch sampling were exacerbated because only 2-3 patches were used to assess hydrocarbon loading for the entire surface of the body. Due to these limitations dose extrapolations were not estimated.

A dermal transfer coefficient was determined in the second part of this study; however there were uncertainties in the estimate because of the various petroleum products that were handled by the attendant during a work shift. As a result, hand loading could be the result of a direct transfer from equipment surface as well as contact with other aerosols, vapours, and splashed liquids. Other factors that could be affecting the DTC determination include observations showing that (i) the equipment surfaces contained principally by heavy hydrocarbon components rather than the light hydrocarbons which tended to evaporate, and (ii) the attendant came into contact with surfaces other than the fuel dispenser which could transfer the hydrocarbons to the skin by an alternative transfer mechanism. Regardless, the findings from this study may provide an important means of assessing applied dermal dosages by first evaluating the levels found on equipment surfaces that are routinely found in service stations.

5. CONCLUSIONS

This study examined the levels of surface concentrations and dermal transfer of petroleum hydrocarbons in service station attendants dispensing diesel and petrol fuels. Hydrocarbon measurements were performed following the collection of skin and clothing patch samples, surface wipe samples, and hand washing samples. Individual C_6-C_{28} tracers were quantitated as were the resolved tracer hydrocarbons in diesel and petrol fuel and the total (resolved and unresolved) hydrocarbons in samples where liquid fuel contact may have occurred. In addition to these measurements, benzene, toluene, ethylbenzene, *m,p*-xylene, *o*-xylene, and methyl *t*-butyl ether were also evaluated for use as tracers of fuel exposure.

Diesel and petrol dispenser nozzle grips, button panel, and dispenser hoses were all found to have surface concentrations of varying levels of heavy hydrocarbon components (C_{14}-C_{28}). The diesel dispenser nozzle possessed the most hydrocarbons expressed as the sum of the C_{14}-C_{28} tracers. Levels were 20 times higher for the dispenser nozzle than for the button panel. The levels found on the diesel dispenser nozzle and button panel were significantly related to the levels found in hand washing samples, suggesting a common mechanism of transfer.

After normalizing the measurements relative to the amount of fuel dispensed at each of the three stations examined, dermal loading of hydrocarbons onto the hands of the attendants was calculated from hand washing samples. Hydrocarbon tracers of C_{14} or less were not detected on the hands due to their volatility. An examination of the relationship between diesel fuel measurements and tracer level on the hands indicated that the strongest correlation occurred for the C_{21} tracer, which accounted for 0.9% of the diesel fuel hydrocarbons. Heavier hydrocarbons greater than C_{21} were found in smaller quantities and their presence may have been associated with the handling of other petroleum products, such as engine oils and lubricants. None of the attendants were found to be wearing gloves during the work shift.

Patch samples placed inside and outside the clothing at the level of the chest and forearms showed variable levels of transfer at these sites that were dominated by the light petrol hydrocarbons possessing a carbon number of C_{12} or less. The transfer of heavy hydrocarbons only occurred only after direct contact with a equipment surface or from the deposition of liquid aerosols or splashes. The patch samples revealed that the amount of petrol dispensed during the work shift greatly affected the hydrocarbon loading onto skin areas other than the hands. Measurement of hydrocarbon levels inside and outside the clothing worn on the chest or forearm showed that the cotton t-shirts worn by the attendants did reduce the hydrocarbons reaching the skin surface by fifteen to sixty four percent based on median values. However working clothes did not provide appreciable skin protection when splashes occurred.

A dermal transfer coefficient was calculated in a separate phase of the study that focused on the transfer of C_{14}-C_{29} tracers from equipment surfaces to the hands. Loading onto the hands of a single attendant was determined at hourly intervals for a period of 4 hours on each of three work days. The dermal transfer coefficient was calculated as the ratio of the hand loading expressed in ng/hr to the levels on nozzle grips and button panels expressed ng/cm^2. The median value for the twelve measurements was 25 cm^2/hr. This number provided a means for calculating the hydrocarbon load to the hands after measuring the sum of C_{14}-C_{28} hydrocarbon concentration on an equipment surface.

This study has both strengths and limitations. Its primary strengths are as follows:

- First ever analysis screening of the potential dermal exposures to petroleum hydrocarbons in service station attendants.
- Examination of multiple employees working at different service stations
- Examination of dermal exposure to both petrol and diesel.
- Speciation of the exposure level to individual hydrocarbon congeners found in fuel.
- Determination of wiping efficiency for different hydrocarbons found on equipment surfaces.
- Measurement of the evaporation potential for the different hydrocarbon tracers found in petrol and diesel fuel.
- Consideration of dermal contact with both liquids and vapours through the use of patch samples.
- Evaluates the protective qualities of service station uniforms.
- Identification of the equipment surfaces responsible for direct dermal transfer.
- Identification of those hydrocarbon tracers showing the greatest probability for transfer to the hands.
- Dermal transfer coefficients provided for exchange of fuel hydrocarbons from equipment surfaces to the hands.
- Preliminary information made available on the impact of cigarette smoking.

The major limitations of this study were as follows:

- A limited number of dermal sampling patches were used to represent the entire body surface area.
- A separate determination of hydrocarbon exposure from liquid and vapour phase hydrocarbons was not possible.
- The impact of hydrocarbon evaporation form the skin surface was not specifically evaluated.
- The impact of dermal absorption was not evaluated.
- No determination of the actual absorbed dose.
- Impact of splashes and incidental contact with liquid fuels was not determined.

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7. GLOSSARY

C_7 – alkane chain length of seven carbons

C_{28} – alkane chain length of twenty-eight carbons

CV – coefficient of variation

DTC – dermal transfer coefficient

ECETOC – European Centre for Ecotoxicology and Toxicology of Chemicals

LOQ – limit of quantitation

MTBE – methyl *t*-butyl ether

OSHA – Occupational Safety and Health Administration

SD – standard deviation

TBS – total body surface

TIC – total ion chromatograph

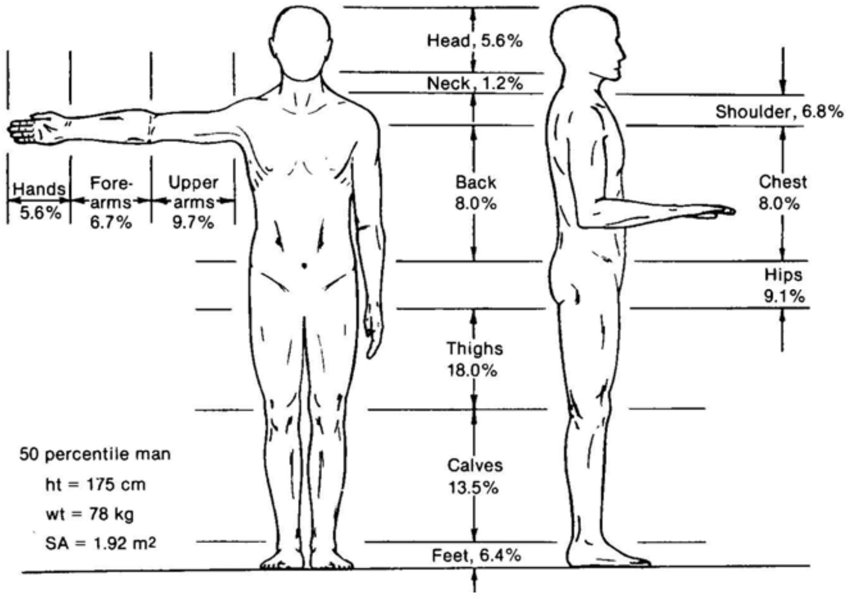
UCM – unresolved complex carbon mixture

APPENDIX 1 BODY SURFACE AREA AND QUESTIONNAIRES

A. Body surface area

For each attendant, the dermal contact on areas other than the hands was determined using a variety of metrics for both the individual tracers, diesel and petrol fuel measurements and petroleum hydrocarbon tracer levels found on the patches samples. Dermal exposure estimates were obtained for different anatomical regions of the body by multiplying the concentration detected on each patch sample (ng/cm^2) with the total surface area for the region being examined. The percentages for each region relative to the total body surface are shown in **Figure A1.1**.

Figure A1.1 Anatomical representations of skin surface areas [14]



The total body surface (TBS) area was calculated for each attendant using Du Bois' formula given below which considers an individual's height and weight [9]. These measurements were obtained from the responses to the questions in form 2 shown in **Table A1.3**.

$$\text{TBS(cm}^2\text{)} = 71.84 \times \text{weight(kg)}^{0.425} \times \text{height(cm)}^{0.725}$$

For the attendants wearing long-sleeved shirts, the patch placed outside the garment at the level of the forearm was considered to be representative of the unprotected skin on the head, neck, and hands. The patch placed in contact with the skin below the clothes on the forearm was indicative of skin exposures for all areas covered by clothing. For the attendants wearing short-sleeved shirts, the patch placed onto their clothing at the chest was considered to be representative of exposures to the head and neck, while the patch on the forearm was representative of the forearms, arms, and hands. The patch placed in contact with the skin on the chest was considered to be indicative of skin exposures in all skin areas covered by clothing.

The above mentioned approach gives only a rough estimate of the skin exposures since only a few patches were used to represent the entire surface of the body. **Table A1.1** indicates the skin surfaces that were associated with each individual patch sample and the percentages of the total skin surface area represented by those samples.

B. Questionnaires

The following questionnaires were administered to service station attendants and managers to obtain crucial background information.

Table A1.1 Questionnaire Form 1 – Service station information

Types of fuels dispensed	Unleaded petrol	Diesel	LPG	Other (specify)
Number of served dispensers per fuel type	Unleaded petrol	Diesel	LPG	Other (specify)
Work shifts with active service				
Number of employees per shift				
Self-Service Service	YES	NO	Only at night	
Average daily activity	number of petrol vehicles	number of diesel vehicles	number of diesel vehicles	large lorries and heavy vehicles
Fuel dispensed on average per day	Unleaded petrol	Diesel	LPG	Other (specify)
Other activities besides fuel sales	Bar/Restaurant	Sale of car accessories	Car wash	Other (specify)

Table A1.2 Questionnaire Form 2 - Personal information of the monitored attendants

Age (years) Weight (Kg) Smoking (cig/day)	....	Length of service (years) Height (cm)	....		
Personal protective equipment (PPE) or work clothing used on the job					
When is the work garment taken off?			At the end of the shift, in the workplace At home, after returning from work Other (specify)		
How long does it take for the PPE or work garment to get changed?			Every day Once a week Other (specify)		
Who takes care of the cleaning of the work garments?			The Company Washed at home Other (specify)		
Do you normally wear gloves while working?			YES	NO	Occasionally
How many times do you generally wash your hands during the day?					
Do you use protective hand creams (before work) or moisturizing hand creams (after work)?			YES	NO	Occasionally
Have you ever had hand skin irritation when working at the petrol station?			YES	NO	Occasionally

APPENDIX 2 EQUIPMENT SURFACE CONCETRATION RESULTS

Table A2.1 Concentrations of hydrocarbonts on the button panel in ng/cm^2 (9 measurements)

Hydrocarbon	% data >LOQ	Min-Max	25th percentile	Median	75th percentile	Mean ± SD
C_{14}	22	0-10	0.0	0.0	0.0	2±4
C_{15}	22	0-24.4	0.0	0.0	0.0	4.3±8.9
C_{16}	89	0-68.7	15.9	23.8	41.7	29.5±22.9
C_{17}	78	0-41	2.6	4.5	12.4	10.5±13.9
C_{18}	100	2.6-54.8	3.1	6.1	17.9	14±17
C_{19}	100	3.4-55.3	5.7	12.4	17.2	15.6±15.9
C_{20}	100	2.5-38.8	5.0	7.3	11.7	11.4±11.3
C_{21}	100	4.6-48.6	7.4	10.9	12.9	14.5±13.5
C_{22}	100	2.2-38	4.3	8.9	10.2	10.4±10.8
C_{23}	89	0-30.8	4.6	5.9	7.0	7.9±8.9
C_{24}	100	22.2-517.6	78.3	159.7	256.2	206.8±162.2
C_{25}	89	0-14.6	2.2	4.3	5.0	4.7±4.1
C_{26}	56	0-11	0.0	3.0	4.8	3.1±3.7
C_{27}	56	0-10.5	0.0	2.7	6.8	3.3±3.9
C_{28}	89	0-210.3	20.0	59.6	165.9	92.5±84.6
total hydrocarbons	100	102.1-1292.7	219.4	413.3	573.4	473.6±371.8

Table A2.2 Concentrations of hydrocarbons on the petrol hose in ng/cm^2 (9 measurements)

Hydrocarbon	% data >LOQ	Min-Max	25th percentile	Median	75th percentile	Mean ± SD
C_{14}	0	0-0	0.0	0.0	0.0	0±0
C_{15}	56	0-55.6	0.0	0.0	0.0	6.6±18.4
C_{16}	89	0-108.5	36.4	55.8	67.1	54.3±35.2
C_{17}	78	0-34.4	2.9	3.9	8.1	7.8±10.7
C_{18}	78	0-16.6	1.6	4.8	7.8	5.5±5.2
C_{19}	100	3.4-22.1	8.0	11.0	13.7	11.7±5.7
C_{20}	67	0-12.9	0.0	5.0	5.2	4.4±4.1
C_{21}	100	4.6-24.1	10.4	11.4	15.7	12.4±5.8
C_{22}	78	0-7	4.6	5.3	5.8	4.4±2.6
C_{23}	78	0-6.9	4.0	5.2	6.1	4.3±2.6
C_{24}	100	108.3-569.2	189.8	244.5	293.3	273.6±144.8
C_{25}	56	0-6.8	0.0	2.6	3.8	2.3±2.5
C_{26}	66	0-6.7	0.0	1.7	2.8	2.2±2.3
C_{27}	78	0-15.2	2.1	4.2	5.6	5±4.7
C_{28}	100	23.3-327.6	54.6	94.2	178.3	135±107.2
total hydrocarbons	100	359.4-3264.8	719.2	1083.8	1380.0	1256.5±922

Table A2.3 Concentrations of hydrocarbons on the diesel hose in ng/cm2 (9 measurements)

Hydrocarbon	% data >LOQ	Min-Max	25th percentile	Median	75th percentile	Mean ± SD
C_{14}	22	0-9	0.0	0.0	0.0	1.5±3.2
C_{15}	100	2.4-90	3.8	4.5	6.8	16.8±28.8
C_{16}	100	9.9-132.6	40.1	42.6	46.9	47.2±35.8
C_{17}	100	5.1-102.7	18.0	21.4	36.5	31.5±29.1
C_{18}	100	4.4-145.9	23.0	29.7	35.7	42.3±41.9
C_{19}	100	11.4-154	27.0	30.3	44.7	47.2±42.6
C_{20}	100	3.8-142	15.5	24.1	40.0	41.3±43.9
C_{21}	100	7.8-135.3	18.5	34.6	43.2	43.2±39
C_{22}	100	2.4-89.9	9.4	27.0	27.9	29±27.4
C_{23}	100	5.3-49.5	6.6	15.9	27.3	19.4±14.2
C_{24}	100	67.1-530.7	230.9	333.5	441.7	321.5±159.9
C_{25}	89	0-154.7	3.3	8.3	12.1	23.4±49.4
C_{26}	78	0-936.2	2.0	4.2	7.9	109.8±310
C_{27}	100	2-270.2	3.6	5.4	18.9	43.2±88.2
C_{28}	89	0-395.7	95.4	136.8	213.0	159.4±122
total hydrocarbons	100	206.6-2882.7	633.9	854.7	1242.5	1018.8±784.5

Table A2.4 Concentrations of hydrocarbons on the nozzle grip of the petrol dispenser in ng/cm2 (9 measurements)

Hydrocarbon	% data >LOQ	Min-Max	25th percentile	Median	75th percentile	Mean ± SD
C_{14}	22	0-6.9	0.0	0.0	0.0	1.5±3
C_{15}	89	0-15.5	2.9	3.3	7.8	6.2±5.6
C_{16}	100	4.6-88.3	24.9	29.9	75.8	41.4±32.1
C_{17}	100	1.7-47.6	8.3	14.7	38.0	21±16.3
C_{18}	100	3.9-81.4	12.4	24.4	42.1	31.8±24.7
C_{19}	100	10.5-89.1	19.4	43.9	53.9	40.8±25.1
C_{20}	100	6.6-95.2	16.9	27.4	41.0	35±27
C_{21}	100	16.3-110.2	21.6	36.7	57.3	45.1±30.5
C_{22}	100	8.6-120	11.7	30.2	48.2	37.4±34.8
C_{23}	100	6.3-89.9	9.5	20.9	32.1	27.9±26
C_{24}	100	585.9-5856.9	1120.4	1817.7	2036.6	2127±1606.6
C_{25}	89	0-44.2	4.1	10.5	19.5	13.9±13.6
C_{26}	89	0-32.5	4.7	6.0	7.9	8.5±9.6
C_{27}	78	0-93.2	3.5	7.5	12.4	17.2±29.3
C_{28}	100	55.9-446.8	123.0	168.6	313.6	224.4±131.3
total hydrocarbons	100	999.7-6514.6	1589.9	2458.2	3652.6	2864.5±1709.2

Table A2.5 Concentrations of hydrocarbons on the nozzle grip of the diesel dispenser in ng/cm2 (9 measurements)

Hydrocarbon	% data >LOQ	Min-Max	25th percentile	Median	75th percentile	Mean ± SD
C_{14}	100	6.2-655.6	15.0	42.6	144.3	158.3±224.4
C_{15}	100	18.2-1542.6	39.2	86.3	383.8	378.2±543.8
C_{16}	100	43.4-2209.6	84.8	134.7	656.8	537.7±761.1
C_{17}	100	137-2753.4	246.8	287.6	681.0	759.9±943.7
C_{18}	100	221.2-2684.8	254.8	373.9	751.2	811.3±897.9
C_{19}	100	178.6-1809.8	236.1	328.8	484.0	586.7±583
C_{20}	100	165.2-1283.5	226.4	299.8	357.2	462.4±408.2
C_{21}	100	159.6-1060.1	217.0	253.4	284.9	383.7±317.1
C_{22}	100	144.2-801.3	181.7	199.5	237.3	305.4±231.8
C_{23}	100	116.4-548.4	127.5	153.0	177.5	219.6±154.3
C_{24}	100	911-5750.2	1239.5	1975.8	2319.6	2203.2±1460.5
C_{25}	100	61.6-267.7	65.8	83.2	94.1	112.4±75.8
C_{26}	100	35.3-172.6	40.1	47.1	61.1	68±48.9
C_{27}	100	13.6-97.6	17.9	19.6	59.6	39.1±32.3
C_{28}	100	83.2-398.2	150.6	166.4	341.6	232.9±116.3
total hydrocarbons	100	3346.9-18288.7	4699.2	5256.5	8362.6	7456±5069.4

APPENDIX 3 LINEAR REGRESSION ANALYSIS AND DERMAL TRANSFER COEFFICIENT CALCULATIONS

Figure A3.1 Linear regression analysis comparing C_{21} concentration on the nozzle grip of the diesel dispenser with loading onto the hands

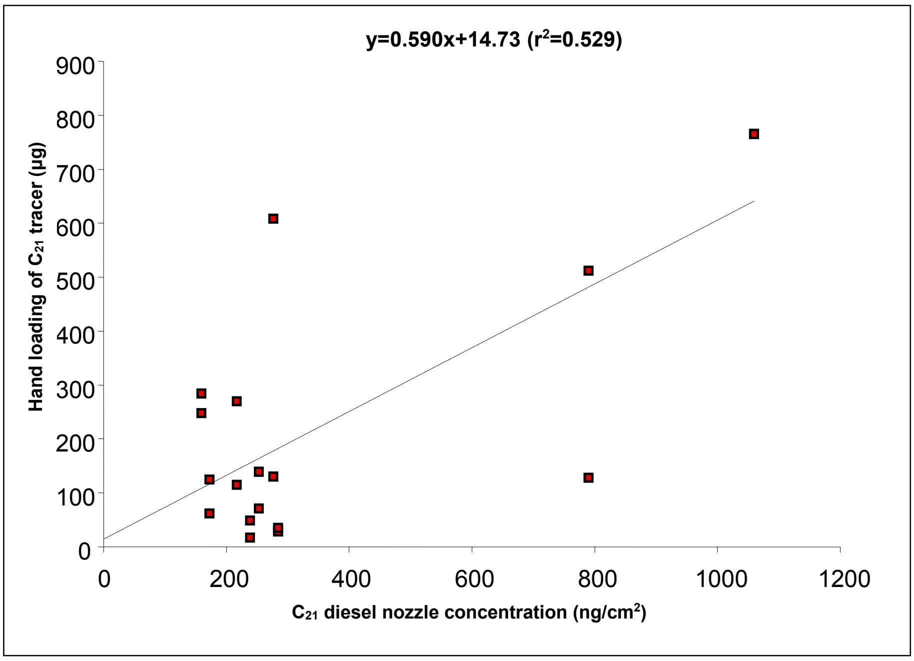


Figure A3.2 Linear regression analysis comparing C21 concentration on the nozzle grip of the petrol dispenser with loading onto the hands

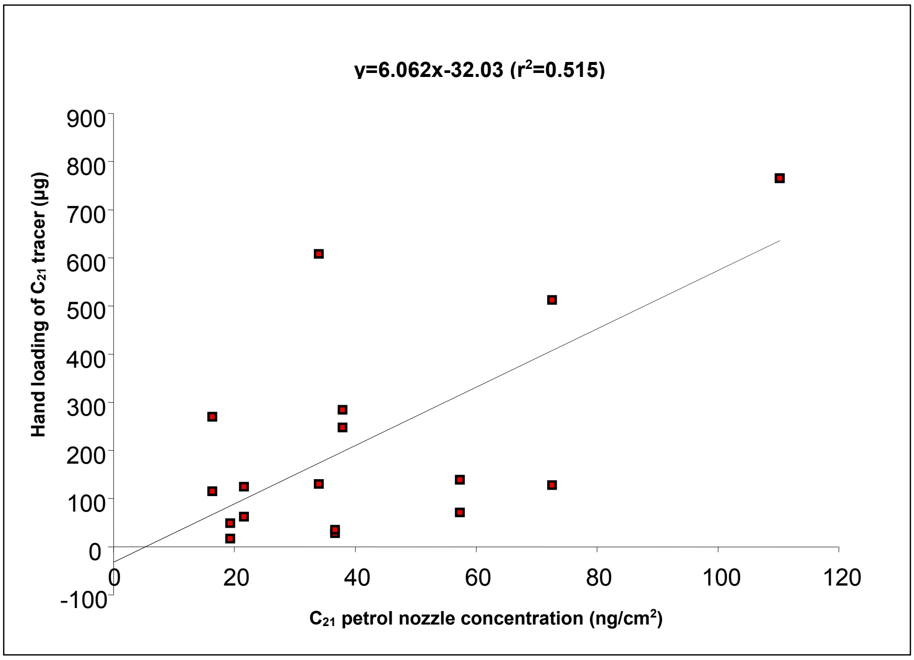


Figure A3.3 Linear regression analysis comparing C_{21} concentration on the button panel with loading onto the hands

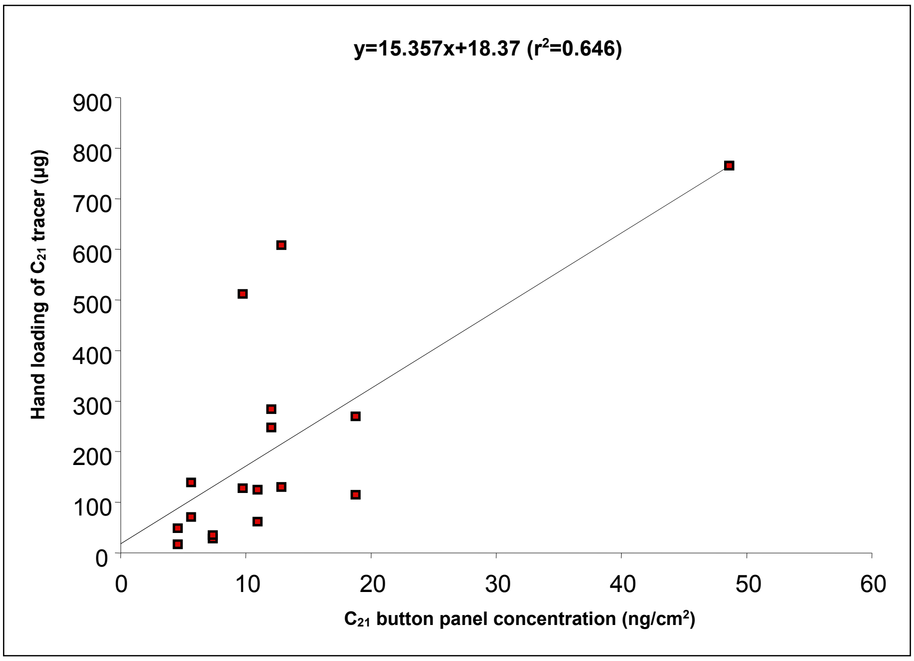


Figure A3.4 Linear regression analysis comparing C_{21} concentration on the diesel hose with loading onto the hands

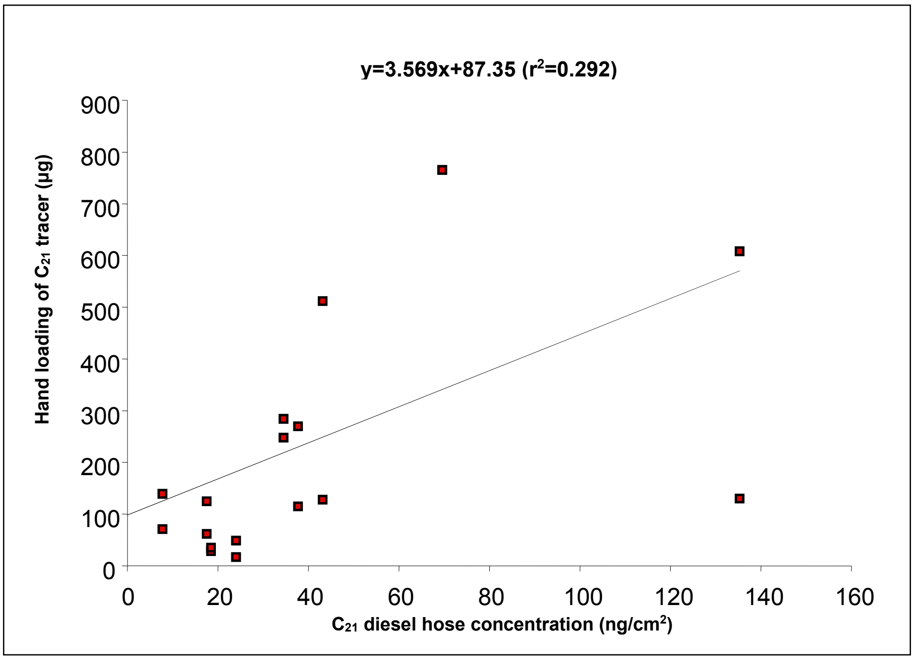
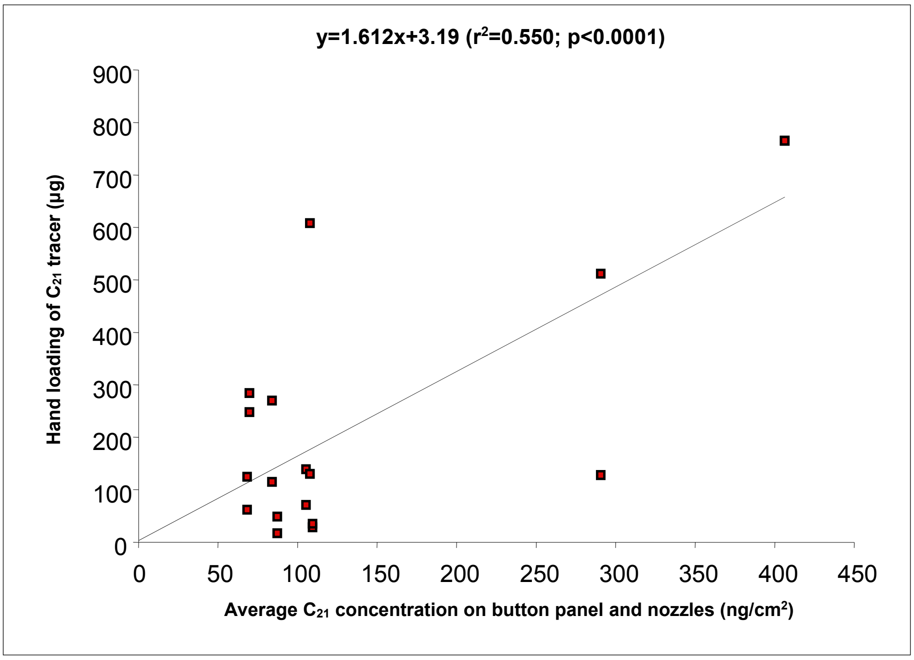


Figure A3.5 Linear regression analysis comparing C_{21} concentration on the button panel and nozzle grips with loading onto the hands



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