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Occupational Dermal Exposure to Heavy Fuel Oils

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Heavy fuel oil (HFO) consists of a wide variety of blended hydrocarbon residues from refinery distillation and cracking processes. Dermal exposure to HFO may cause oil folliculitis and dermatitis and it is known to contain compounds that may cause skin cancer, including benzo(a)pyrene. There is no standard and validated method for determining dermal exposure to HFO and hence no exposure data are available. Concawe has funded this study to obtain exposure data in order to inform health risk assessment for HFO exposure.

A validated method for the collection and analysis of dermal exposure to HFO was developed. Subsequently, quantitative data were collected from the relevant industries under production (oil refineries), distribution (fuel terminals) and use (fuel for power stations, heating, marine and feedstock) scenarios. Attempts were also made to validate and calibrate a semi-quantitative method for dermal exposure assessment (DREAM).

We concluded that, for the scenarios investigated, dermal exposures were relatively low. There was no relationship between quantitative dermal exposure measurements and semi-quantitative estimates of dermal exposure, most likely due to the limited range in dermal exposure levels. We advise that exposure data should be collected using the validated method for dermal exposure measurements of HFO developed in this study. While we were able to capture exposure data for some of the main scenarios for which there is a potential for HFO exposure, there are other important exposure scenarios (e.g. engine-building) which were not included. The low frequency and levels of exposure obtained for the scenarios investigated in this study are not necessarily indicative of exposure levels for situations that have not been investigated here.

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SUMMARY

Heavy fuel oil (HFO) is a term used to describe a wide variety of blended hydrocarbon residues from refinery distillation and cracking processes. HFO is used in industry as fuel for power stations and for heating of large industrial sites. In Scotland, HFOs are also used as heating fuel in hospitals and distilleries in remote areas. Due to its physico-chemical properties dermal exposure is likely to be the main route of exposure for employees involved in production, transport and use of HFO. Among the health effects of HFO exposure are oil acne, oil folliculitis and dermatitis. Additionally, HFO contains compounds that may cause skin cancer, including benzo(a)pyrene.

Concawe is undertaking a risk assessment of HFO. However, there is no standard and validated method for determining dermal exposure to HFO and hence no exposure data are currently available. Consequently, Concawe funded a study to develop a validated method for measuring dermal exposure and to collect quantitative and semi-quantitative dermal exposure data. Additionally we aimed to use the quantitative data to validate the semi-quantitative methods and use the validated semi-quantitative method to estimate dermal HFO exposure in various exposure scenarios.

Field surveys were carried out at five different sites – one refinery, two fuel terminals and two power stations. Dermal exposure samples were obtained with a removal method using moist wipes. The dermal measurement method was validated prior to the workplace surveys and the average recovery efficiency for the sample preparation and analysis procedure approached 100%.

A total of 38 sets of dermal samples from 5 anatomical locations (palmar surfaces, forearms and neck) were collected from the five facilities during five different groups of tasks – loading/unloading, different cleaning and maintenance activities, sampling and during general operations. Detectable levels of HFO were found mostly on the hands (arithmetic mean = 0.6 – 0.9 μg/cm^2). HFO levels on the forearms and the neck were generally below the limit of detection, although the arithmetic mean levels for the forearm were higher than those for the hand (arithmetic mean 0.6 – 0.9 μg/cm^2). There was a moderate correlation between the log-transformed hand and forearm exposure (Pearson correlation coefficient = 0.61).

Calculations of the within- and between-worker variance for hand exposure for the loading/unloading and maintenance tasks indicated that the main variance component was the within-worker variance for loading/unloading while for the maintenance task the between-worker variance component was the dominant factor.

Using a modification of the semi-quantitative method for dermal exposure assessment (DREAM), fifty-eight DREAM assessments were completed from 11 sites. These data described potential and actual hand, forearm and body exposures during activities carried out in refineries, fuel terminals, power stations and engine building sites. Potential exposure is equivalent to the dermal exposure assuming no personal protective equipment (PPE), such as gloves, overalls, or other protective clothing were used, while the actual exposure is an estimate of the dermal exposure after taking into account the protective effects of any PPE used by the employees. Results are expressed in "Dream Units" or DU, per cm^2 of skin. A subset of these data (N=16) were compared with dermal measurements collected at the same time.

The actual hand exposure was much lower than potential exposure levels (AM actual: 0.2–0.4 DU/cm^2; AM potential: 0.6–5.2 DU/cm^2) with the potential hand exposure being lowest at engine building sites. Whole body exposure was also relatively low. There was no correlation

between the DREAM estimates and the results of the dermal exposure measurements, which is in contrast with the correlation found between measured and estimated dermal exposure observed by the scientist who developed the DREAM method. However, the range of exposure levels was relatively narrow. Comparison of our data with the datasets used by the developers of the DREAM model for the validation exercise indicated that our data are compatible with their overall comparison between DREAM and measured dermal exposure data.

This study has been successful in developing a validated method for sampling dermal exposure to HFO. Both the levels and frequency of dermal exposure levels to HFO appeared to be generally low for workers at the sites and companies included in this study. However, this may not be the case for HFO exposure scenarios for which dermal measurements were not collected.

As there was no relationship between quantitative dermal exposure measurements and semi-quantitative estimates of dermal exposure, the semi-quantitative method may not be appropriate for estimating HFO exposure. Consequently, further data collection for these and other exposure scenarios should be collected using the method for dermal exposure developed and validated during this study.

1 INTRODUCTION

Heavy fuel oil (HFO) is a general term for a wide variety of blended hydrocarbon residues from refinery distillation and cracking processes. They are viscous liquids with high boiling points (typically 350 to 650°C) that require heating for storage and combustion. HFOs contain a range of high molecular weight compounds, including aromatic, aliphatic and naphthenic hydrocarbons, along with asphaltenes and some heterocyclic compounds containing sulphur, nitrogen and oxygen. In addition, they may also contain traces of vanadium and other metals. The composition of HFO can vary widely between refineries and over time, due to the refinery configuration, the crude oils being processed and the overall refinery demand (Concawe, 1998). Refineries in the United Kingdom obtain crude oil predominantly from the North Sea and among the products resulting from the atmospheric distillation of the crude is heavy fuel oil. A barrel of North Sea crude oil will usually yield about 12% of HFO.

No consistent terminology for HFO is used in the refinery and user industry and in addition to HFO there are other names commonly used to describe this range of products, including residual fuel oil, bunker fuel, marine fuel oil and black oil. Concawe (1998) produced a list of oils with associated CAS-numbers that are included in the category of HFOs (Appendix I). This list includes blends of HFO with gas oils and can also include oils described in the industry as medium fuel oils.

Use of HFO is restricted to industrial use as a fuel for boilers, furnaces and as marine or bunker fuel in engines of seafaring vessels. In the UK, HFOs are used as an industrial fuel for power stations and for heating of large industrial sites. In Scotland, HFOs are used as heating fuel in hospitals and distilleries in remote areas such as the Scottish Highlands.

Due to its high boiling point and low vapour pressure, inhalation exposure for HFO is generally considered to be of low importance. Dermal exposure is likely to be the main route of exposure for employees involved in production, transport and use of HFO. Prolonged repeated contact with the skin may cause oil acne, oil folliculitis and dermatitis. In addition, HFOs contain compounds that may cause skin cancer, including benzo(a)pyrene and other polyaromatic hydrocarbons (PAHs).

Concawe, established in 1963, is the oil refineries' European association for environment, health and safety in refining and distribution. Its membership comprises most oil companies operating in Europe and issues concerning occupational health and safety come under its scope of activities (http://www.concawe.be/). They are currently undertaking a risk assessment for HFO according to the methodology used by the European Union for Existing Substances – described in a Technical Guidance Document (TGD) available at http://ecb.jrc.it/existing-substances/. However, due to the absence of a standard and validated method for determining dermal exposure to HFOs, there are currently no data available for dermal exposure to HFO in various exposure scenarios during the product's lifecycle. There are a limited number of predictive models that can be used to provide semi-quantitative estimates of dermal exposure, such as the EASE (Tickner *et al*, 2005) and DREAM models (van Wendel de Joode et al., 2003). These approaches are usually less expensive than quantitative measurement in workplaces, although the data are usually less reliable and accurate compared to measured exposure data.

In order to collect quantitative and semi-quantitative data on dermal HFO exposure, Concawe funded a study to develop a validated method for measuring dermal exposure and to collect quantitative and semi-quantitative dermal exposure data. An additional aim of the study was to use the quantitative data to validate the semi-quantitative DREAM method. It was proposed to use this validated semi-quantitative method to estimate dermal HFO exposure in various exposure scenarios where measurement data were unavailable.

2 AIMS

The main aim of this study was to collect data on dermal exposure to HFO during production, transport and use of HFOs and to provide exposure estimates for various exposure scenarios during its lifecycle. To achieve this aim we addressed the following key objectives:

i). To develop a validated method for measuring dermal HFO exposure;
ii). To identify and approach a number of companies and workplace situations where there is potential for exposure to HFO;
iii). To collect contextual exposure information from these sites and use these data to apply a semi-quantitative dermal exposure assessment method;
iv). To carry out quantitative dermal exposure measurements using the validated method at a small number of sites;
v). To compare the quantitative measurement data with the semi-quantitative estimates; and
vi). To provide HFO dermal exposure estimates for relevant workplace scenarios.

3 METHODS

3.1 WORKPLACE SCENARIOS

Relevant industries and workplace scenarios were identified within manufacturing, distribution and user industries, using information from literature, the internet and experts in the field. Companies within these industries were contacted to engage their participation.

3.2 RECRUITMENT OF COMPANIES

Companies were recruited with the assistance of Concawe, who provided contact details for the petrochemical industry. Information on user companies was obtained though contacts within the refinery and oil distribution industry and through internet searches. In particular, power generation plants, ship and dockyards, carbon black manufacturers, tank cleaning and oil recycling companies and relatively small scale users of HFO were approached. Towards the end of the study, Concawe approached an engine building and maintenance company to participate in the study. Most of the companies approached were based in the UK, although data were also collected from one company in Belgium and two companies in Finland.

The companies were contacted by telephone and email and were provided with information about the study. Subsequently, it was established whether HFO was produced or used within the company using the list of CAS numbers obtained from Concawe (1998) (Appendix 1) and, if so, whether they would be interested in participating in the study. With the exception of the carbon black manufacturing companies and several companies in the tank cleaning and oil recycling industry, all companies that were approached and confirmed use of HFO agreed to participate. However, a number of sites, such as hospitals and distilleries in the Highlands of Scotland, were excluded from the study since they were relatively small users of HFO and none of their employees would usually come in contact with HFO.

Subsequently, information on HFO exposure scenarios was requested from participating companies in the form of risk assessments, such as assessments made under the Control of Substances Hazardous to Health (COSHH) regulations in Great Britain.

3.3 QUANTITATIVE EXPOSURE MEASUREMENTS

3.3.1 Dermal sampling method

As part of this project a validated method was developed using skin cleansing clinical wipes saturated with 70% isopropyl alchohol (Safety First Aid Group Limited). The principle behind the method is the use of a specific PAH as a marker of HFO exposure. A comprehensive report of the method development is included in Appendix II.

To identify a suitable marker, nine HFO samples from different sources were analysed for their PAH content. The results showed that a wide range of PAHs can be present in a sample and the levels of these PAHs can vary extensively between samples (Table 1). The most common PAHs in the HFO samples were naphthalene, with levels ranging from <2 to 5.2 x 10^4 mg/kg, and phenanthrene, with levels ranging from <2 to 5.3 x 10^2 mg/kg. These results clearly show that, if naphthalene or phenanthrene were to be used as markers of HFO exposure then for each set of dermal samples collected, a corresponding bulk sample needs to be obtained from the same exposure source as the dermal samples. These bulk samples can subsequently be used to develop calibration curves for the analysis.

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Table 1 PAH levels in oil samples provided to IOM

PAH Compound	PAH Concentrations in Oil (mg/kg)								
	Oil 1	**Oil 2**	**Oil 3**	**Oil 4**	**Oil 5**	**Oil 6**	**Oil 7**	**Oil 8**	**Oil 9**
Naphthalene	1.6 x 10^{3}	3.4 x 10^{3}	5.2 x 10^{4}	<2	<2	7.2 x 10^{2}	56	1.1 x 10^{2}	2.2 x 10^{3}
Acenaphthalene	<2	43	3.3 x 10^{3}	<2	<2	30	3	11	<2
Acenaphthene	35	3.1 x 10^{2}	44	<2	<2	2.9 x 10^{2}	8	77	34
Fluorene	48	3.3 x 10^{2}	4.2 x 10^{2}	<2	<2	5.2 x 10^{2}	39	3.1 x 10^{2}	45
Phenanthrene	95	6.5 x 10^{2}	5.3 x 10^{2}	20	<2	2.8 x 10^{2}	84	9.4 x 10^{2}	2.7 x 10^{2}
Anthracene	93	92	9.8 x 10^{2}	22	<2	5.2 x 10^{2}	83	74	18
Fluoranthene	13	28	4.3 x 10^{2}	17	<2	3.1 x 10^{2}	<2	31	11
Pyrene	48	77	7.7 x 10^{2}	25	<2	1.6 x 10^{3}	24	1.2 x 10^{2}	2.5 x 10^{2}
Benz(a) anthracene	43	8	2.0 x 10^{2}	<2	<2	6.4 x 10^{2}	<2	<2	1.1 x 10^{2}
Chrysene	43	11	2.0 x 10^{2}	<2	<2	1.2 x 10^{3}	<2	<2	95
Benzo(b) fluroanthene	14	5	27	15	<2	1.4 x 10^{2}	11	<2	16
Benzo(k) fluroanthene	6	3	<2	15	<2	17	9	<2	<2
Benzo(a)pyrene	46	7	39	27	<2	3.7 x 10^{2}	15	<2	71
Indeno(1,2,3-cd) fluoranthene	<2	<2	<2	<2	<2	<2	<2	<2	<2
Dibenz(a,h) anthracene	<2	<2	<2	<2	<2	<2	<2	<2	<2
Benzo(ghi) perylene	<2	<2	<2	32	<2	1.9 x 10^{2}	<2	<2	97

Oil 1 = HFOl TK-624 (EC No 270-675-6),
Oil 2 = Bunker fuel oil TK-225 (EC No 270-675-6),
Oil 3 = PFO TK-339 (Cas No 64742-90-1),
Oil 4 = Wax job 66 (Cas No 64741-87-7),
Oil 5 = Residue job 66 (Cas No 68955-27-1),
Oil 6 = HCO job 67 (Cas No 64741-61-3),
Oil 7 = HGO job 63 (Cas No 68783-08-4),
Oil 8 = VGO job 66 (Cas No 70592-77-7),
Oil 9 = HFO S502 (EC No 270-675-6)

Further tests were carried out with Oil 1 in Table 1 to determine the desorption efficiency, limit of quantification, storage stability and stability on the skin. The desorption efficiency from spiked wipe samples ranged from 95% to 106%. The sampling efficiency, determined by spiking HFO solutions on pig skin, followed by sampling the skin with the wipes, ranged from 85% to 109%. However, at lower levels (i.e. below 20 µg of HFO on the skin) the recoveries were reduced. The detection limit for individual PAHs by Gas Chromatography-Mass Spectroscopy (GC-MS) was 0.1 µg/ml. Although, in practice the detection limit for some individual PAHs is much lower. The calibration for the HFO analysis was based on weighed masses of HFO. One single PAH peak was used for quantification. It was assumed that the relative proportion of different components of the HFO was the same in the bulk material used to establish the calibration as that in the samples. The estimated detection limit for HFO was 1 µg/ml. This was based on the peak areas of the calibration standards and consideration of the height of the peak relative to the background. However, the limit of detections for the other oils (oils 2 to 9) will be different due to the different PAH content. The spiked samples were found to be very stable with a 90% recovery from samples stored for 14 days at room temperature. HFO levels spiked on the skin were found to be stable for up to 4 hours.

3.3.2 Field survey

Dermal exposure measurements from employees who are potentially exposed to HFO were carried out at a 5 of different sites. Dermal samples were obtained using a removal method using clinical wipes saturated with 70% isopropyl alchohol. In contrast to the laboratory trials where we used small clinical sterets (2.5 x 2.5 cm) for HFO sampling, in the field surveys we used larger wipes (13 x 13 cm) for practical reasons.

The anatomical areas sampled were the hands, the forearms and the neck. Wipe samples were collected from the entire palmar surface of each hand. An acetate template with an open aperture of 25 cm^2 was used to collect wipe samples from the inner surface of each forearm and one side of the neck. Each sample comprised three sequential wipes from the same anatomical area and stored in a single container. To avoid cross contamination via transfer between anatomical sites and between workers, the researcher used a fresh pair of gloves after each set of 3 wipe samples. A clean template was also used for each worker and anatomical area.

Samples were generally collected immediately following the completion of a task or before rest breaks. In this way contamination was not lost from the skin as a result of washing and was therefore representative of the level of skin contamination immediately upon completion of the task. A limited number of pre- and post task sampling was carried out. Dermal wipe samples were collected during site visits whenever a relevant task was carried out. This included some repeat samples of tasks and individuals.

A field blank sample was obtained for each subject sampled to check for contamination introduced during the sampling procedure. The field blanks comprised a series of three wipes which were handled in the same way as the exposed samples but without being wiped over the workers' skin. Bulk HFO samples were collected for each measurement visit and from each area where dermal samples were collected.

3.3.3 Analysis

The samples were analysed at the IOM analytical laboratory, which had previously developed and validated the method to determine the mass of HFO based on PAH content of the bulk and wipe samples (Appendix II).

All wipe samples were transferred to the laboratory in 30 ml glass jars and were extracted with 10 to 20 ml dichloromethane. Extracts were dried over calcium chloride and analysed by GC fitted with a 30 m DB5-MS capillary column[1] and which was programmed to heat from 60 to 310^{o}C. The MS was set in selected ion monitoring (SIM) mode for the specific ions corresponding to naphthalene, phenanthrene and benzo(a)pyrene. The ion chromatograms generated were examined for these specific ions. Calibration standards were prepared from known weights of the HFO in the desorption solution using relevant bulk samples. Calibration curves were developed using phenanthrene or naphthalene as markers for exposure to HFO. The decision on which PAH to use was based on the quality of the calibration curve.

The quantity of HFO in each sample was used to calculate the dermal surface loading for each anatomical area, expressed in terms of mass per unit area (μg/cm^2). None of the field blanks contained any detectable levels of HFO, and therefore no correction was required for the field samples. The surface load for each hand was calculated using a palmar surface area of 210 cm^2. For calculating the surface load on the inner forearms and the neck the surface area defined by the acetate template (25 cm^2) was used.

[1] The IOM has a quality assurance (QA) system in place for GC-MS that is equivalent to those required for laboratory analyses under UKAS accreditation. Quality measures include ensuring that work is undertaken by appropriately trained analysts, reports are checked, replicate analysis is conducted and equipment is regularly maintained. UKAS accreditation has not been sought for GC-MS work as the work largely involves non-routine analysis whereas UKAS accreditation is designed for routine testing.

Surface load on hands (μg/cm²) $= \dfrac{mass\ on\ hands\,(\mu g)}{210\,(cm^2)}$

Surface load on neck (or forearm) (μg/cm²) $= \dfrac{mass\ on\ neck\,(or\ forearm)(\mu g)}{25\,(cm^2)}$

3.4 SEMI-QUANTITATIVE EXPOSURE MEASUREMENTS

3.4.1 DREAM method

A generic semi-quantitative method for estimating dermal exposure was developed by van Wendel de Joode *et al* (2003) (DeRmal Exposure Assessment Method – DREAM). This method is based on a conceptual model develop by Schneider et al (1999). The following contextual information is collected, preferably during observations of the tasks for which an assessment is required:

- job, tasks and department variables;
- agent specific variables – determinants for intrinsic emission estimates;
- exposure route variables – direct emission, transfer and deposition;
- clothing related variables, including personal protective equipment;

The evaluation module within DREAM is based on information from about 33 variables for nine separate body parts (face, upper arms, forearms, hands, front torso. back torso, lower body, lower legs and feet).

In this study the contextual information was collected in a variety of ways. First of all, during the field surveys, dermal measurements as well as DREAM observations were carried out by one of the researchers (YC). Secondly, DREAM observations were carried out by occupational hygienists at the companies in Belgium and Finland. Finally, for the remaining companies DREAM assessments were completed as far as possible by one of the researchers (YC) based on information contained in the risk or COSHH assessments that were made available by the companies. These partly completed assessments were subsequently returned to the companies, with a request to check, update and complete the information. Follow-up telephone interviews were carried out, where necessary, to complete the assessments.

The original DREAM method is based on three different modes by which dermal exposure may occur (emission, transfer and deposition). However, the deposition route was not considered to be relevant for dermal HFO exposure due to its physico-chemical properties, and, hence, in this study we only considered the emission and transfer modes of transfer. Appendix III presents the truncated form for the DREAM assessment.

A set of algorithms was used to transform the contextual information into semi-quantitative exposure estimates. A SAS for Windows (version 9.1; SAS Institute Inc, NC, USA) procedure was obtained from the scientist at the Institute for Risk Assessment Sciences (IRAS) who developed the method. The semi-quantitative estimates were expressed as arbitrary Dream Units (DU) per cm² of skin surface. The algorithms provide estimates of potential and actual dermal exposure. Potential exposure is equivalent to the dermal exposure assuming no personal protective equipment (PPE), such as gloves, overalls, or other protective clothing were used, while the actual exposure is an estimate of the dermal exposure after taking into account the protective effects of any PPE used by the employees.

3.4.2 Confidence rating of DREAM

Each questionnaire was given a confidence rating using a Likert Scale that rated confidence in the overall validity and completeness of each DREAM questionnaire returned by participants. Confidence was rated on a scale of 1 to 5 with a rating of 1 representing questionnaires that were completed from direct observations by one of the researchers and a rating of 5 representing incomplete questionnaires (Table 2).

Table 2 Scaling used to rate confidence in DREAM estimates

Scale	Description
1	Direct observation by researcher
2	Direct observation by company occupational hygienist
3	Observed at least once by observer
4	Never observed and based on indirect information
5	Incomplete questionnaire

3.5 STATISTICAL METHODS

3.5.1 Data handling and analysis of quantitative exposure data

Samples with exposure values below the limit of detection were given the value of the limit of detection divided by the square root of two. Exposure data were analysed using SAS for Windows (version 9.1). Measured dermal exposure data were summarised by anatomical location. For each individual sample set the mean HFO exposure on the hands and on the forearms was calculated. These were subsequently described by industry sector and task group in terms of arithmetic mean (AM), geometric mean (GM), geometric standard deviation (GSD), median, 90th percentile and the range. In addition, the Proc Nested in SAS for Windows procedure was used to determine the within- and between-workers variability when sufficient repeated measurements were available.

3.5.2 Analysis of DREAM data

DREAM exposure data were also summarised by industry sector and task group and described in terms of AM, median, 90th percentile and range, for the hands, forearm and the remainder of the body (i.e. whole body minus hand and forearms).

3.5.3 Comparison of quantitative and semi-quantitative data

We were able to compare the results of the dermal exposure measurements with the DREAM estimates using a subset of the data. These consisted of tasks for which a measurement and a DREAM observations was carried out simultaneously. This subset of the data was used to validate and if possible calibrate the semi-quantitative DREAM method for assessing HFO exposure. Results were plotted and Pearson's correlation coefficients were calculated for hands and forearm based on log-transformed exposure estimates, after combining the measurement results for the left and right hand and forearm.

4 HFO EXPOSURE SCENARIOS

Figure 1 provides a simple overview of the life cycle of heavy fuel oil. Subsequent to its production at a refinery, HFO is shipped via distribution terminals to various users. Use of HFOs (at least in the UK) can be broadly categorised into power stations, industrial heating (for example in hospitals and distilleries in the Scottish Highlands), marine fuel, and feed stock oil in manufacture of chemicals such as carbon black. Exposure scenarios may exist for tank cleaning and recycling of HFO.

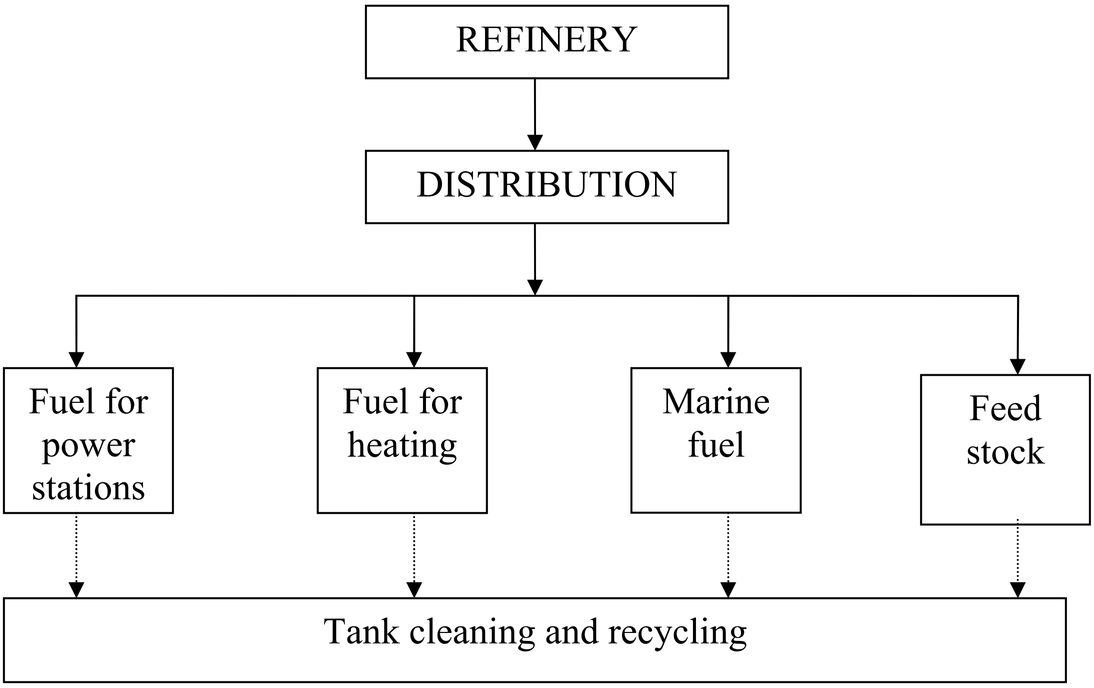

Figure 1 The life-cycle of Heavy Fuel oil

Table 3 gives an overview of the main exposure scenarios within each part of the HFO life cycle. This shows that some of the exposure scenarios are common to more than one life-cycle stage. Dermal exposure during these activities such as sampling/testing, tank dipping, cleaning of filters and pump maintenance may depend more on the local exposure conditions and personal working practices than on whether this occurs within a refinery or power station. However, frequency and duration of activities are likely to differ between industries and sites and this will lead to differences in the overall dermal HFO exposure.

Table 3 HFO life cycle showing the distribution of tasks among the different areas

HFO life cycle	Exposure Scenarios	Broad scenario categories
PRODUCTION	Operation	General Operation
	Line spading	Maintenance
	Cleaning	Cleaning
	Filter cleaning	Cleaning
	Sampling	Sampling and testing
	Testing	Sampling and testing
	Tank cleaning	Cleaning
	Pump maintenance	Maintenance
DISTRIBUTION	Loading road tankers	Loading/unloading
	Loading ships	Loading/unloading
	Sampling/testing	Sampling/testing
POWER STATIONS	Sampling/testing	Sampling/testing
	Pump maintenance	Maintenance
	Filter cleaning	Cleaning
	Cleaning burner tips	Cleaning
	Unloading	Loading/unloading
	Tank dipping	Sampling/testing
HEATING FUEL	Unloading	Loading/unloading
	Maintenance	Maintenance
MARINE FUEL	Clean filters/other equipment	Cleaning
	Pump maintenance	Maintenance
	Tank dipping	Sampling/testing
	Engine building/maintenance	Maintenance
FEED STOCK	Tank dipping	Sampling/testing
	Filter Cleaning	Cleaning
	Pump maintenance	Maintenance
TANK CLEANING/OIL RECYCLING	Tank cleaning	Cleaning
	Testing	Sampling/testing
	Tank dipping	Sampling/testing

5 FIELD SURVEYS

5.1 WORKPLACE AND TASKS DESCRIPTIONS

Field surveys were carried out at four different sites, one refinery, two fuel terminals and one power plant. However, the refinery site also included a power plant, and in the rest of this report this power plant will be regarded as a separate site. The following section provides a description of these sites and relevant activities.

5.1.1 OIL REFINERY

The refinery and petrochemicals facility visited during the survey was located on a site of 2 square kilometre. The petrochemicals facility manufactures over 2 million tonnes of chemical products per annum and the refinery has an annual capacity of 10 million tonnes. The site uses crude oil and natural gas liquids from the North Sea and transforms them into petrol, fuel products and a range of olefins and polymer products. The refinery processes around 200,000 barrels per day of crude oil. There was a total 2,000 workers employed at this oil refinery. The following tasks were identified as having potential for dermal exposure to HFO:

- Spading the line;
- Pump maintenance;
- Cleaning of spillages;
- Sampling of HFO;
- Testing of HFO in the laboratory.

During the survey at the oil refinery dermal samples and observations were only carried out for the spading of an HFO. This activity is described below.

Spading the line

The mechanical fitters are responsible for maintenance activities around the plant. These sometimes require isolation of HFO-containing pipe lines using isolation spades. These are round pieces of metal with a small tab that is placed between two pipe flanges to give a positive isolation from the central section. The isolated pipe section is subsequently opened and residual oil drained into a large tray under the pipe and then pumped away. This is potentially a messy job when there may be a lot of residual oil in the line and therefore the potential for exposure is high.

5.1.2 OIL DISTRIBUTION TERMINALS

Dermal measurement surveys were conducted at two oil fuel terminals. The main activity of both terminals is distribution of HFO to user industries e.g. power stations, remotely located distilleries and hospitals. One terminal operated only via road tankers, while the second terminal serviced road tankers as well as sea-going vessels with an HFO/gas oil fuel blend. Distribution of HFO via road tankers was contracted out to haulage companies and therefore potential for dermal exposure was not limited to employees of the company operating the terminal. The number of road tanker drivers visiting the terminals on any one day can vary depending on demand. Drivers employed by the haulage companies were asked to participate in the study. Other occupations with possible exposure include gantry operators and mechanical fitters/maintenance operators; these workers are employed by the company operating the terminal.

Use of safety helmet, coveralls, hi-visibility vest and safety boots is mandatory at both sites. Additional protective equipment – safety glasses and impervious gloves were used by the road tanker drivers when loading and by the gantry operators and fitters during certain maintenance activities.

Top loading road tanker
Road tankers are top loaded with HFO from dedicated loading bays. The driver positions his tanker directly under the rails of the loading bay, allowing him to step down from the stationary platform of the bay onto the top of the tanker. This is further facilitated by a fixed metal grill on top of the tanker. The top loading arm is manually swung into place above the tanker and the driver positions it into the tank inlet. To reduce the risk of splashing, the driver covers the manhole of the tanker and the end of the loading arm with a rag. HFO loading is generally at a rate of about 2,700 litres per minute and with an average tanker capacity of 31,000 litres, the filling usually is completed in 10-15 minutes. The actual flow rate is influenced by the temperature of the oil, which is kept at a temperature between 54-70^{o}C. When loading is complete, the driver once again climbs on top of the tanker and removes the loading arm. He removes any excess HFO from the loading arm by wiping with the rag that is used to prevent splashes, usually after first soaking it with a solvent. There is potential for considerable transfer of oil from the loading arm onto the gloves of the driver and during the observations the driver wiped his gloves with the solvent soaked rag. The rags are generally re-used and usually stored on top of the tanker in a plastic bag.

All surfaces of the loading bay at the sites visited, such as the handrails and control panels, were heavily contaminated with oil, which can potentially lead to dermal exposure. For example, drivers usually remove their gloves before operating the control panels.

Bottom unloading/Ship loading (coupling/uncoupling)
Tankers at one of the sites are bottom-unloaded during ship fuelling. This process involves a hose coupling/uncoupling scenario where the driver connects the transfer hose of the tanker to the loading point of the transfer line of the ship. Discharge to ships takes between 45 minutes to 1 hour.

Gantry cleaning/maintenance
The gantry operator spends most of his day around the gantries doing miscellaneous duties including cleaning tasks and maintaining sample points. These tasks do not necessarily involve HFO handling, as most of the loading bays are for other fuels, such as petrol and diesel. Potential for HFO exposure exists due to his presence around the HFO loading bays as many surfaces of the loading bay can be contaminated with oil and during cleaning of the sample points. Sample points are cleaned three times a day by applying a solvent to the sample point and allowing the solvents to drip into a tray before disposal.

5.1.3 POWER STATIONS

Two power stations with different capacities were visited. The first of these had a relatively large capacity whereas the second one serviced a large oil refinery and had a lower capacity.

The first power station is a coal-fuelled power station which was built in 1968 and has 4 units (one boiler for each unit) with a total capacity of 300 kW. Fuel oil is used to heat the boiler at start up before it is ready to burn coal. This is only necessary after the boilers have been switched off. Each boiler has a set of 36 fuel burners but generally eighteen are used at a time. Fuel burner tips are specialised tubes which direct fuel and combustion air into the combustion zone. The arrangement and performance of burners have a direct impact on the distribution of air, the stability of the flame in the boiler and the combustion efficiency. Each burner consists of a fuel pipe and nozzle with a nozzle tip at the end of the nozzle at the interior wall of the boiler. Fuel burner tips are cleaned prior to start up of the boilers to ensure efficiency of combustion.

The start up of the boilers takes between 1 and 5 hours, depending on the temperature of the boiler. The use of fuel burners depends on the electricity demand. If electricity demand is relatively low and units are turned off at night or over the weekend, then more fuel oil is needed for start up. In contrast, if demand is continuously high, for example during the winter months and units are producing electricity continuously then there is no need for fuel burning.

HFO is delivered to the power station by road tanker and pumped into a fuel storage tank. Depending on the demand, this occurs about three times a week, with 3-5 tanker loads being received each time. There are two storage tanks on the site, although at the time of the survey only one was in use. These fuel tanks are rarely cleaned. During loading the driver connects the hose between the road tanker and delivery point (loading bay). During transfer either the driver or the water treatment operator takes an oil sample using a bucket lined with a plastic bag which is kept in a cupboard suspended on a wall about 1.5 metres from the loading bay. The entire area was heavily contaminated with HFO at the time of the survey. The fuel is pumped via the fuel pump house, heated, filtered and piped to the burners. There are 2 filters in the pump house, which are cleaned about 10 times a year.

The second power station included in this survey was based on the site of a large oil refinery and provided electricity predominantly to the refinery and surrounding industries. This power station runs predominantly on gas and uses HFO as a back up approximately 2-3 times per month for a few hours. The station operates a twelve hour shift system with four power station operators on work rotations. This power station has seven boilers with eight fuel oil burning tips per boiler, which are cleaned after use. HFO is stored in two storage tanks next to the power station. At the start of each shift the tanks are dipped to check the level of oil.

The following tasks descriptions apply to both power stations unless stated otherwise.

Sample collection
HFO samples are collected for analyses in the first power station on a daily basis. This involves tapping about 0.5-1 litre of oil from a sample tap at the side of the storage tank. In the laboratory the sample is then bottled for transport to an external laboratory that was contracted to conduct the sample analyses for this company. The laboratory technician handled HFO for about 15 minutes per day. In addition to the standard PPE, nitrile gloves were used during sample collection.

Cleaning loading bay
The unloading bay at the first power station gets contaminated during transfer of oil from road to storage tankers. A small sump under the connector for the hoses collects any drippings of oil from the hoses. At the time of the study there had been a major spill and the oil in the sump was about 25 cm high. The operator attempted to clear the sump of oil using broom, bucket and absorbent rags. The job was aborted since it required more than one operator to complete the work. The operator wore a full tyvek suit over his regular overalls, impervious PVC gloves, safety glasses and boots.

Cleaning spillage and equipment
The equipment in the pumphouse in the first power station is cleaned daily. The external frame of the pump is wiped down with absorbent rags wetted with a solvent. The task takes about thirty minutes, but could be longer if the contamination of surfaces is very heavy.

Burner tip cleaning
Before start up of the boiler all the fuel burner tips need to be cleaned. First, steam is blown through the fuel burner tips to remove any excess HFO. The burner is subsequently taken out of

the boiler and the nozzle tip is cleaned with a brush. The nozzle cap is then removed and oil is wiped from the cap using a rag and degreaser. There is potential for exposure from the oil containing lance tip as well as from leaking hoses and pumps in the vicinity. The cleaning of the lance and burner tip is predominantly carried out at nights and at the weekends, as, due to lower demands, some of the units may be taken off line.

Tank dipping
Tank dipping is carried out using a dip stick, which is a retractable measuring tape with a cylindrically-shaped brass graduated weight. The operator lowers the dip stick into the hatch at the top of the tank, and after removing it, reads the oil level and wipes away the fuel oil with a rag. The operator observed during the survey carrying out this task wore the basic personal protective equipment required on site including rigger gloves and safety boots.

Filter changing/cleaning
Pumps are drained of oil prior to cleaning of the pumps and changing of the filters. Dirty filters are placed in a container and cleaned by pouring a solvent over it and wiping with a rag. Absorbent tissues are used to collect oil drips at the bottom of the container. Rags and absorbent tissues were disposed upon completion of the task. The operator observed carrying out this task wore the basic PPE required on site in addition to rigger gloves. When handling heavily contaminated surfaces such as the contaminated filter he wore impermeable PVC gloves.

5.1.4 RESULTS - QUANTITATIVE DERMAL EXPOSURE MEASUREMENTS

Analysis of bulk samples
The bulk samples collected during the field surveys were compared with the nine oil samples tested during the method development. The levels of the analytes naphthalene, phenanthrene and benzo(a) pyrene found in the bulk samples collected during the surveys were within the range found in the samples tested during the validation exercise. However, there was much less variation in analyte levels within the 5 bulk samples tested than the oil samples tested (GSDs of bulk samples for naphthalene, phenanthrene, benzo(a)pyrene were 6, 2, and 1, respectively while the GSDs of the original oil samples were 33, 14 and 14, respectively) (Table 4).

Table 4 Comparison between bulk samples collected during the field surveys and samples tested during analytical validation of method.

	Concentration (mg analyte /kg HFO)		
	Bulk samples from field survey		
	Naphthalene	Phenanthrene	Benzo(a)pyrene
Bulk 01	6.6×10^4	4.5×10^2	No peak
Bulk 03	1.3×10^3	6.0×10^4	No peak
Bulk 04	1.1×10^4	1.1×10^3	<0.1
Bulk 05	1.2×10^4	1.3×10^3	<0.1
Bulk 06	8.1×10^2	6.2×10^2	<0.1
Range	8.1×10^2 - 6.6×10^4	$4.5 \times 10^2 – 1.3 \times 10^3$	<0.1
GM	$6.26.6 \times 10^3$	7.5×10^2	<0.1
GSD	6	2	1
N	14	14	12
<LOD	0	0	3
	Samples tested during analytical method validation		
Oil 1	1.6×10^2	95	46
Oil 2	3.4×10^3	6.5×10^2	7
Oil 3	5.2×10^4	5.3×10^3	39
Oil 4	<2	20	27
Oil 5	<2	<2	<2
Oil 6	7.2×10^2	2.8×10^3	3.7×10^2
Oil 7	56	84	15
Oil 8	1.1×10^2	9.0×10^2	<2
Oil 9	2.2×10^2	2.7×10^2	71
Range	<2 – 5.2×10^4	<2 – 5.3×10^3	<2 – 3.7×10^2
GM	1.4×10^2	1.9×10^2	1.9×10^2
GSD	33	14	14
N	9	9	90
<LOD	2	1	1

<LOD – number of samples that were less than the limit of detection

Results of dermal measurements

The limit of detection (LoD) for hands ranged from 0.05 to 0.10 μg HFO/cm², while for the neck and forearms the LoD ranged from 0.4 to 0.8 μg HFO/cm².

A total of 40 sets of dermal samples from 5 anatomical locations (200 measurements) were collected from the five facilities previously described: one oil refinery; two fuel terminals and two power stations. At the oil refinery dermal samples were collected following the isolation of the line which was conducted to facilitate changing and cleaning of valves. The operator indicated that the line was much drier than usual. The fitters wore impermeable gloves including the basic personal protective equipment required on site. At the oil distribution terminals, dermal exposure measurements were collected from road tanker drivers and one gantry operator. In the first power station dermal measurements were collected during sample collection (pumphouse), cleaning of the HFO loading bay and during clean-up of spillage and equipment in the pumphouse. In the second power station, dermal measurements were collected during cleaning of burner tips, tank dipping of storage tanks and filter cleaning.

Due to the lack of an appropriate bulk sample, two sets of samples were discarded resulting in a working dataset of 190 measurements. These samples were collected from 18 different workers with eleven workers being sampled more than once. Repeated measurements also included two sets of pre- and post- task measurements on two different workers. Of the samples analysed, 144 (76%) were less than the LoD. These were set to the value of the LoD divided by the square root of 2 in order to facilitate statistical analyses. Raw data from these measurements are presented in Appendix IV.

The results of the dermal monitoring survey are shown in Tables 5 to 9. These indicate the number of samples below the LoD and describe the data in terms of arithmetic mean (AM), geometric mean (GM), geometric standard deviation (GSD), median, 90th percentile and the range.

Table 5 presents the results by anatomical site. The majority of forearm and neck samples were below the LoD with only one neck sample having a value above LoD. For the hands, approximately half of the measurements had detectable levels of HFO. The arithmetic mean levels for the forearm (1.5 µg/cm^2 (right) and 2.1 µg/cm^2 (left)) were higher than those for the hand (0.6 µg/cm^2 (right) and 0.9 µg/cm^2 (left). This is partly due to the higher LoD for the measurements of the forearm compared with the measurements of the hand, and partly due to the fact that the peak levels for the forearm were higher than for the hand. There was a reasonably strong correlation between the log-transformed hand and forearm exposure (Pearson correlation coefficient = 0.61).

Table 5 Dermal exposure by anatomical site

Bodypart	<LoD		N	AM	GM	GSD	Median	90th %tile	Range
	N	%							
left hand	16	*42*	38	0.87	0.21	5.2	0.09	3.1	*0.03* - 5.7
right hand	20	*53*	38	0.61	0.16	4.4	0.07	2.6	*0.03* - 5.5
left forearm	32	*84*	38	1.5	0.59	2.9	0.57	4.5	*0.28* - 15
right forearm	31	*82*	38	2.1	0.68	3.4	0.57	10.7	*0.28* - 18
neck	37	*97*	38	0.46	0.43	1.5	0.57	0.57	*0.28* - 1.3

N: number of samples; %<LoD: percentage of samples with results for both hands below the limit of detection; 90th %tile: 90th percentile of the exposure distribution.

Tables 6 and 7 provide the average hand and forearm exposure, respectively, by type of facility. The dermal hand and forearm exposure levels for workers in the distribution facilities were higher than for workers in the other two types of facilities. As some repeated measurements on the same worker were available, we were able to estimate the within- and between-worker variability for the distribution and power stations. The between-worker GSD (GSD_{bw}) for the hand exposure was higher than the within-worker GSD (GSD_{ww}) (fuel terminals: GSD_{bw} = 4.4 and GSD_{ww} = 2.0; power stations GSD_{bw} = 3.2 and GSD_{ww} = 2.1). The within-and between-worker GSDs for the forearm exposure could not be estimated as the majority of the results were below the LoD.

Table 6 Dermal Total Hand Exposure (µg/cm^2) by facility type

Industry	N_s	N_w	%<LoD	AM	GM	GSD	Median	90th%tile	Range
Oil Refinery	1	1	100	*0.07*					
Distribution	29	17	31	0.89	0.25	5.0	0.14	3.5	0.1 – 5.1
Power stations	8	4	63	0.26	0.11	3.6	0.07	1.4	0.03 - 1.4

N_s: number of samples; N_w: number of workers; %<LoD: percentage of samples with results for both hands below the limit of detection; 90th %tile: 90th percentile of the exposure distribution.

Table 7 Dermal Total Forearm Exposure (μg/cm^2) by facility type

Industry	N_s	N_w	%<LoD	AM	GM	GSD	Median	90th%-ile	Range
Oil Refinery	1	1	100	*0.57*					
Distribution	29	17	83	2.07	0.68	3.6	0.57	7.6	*0.28*-15
Power station	8	4	75	0.76	0.59	2.1	0.49	2.2	*0.28*-2.2

N_s: number of samples; N_w: number of workers; %<LoD: percentage of samples with results for both hands below the limit of detection; 90th%-ile: 90th percentile of the exposure distribution.

Tables 8 and 9 show the results of the dermal exposure measurements by task group. The task group with the highest dermal exposure was maintenance, with an AM of 2.5 μg/cm^2 for the hands and an AM of 7.3 μg/cm^2 for the forearms. Pre-task measurements were collected from a worker during 'tank dipping' and from a worker during 'filter cleaning'. Results of all pre-tasks measurements and post tank-dipping were less than LoD, while results for post filter-cleaning were all greater than LoD with values ranging from 0.24 μg/cm^2 (left-hand) to 1.44 μg/cm^2 (right forearm). All results for the forearm collected after loading/unloading were below the LoD, whilst for the hands only 39% of the samples after loading/unloading were below the LoD.

The within- and between-worker GSDs were estimated for the loading/unloading and maintenance tasks. Interestingly, for the loading/unloading task, the main variance component was the within-worker variance (GSD_{ww} = 2.2 compared to GSD_{bw} = 1.8); while for the maintenance task the between-worker variance component was the dominant factor (GSD_{ww} = 1.5 compared to GSD_{bw} = 5.5). These results may indicate that the dermal hand exposure for loading and unloading activities are relatively stable between different workers and different sites, but that the exposures for different maintenance activities can vary widely between workers and/or sites.

Table 8 Dermal Hand Exposure (μg/cm^2) by task group

Task group	N_s	N_w	%<LoD	AM	GM	GSD	Median	90th%-ile	Range
Pre-task	2	2	100	*0.05*	*0.05*	*1.6*	*0.05*	*0.07*	*0.03 - 0.07*
Loading/unloading	23	15	39	0.23	0.13	2.7	0.07	0.89	*0.05* - 1.2
Cleaning	3	2	0	0.62	0.44	2.7	0.28	1.4	*0.23* - 1.4
Maintenance	7	3	14	2.5	1.9	4.5	3.2	5.1	*0.07* - 5.1
Sampling	2	2	100	*0.04*	*0.04*	*1.3*	*0.04*	*0.05*	*0.03 - 0.05*
General duties	1	1	100	*0.07*					

N_s: number of samples; N_w: number of workers; %<LoD: percentage of samples with results for both hands below the limit of detection; 90th%-ile: 90th percentile of the exposure distribution.

Table 9 Dermal Forearm Exposure (μg/cm^2) by task group

Task group	N_s	N_w	%<LoD	AM	GM	GSD	Median	90th%-ile	Range
Pre-task	2	2	100	*0.42*	*0.40*	*1.6*	*0.42*	*0.57*	*0.28 - 0.57*
Loading/unloading	23	15	100	0.41	0.38	1.4	0.28	0.57	0.28 - 0.57
Cleaning	3	2	67	0.74	0.63	2.0	0.42	1.4	*0.42* - 1.4
Maintenance	7	3	29	7.3	4.3	4.1	7.4	14.8	*0.57* - 15
Sampling	2	2	50	1.2	0.79	4.3	1.24	2.2	*0.28* - 2.2
General duties	1	1	100	*0.57*					

N_s: number of samples; N_w: number of workers; %<LoD: percentage of samples with results for both hands below the limit of detection; 90th%-ile: 90th percentile of the exposure distribution.

6 RESULTS - SEMI-QUANTITATIVE DERMAL EXPOSURE ASSESSMENT

6.1 INTRODUCTION

Using a modification of the semi-quantitative method for dermal exposure assessment (DREAM) developed by van Wendel de Joode *et al* (2003) we collected dermal exposure information for a number of exposure scenarios. Data were collected either through direct observations by one of the research team (YC), by observations from industry personnel, or by collection of information from industry representatives based on their knowledge of the operation (no actual observations). Information was available from oil refineries, fuel terminals, power stations and engine building sites.

Although the results of the semi-quantitative dermal exposure estimates are available for all anatomical locations, we only present results from the hands, the forearms and the remainder of the body i.e. total body minus hands and forearms. Results are presented as potential exposure and actual exposure.

6.2 CONFIDENCE RATING OF DREAM ESTIMATES

Fifty eight DREAM assessments were completed by ten different observers including the researchers. Of these assessments 42% of the assessments were given a confidence rating of 1 or 2 as these were based on direct observations of tasks (either by a researcher or an employee of the company) (Figure 5). Thirty-three percent of the DREAM assessments were based on direct knowledge of the tasks (confidence level 3), although no observations were carried out using the DREAM method. Ten percent of the assessments were based on existing information such as risk or COSHH assessment records(confidence scale 4) and 16% of the assessments were incomplete (confidence scale 5).

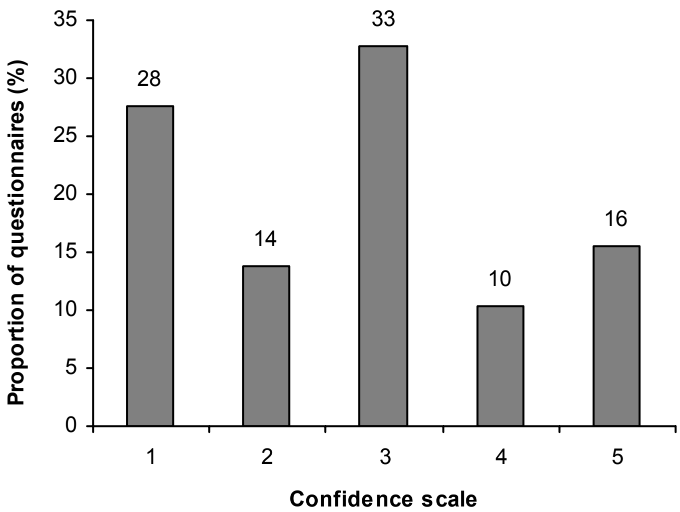

Figure 2 Confidence rating of dream estimates

6.3 RESULTS

Estimates of exposure were available for 58 situations for 13 different tasks from 8 different companies (at 11 different sites). Tables 10, 11 and 12 give the actual and potential hand, forearm and body exposure, respectively, by type of facility. The results are expressed in arbitrary units (DREAM Units (DU) per cm^2). The potential hand exposure levels were lower at engine building sites compared to the other three type of facilities (Table 10). The actual hand exposure was much lower than potential exposure levels, with AM of exposure ranging from 0.2 to 0.4 DU/cm^2 for oil distribution, energy provider and oil refinery, and less than 0.1 DU/cm^2 for engine building.

Table 11 shows the potential and actual forearm exposure by facility type. The levels for engine building were very low compared with the other facilities. Although forearm exposure for the oil refinery is low, it is of interest to note that the potential and actual forearm exposures are identical, indicating lack of control for forearm exposure.

Table 12 shows the results for dermal exposure for the whole body, (minus hands and forearms). The estimated dermal exposure for the remainder of the body are again low, but similar levels of potential and actual exposure, suggest that personal protective equipment was not used or ineffective.

Table 10 Potential and actual hand exposure (in DREAM units / cm^2) by facility type

Type of Facility	N	Potential exposure				Actual exposure			
		AM	Median	90^{th} %tile	Range	AM	Median	90^{th} %tile	Range
Oil Refinery	8	5.2	1.1	23.8	0.1 – 23.8	0.3	0.0	1.9	0.0 – 1.9
Distribution	16	5.1	2.8	24.8	0.1 – 26.8	0.4	0.3	1.4	0.0 – 2.2
Power stations	30	3.2	1.1	12.2	0.0 – 15.9	0.2	0.0	0.7	0.0 – 1.4
Ship and Power Plant Engine Building	4	0.6	0.4	1.5	0.0 – 1.5	0.0	0.0	0.0	0.0 – 0.0

N: number of DREAM assessments; AM: arithmetic mean; 90^{th} %tile: 90^{th} percentile of the exposure distribution.

Table 11 Potential and actual forearm exposure (in DREAM units / cm^2) by facility type

Type of Facility	N	Potential exposure				Actual exposure			
		AM	Median	90^{th} %tile	Range	AM	Median	90^{th} %tile	Range
Oil Refinery	8	0.6	0.0	3.8	0.0 – 3.8	0.6	0.0	3.8	0.0 – 3.8
Distribution	16	1.1	0.6	2.4	0.1 – 7.3	0.1	0.0	0.2	0.0 – 0.4
Power stations	30	0.6	0.1	2.3	0.0 – 6.0	0.3	0.0	1.3	0.0 – 3.6
Ship and Power Plant Engine Building	4	0.0	0.0	0.1	0.0 – 0.1	0.0	0.0	0.1	0.0 – 0.1

N: number of DREAM assessments; AM: arithmetic mean; 90^{th} %tile: 90^{th} percentile of the exposure distribution.

Table 12 Potential and actual body (minus hands and forearms) exposure (in DREAM units / cm^2) by process

Type of Facility	N	Potential exposure				Actual exposure			
		AM	Median	90^{th} %tile	Range	AM	Median	90^{th} %tile	Range
Oil Refinery	8	0.2	0.0	0.8	0.0 – 0.8	0.2	0.0	0.8	0.0 – 0.8
Distribution	16	0.4	0.2	0.7	0.0 – 2.6	0.4	0.2	0.7	0.0 – 2.6
Power stations	30	0.2	0.0	0.6	0.0 – 2.4	0.1	0.0	0.4	0.0 – 1.5
Ship and Power Plant Engine Building	4	0.0	0.0	0.1	0.0 – 0.1	0.0	0.0	0.1	0.0 – 0.1

N: number of DREAM assessments; AM: arithmetic mean; 90^{th} %tile: 90^{th} percentile of the exposure distribution.

For ease of comparison all tasks were grouped into 5 task categories; loading/unloading of HFO into road tankers or ships (n=17 assessments), maintenance activities (n=19 assessments), cleaning of equipment (n=13 assessments), sampling of HFO (n=8 assessments) and general process operations (n=1 assessment, operating fuel oil heater). Tables 13 to 15 show the results for the DREAM estimates by task groups. Potential hand exposure was relatively high for loading/unloading (AM=4.7 DU/cm^2), maintenance (AM=4.2 DU/cm^2) and cleaning (AM=4.3 DU/cm^2) (Table 13), with lower estimates for sampling and general operations. Use of gloves reduced the hand exposure, as indicated by the much lower actual hand exposure. The highest potential dermal exposure levels were observed for top loading of road tankers (26.8 DU/cm^2), bottom unloading of road tanker (24.8 DU/cm^2) and spading of an oil line at a refinery (23.8 DU/cm^2).

The highest potential and actual forearm and body exposures were observed for the maintenance tasks (Tables 14 and 15).

Table 13 Potential and actual hand exposure (in DREAM units / cm^2) by task group

Task	N	Potential exposure				Actual exposure			
		AM	Median	90^{th} %tile	Range	AM	Median	90^{th} %tile	Range
Loading/unloading	17	4.7	2.3	24.8	0.2 – 26.8	0.4	0.3	1.4	0.0 – 2.2
Maintenance	19	4.2	1.2	12.5	0.1 – 23.8	0.2	0.0	1.0	0.0 – 1.9
Cleaning	13	4.3	0.8	13.5	0.0 – 15.9	0.2	0.0	0.2	0.0 – 1.4
Sampling	8	0.8	0.3	1.9	0.0 – 1.9	0.1	0.0	0.5	0.0 – 0.5
Operation	1	0.0	0.0			0.0	0.0		

N: number of DREAM assessments; AM: arithmetic mean; 90^{th} %tile: 90^{th} percentile of the exposure distribution.

Table 14 Potential and actual forearm exposure (in DREAM units / cm^2) by task group

Task	N	Potential exposure				Actual exposure			
		AM	Median	90^{th} %tile	Range	AM	Median	90^{th} %tile	Range
Loading/unloading	17	0.7	2.3	2.3	0.0 – 2.4	0.1	0.0	0.5	0.0 – 0.8
Maintenance	19	1.2	1.2	6.0	0.0 – 7.3	0.5	0.0	3.6	0.0 – 3.8
Cleaning	13	0.4	0.8	2.3	0.0 – 2.3	0.2	0.0	0.5	0.0 – 2.3
Sampling	8	0.0	0.3	0.1	0.0 – 0.1	0.0	0.0	0.1	0.0 – 0.1
Operation	1	0.0	0.0			0.0	0.0		

N: number of DREAM assessments; AM: arithmetic mean; 90^{th} %tile: 90^{th} percentile of the exposure distribution.

Table 15 Potential and actual body exposure (in DREAM units / cm^2) by task group

Task	N	Potential exposure				Actual exposure			
		AM	Median	90^{th} %tile	Range	AM	Median	90^{th} %tile	Range
Loading/unloading	17	0.3	0.2	0.7	0.0 – 0.7	0.2	0.2	0.6	0.0 – 0.7
Maintenance	19	0.4	0.0	2.4	0.0 – 2.6	0.3	0.0	1.5	0.0 – 2.6
Cleaning	13	0.1	0.0	0.5	0.0 – 0.8	0.1	0.0	0.3	0.0 – 0.5
Sampling	8	0.0	0.0	0.0	0.0 – 0.0	0.0	0.0	0.0	0.0 – 0.0
Operation	1	0.0	0.0			0.0	0.0		

N: number of DREAM assessments; AM: arithmetic mean; 90^{th} %tile: 90^{th} percentile of the exposure distribution.

7 COMPARISON OF SEMI-QUANTITATIVE AND QUANTITATIVE RESULTS

The final aim of the study was to assess HFO exposure for various exposure scenarios within the manufacturing and use industries. We had envisaged that we would be able to validate the results from the DREAM estimates along with the quantitative dermal exposure data to obtain a conversion from DU to µg HFO and subsequently use the DREAM estimates to provide exposure estimates for a wide range of exposure scenarios.

Sixteen DREAM assessments were obtained where measurements and observations were carried out simultaneously. Figures 3 and 4 show scatter plots for the dermal measurements versus the DREAM estimates for hand and forearm exposure plotted on a log scale. We present the DREAM estimates for the actual rather than the potential exposure. It is clear from these figures that there is no correlation between the DREAM estimates and the results of the dermal exposure measurements. Similarly, no correlation was observed when using the potential dermal exposure estimates from DREAM. It was therefore not feasible to use the DREAM method to estimate exposure in the various scenarios.

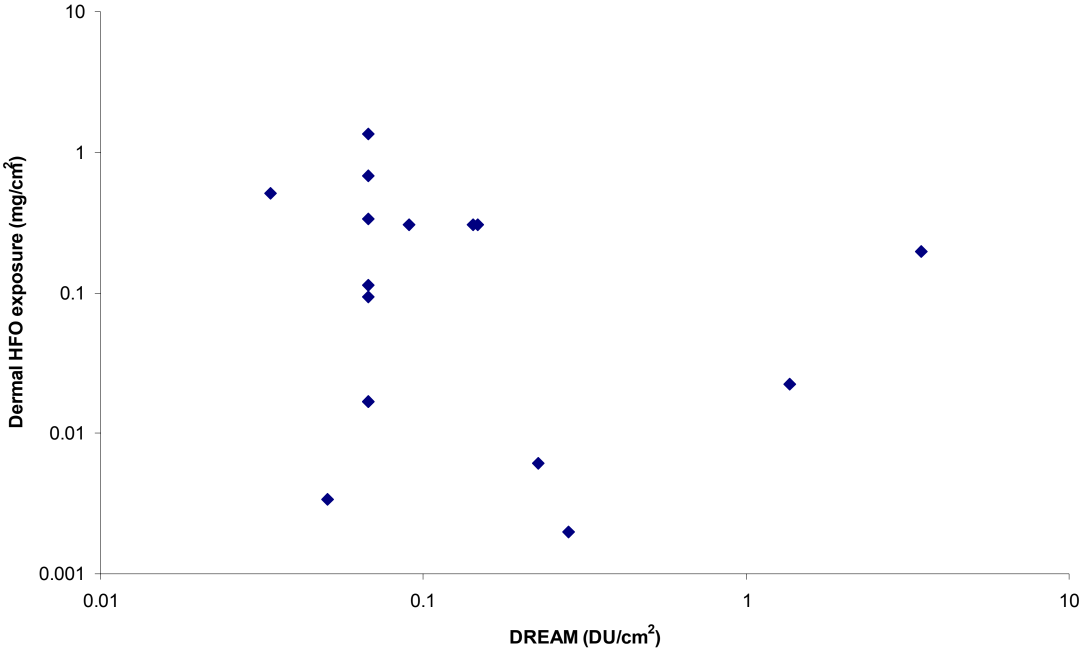

Figure 3 Dermal HFO exposure vs DREAM estimates for hand exposure (log scale)

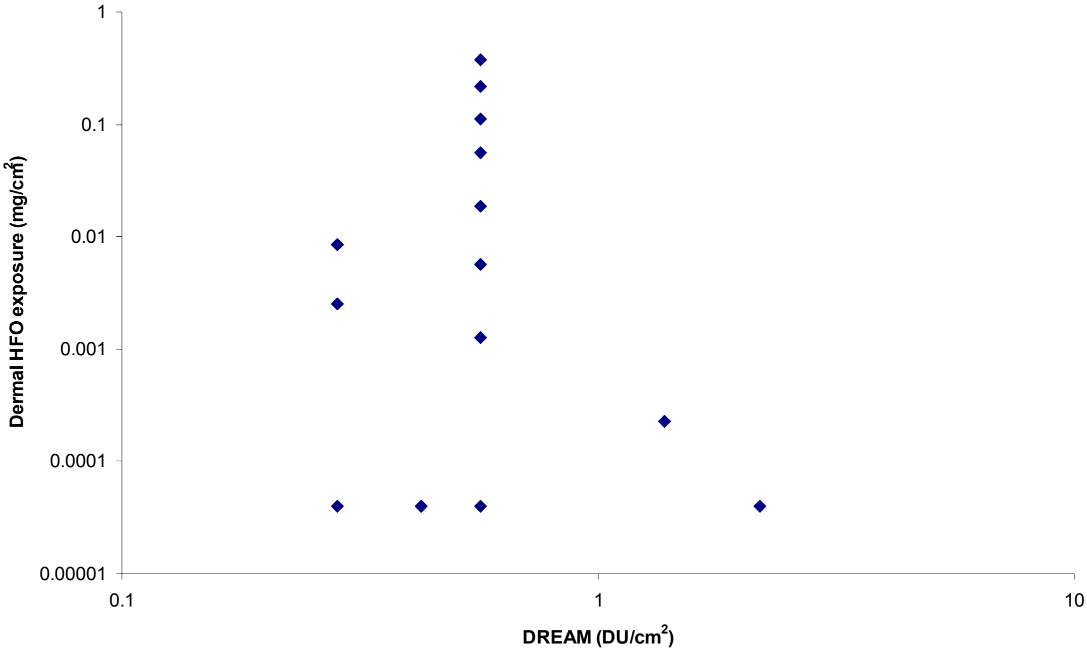

Figure 4 Dermal HFO exposure vs DREAM estimates for forearm exposure (log scale).

Tables 16 and 17 summarise the dermal exposure data and DREAM results for hands and forearms by task group and type of facility. It is clear that there are considerable gaps in the data for both the dermal measurements and the DREAM results. The only conclusion to be drawn from these data is that exposure levels appear to be highest during maintenance activities in the HFO distribution facilities. No clear pattern emerged from the DREAM estimates.

Table 16 Arithmetic mean of dermal hand and forearm exposure (μg/cm^2) by type of facility and task

		Loading	Cleaning	Maintenance	Sampling	Operations	Totals
Production (Refinery)	N			1			1
	Hand	0	0	0.1	0	0	0.1
	Forearm			0.6			0.6
Distribution	N	23		6			29
	Hand	0.2	0	3.4	0	0	0.9
	Forearm	0.4		8.5			2.1
Fuel for Power Plants	N		3		2	1	6
	Hand	0	0.6	0	0.0	0.1	0.3
	Forearm		0.7		1.2	0.6	0.9
Marine fuel	N						
	Hand	0	0	0	0	0	0
	Forearm						
TOTALS	N	23	3	7	2	1	
	Hand	0.2	0.6	2.9	0.0	0.1	
	Forearm	0.4	0.7	7.3	1.2	0.6	

Note: Results from pre-tasks measurements are not included in this table

Table 17 Aritmetic mean DREAM estimates for hand and forearm (actual) exposure by type of facility and task

		Loading	Cleaning	Maintenance	Sampling	Operations	Totals
Production (Refinery)	N	2	0	4	2	0	8
	Hand	0.0		0.6	0.0		0.3
	Forearm	0.4		0.9	0.0		0.6
Distribution	N	13	0	3	0	0	16
	Hand	0.5		0.1			0.4
	Forearm	0.1		0.1			0.1
Fuel for Power Plants	N	2	12	9	6	1	30
	Hand	0.5	0.2	0.2	0.1	0.0	0.2
	Forearm	0.4	0.2	0.6	0.0	0.0	0.3
Marine fuel	N	0	1	3	0	0	4
	Hand		0.0	0.0			0.0
	Forearm		0.0	0.0			0.0
TOTALS	N	17	13	19	8	1	
	Hand	0.4	0.2	0.2	0.1	0.0	
	Forearm	0.1	0.2	0.5	0.0	0.0	

Note: Results from pre-tasks measurements are not included in this table

8 DISCUSSION

This report describes the results of a study to investigate the dermal exposure to HFO in a variety of industries and activities. As part of this study, we developed and validated a method for measuring dermal exposure to HFOs based on the PAH contents of the oils. We subsequently applied this method in a number of surveys collecting dermal measurements from employees at a number of sites. Dermal wipe samples were collected from the hands, forearm and neck. In order to carry out semi-quantitative assessments of dermal exposure we also collected contextual information during observations of a number of tasks during the field surveys and we collected contextual information from industry representatives from a much wider sample of companies (based on observations, direct knowledge or existing risk or COSHH assessments). Finally, the project aimed to provide exposure estimates for a range of exposure scenarios identified during the study.

Method development

Prior to this study there were no standard methods available for measurement of dermal exposure to HFO or other hydrocarbon oils and therefore a method had to be developed during the course of this study. A suitable marker of exposure was required and after reviewing the various components of HFO it was decided to focus on a number of PAHs (e.g. phenanthrene or naphthalene). Analytical methods for PAHs are very sensitive, and using PAH as a marker of exposure would result in sufficiently low detection limits for measuring dermal HFO exposure.

However, the composition of HFO, including its PAH content, can vary greatly due to differences in crude oils and the refinery configurations (Concawe, 1998). One or more suitable bulk samples are therefore required with each set of measurements in order to develop specific calibration curves. It is also important to recognise that PAHs are not specific to HFO and handling diesel and other oils, commonly found at these industrial sites may result in an over-estimation of HFO exposure.

Several dermal sampling methods are available:

a) interception methods such as absorbent patches or absorbent sampling suits;
b) removal techniques involving washing or wiping residues from the skin and
c) in-situ methods that rely on direct observation of the surface contamination e.g. by measuring the fluorescence of the compound or a tracer.

All of these methods can provide estimates of the mass of contaminants in relation to dermal exposure but they do not provide equivalent measures of exposure. For example, samples collected using absorbent patches, which are often used for evaluation of dermal exposure to pesticides, measure the mass of contaminant retained on the patch following exposure over a workday or task. The capacity of a patch may greatly exceed that which could be retained on the skin surface. In contrast, wiping of the skin provides an estimate of the mass of contaminant remaining on the skin (i.e. not absorbed into the body or lost by other means such as evaporation) at the end of a sampling period. Dermal exposure estimates from wipes will be less than or equal to estimates made from patch samples.

In principle any of the three main method types (interception, removal or in-situ) could be used to provide estimates of dermal exposure to HFO. For biologically relevant exposure measurements it is usually necessary to measure the mass or concentration of contaminant in the skin contaminant layer, rather than what might be deposited on the outer clothing. Removal methods are usually more reflective of the skin contaminant layer, whereas interception methods tend to be more representative of the outer clothing contaminant layer, and also give a measure of the total flux of contaminant onto the skin.

Other methods for measuring dermal exposure include skin stripping (Mattorano *et al*, 2004) or biological monitoring. The latter approach is not likely to be suitable for assessing dermal HFO exposure because aromatic hydrocarbons in viscous oils are poorly absorbed through the skin (Potter *et al*, 1999). Skin stripping might seem to be a reasonable method for evaluating the mass of substance present in the *stratum corneum*. However, the method is intrusive, may cause permanent damage to the skin and can only be used on small areas of skin, usually the hands.

Based on the nature of the material we decided to develop a removal method using wipe sampling. To optimise the sampling efficiency of the wiping method, a commercially available skin cleansing clinical wipe saturated with 70% isopropyl alcohol was used. Based on laboratory trials, the sampling efficiency using three consecutive wipes on the same skin area was estimated to be in excess of 85%.

Based on the sampling and analytical method, we obtained a limit of detection for hand exposure to HFO that varied between 0.05 µg HFO /cm^2 and 0.10 µg HFO /cm^2, depending on the PAH content of the bulk sample. The limit of detection or the forearm and the neck varied between 0.4 and 0.8 µg HFO /cm^2. The difference in the limit of detection for the forearm and the hand was due to the difference in sampled surface area - the whole palmar surface of the hand was wiped (210 cm^2), compared to an area of 25 cm^2 for sampling the forearm.

Field measurements
We were able to collect dermal exposure measurements at five different sites, one refinery, two power plants and two oil distribution centres. We also attempted to carry out field surveys at various other facilities, including a dock yard. However, due to the infrequent use of and contact with HFO at these sites, it was not possible to visit these sites during the project. HFO use and contact is infrequent at all facilities, with the possible exception of the oil distribution sites, where road tankers are loaded with HFO for distribution to various customers on a regular basis.

We collected 40 different sets of dermal exposure measurements, each set consisting of two hand, two forearm and one neck dermal wipe sample, although two sets were excluded due to unavailability of a suitable bulk sample. These two measurements were collected from an employee at a power plant during cleaning of the burner tips. We attempted to collect a sample of HFO by wiping oil from some contaminated tips. However, the limit of detection based on the analyses of these samples was much higher than that of the other samples. It was therefore decided to exclude these measurements.

The results suggest that the dermal exposure to HFO was low for the tasks and sites included in this survey. For the hand exposure, the levels were generally below 5 µg HFO/cm^2, while for the forearms the levels were generally below 15 µg/cm^2. The higher forearm concentrations could, at least partly, be due to the higher limit of detection for the forearm. Also the protective effect of gloves may have also contributed to lower exposures found on the hands. The percentage of samples below the limit of detection was high for all anatomical areas, but particularly for the neck and forearm. For the hand approximately 50% of samples were below the limit of detection.

The highest results for the dermal measurements were observed for maintenance tasks, with an overall arithmetic mean of 2.9 µg /cm^2 for both hands and 7.3 µg /cm^2 for both forearms. The results for other tasks were generally much lower. In addition, the dermal exposure levels were generally higher at the distribution sites compared to the other facilities. Pre- and post task sampling was conducted for two tasks 'tank-dipping' and 'filter-cleaning'. The results showed detectable exposure for the 'filter-cleaning' despite the use of gloves during this task. Clearly, exposures are expected to be higher had gloves not been worn.

DREAM estimates

There are a number of semi-quantitative methods available for determining dermal exposure. The modelling approach advocated in the European Union TGD is the EASE model. However, we have demonstrated that for particulate residues on the skin this model provides estimates of dermal exposure that are usually much higher compared to measured data (Hughson & Cherrie, 2005). Furthermore, EASE does not take into account the effect of protective clothing so additional assumptions need to be made to establish how much of the substance of interest comes into contact with the skin. In addition, the EASE model is unlikely to have sufficient resolution to measure the relatively low levels of exposure that are expected for HFOs.

Van Wendel de Joode *et al* (2003) developed a semi-quantitative generic model for estimating dermal exposure, which is based on a conceptual model developed by Schneider *et al* (1999). This model (called DREAM) has been compared to measured dermal exposure in a range of situations and has been shown to produce reasonably good associations between estimates and measurements (van Wendel de Joode *et al,* 2005). The DREAM method takes into account three routes for dermal exposure, emission, transfer and deposition, although for the present study we have assumed that exposure via the deposition route would be insignificant.

We collected contextual DREAM information from 58 tasks from 11 different sites using a combination of methods. Firstly, we carried out 16 full DREAM observations during the field surveys. In addition, we collected information remotely for a further 42 tasks. These data were collected by company personnel either by actual observations or by extracting contextual information from available COSHH assessments and knowledge of the process. In the latter case, we requested COSHH assessments for relevant tasks and completed the modified DREAM assessment as far as possible and returned the partially completed forms to the company representative to complete.

The DREAM assessment requires observations of activities by independent scientists, although the authors of the original paper do suggest that for situations where DREAM data cannot be observed directly, information may be gathered by interviewing workers (van Wendel de Joode *et al,* 2003). However, the authors concede that collection of information by interviewing employees may have implications for the validity of the results. Unfortunately, due to limited resources and infrequent use of HFOs in most industries, it was not feasible within this study to carry out a large quantity of observations, even by representatives of the participating companies. Therefore, the results presented here from the semi-quantitative DREAM assessment need to be interpreted with care.

Comparison of dermal HFO measurements and DREAM estimates

An aim of the project was to validate and, if possible, calibrate the DREAM method for HFO exposure, using quantitative exposure data collected during this study. Unfortunately, comparison of measured dermal exposure with DREAM estimates, showed that at least within the exposure range observed in this study there was no correlation between the two methods. Previous validation studies by van Wendel de Joode *et al* (2005) showed a general good association between measured and estimated dermal exposure over a wide range of circumstances.

The reason for the lack of any correlation between the results from the DREAM method and the dermal measurements is possibly due to the limited range of exposures in this study. Although there was more than two orders of magnitude difference in the results of the DREAM estimates, an even higher contrast in exposure between the various tasks may have resulted in a better correlation between the DREAM estimates and dermal exposure measurements. Van Wendel de Joode *et al* (2005) conducted a validation exercise where they compared DREAM estimates (DU) with measured exposure levels (µg/cm^2) using data from several different surveys. They concluded that the DREAM estimates correlated well with measured data. However, the range in measured exposure levels and DREAM estimates was much larger that observed in this study. Converting our results to total DREAM estimates (DU - rather then concentration, DU/cm^2) and overlaying our results onto the Figure 1 from the paper by van Wendel de Joode *et al* (2005), we can conclude that our data are compatible with their overall comparison between DREAM and measured dermal exposure data.

Exposure assessment for scenarios

Due to the lack of an association between the results from the DREAM method and exposure measurements, it was not possible to use the larger DREAM database for exposure assessments. A general conclusion of the study is that the levels were generally very low, although somewhat higher for maintenance tasks. However, this does not imply that exposure levels are low in all possible exposure scenarios. Dermal exposure may be higher and/or more frequent during the following activities:

- operating sea vessels that use HFO as bunker fuel (cleaning and changing filters);
- repair and maintenance of sea vessels that use HFO (cleaning of pumps, tanks, filters, etc) in dock yards;
- cleaning of large spillages in tank farms; and
- recycling oil.

HFO is generally heated during storage, transport and use. Therefore, employees that work with HFO are careful to avoid contact with the oils. There is, however, potential for dermal exposure through transfer from contaminated surfaces. Areas such as sampling points and loading bays for road tankers were generally heavily contaminated with HFO. However, this did not appear to result in high exposure levels. Again, due to the viscosity of HFO it is likely that employees try to avoid contact with the contaminated surfaces. However, despite this it is important to keep surfaces and work areas clean as HFO is classified in Group 2B by the International Agency for Research on Cancer; it is possibly carcinogenic to humans (IARC 1989).

Conclusions

In conclusion, this study has been successful in developing a validated method for sampling dermal exposure to HFO. The dermal exposure levels for HFO at the sites visited during this study were generally low, although slightly higher for maintenance activities. The low dermal exposure levels are likely to be due to the nature of the substance and the fact that it needs to be heated during storage, transport and use. Exposure to HFO also appeared to be infrequent for workers at the sites and companies included in this study, with the notable exception of drivers of road tankers, who may be loading and unloading road tankers a number of times during the day. It is not possible to conclude that similarly infrequent and low levels of exposure will be found for HFO life cycle stages for which dermal measurements were not collected.

As there was no relationship between quantitative dermal exposure measurements and semi-quantitative estimates of dermal exposure, the semi-quantitative method for estimating exposure should not be used for these scenarios. Consequently, exposure data for these scenarios should be collected using the method for dermal exposure measurements of HFO which was developed and validated during this study.

9 ACKNOWLEDGEMENTS

We thank all the companies that participated in the study and the employees who participated in the measurement surveys. We also thank Hans Kromhout and Wouter Fransman who kindly provided us with the SAS procedure to convert the contextual DREAM information into semi-quantitative exposure estimates. The study was funded by Concawe.

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APPENDIX I – CAS NUMBERS OF HEAVY FUEL OIL AND HEAVY FUEL OIL COMPONENTS (CONCAWE, 1998)

HFO or component	CAS No
Residues (petroleum), atm tower	64741-45-3
Gas oils (petroleum), heavy vacuum	64741-57-7
Distillates (petroleum), heavy catalytic cracked	64741-61-3
Clarified oils, catalytic cracked	64741-62-4
Residues (petroleum), catalytic reformer fractionator	64741-67-9
Residues (petroleum), hydrocracked	64741-75-9
Residues (petroleum), thermal cracked	64741-80-6
Distillates (petroleum), heavy thermal cracked	64741-81-7
Gas oils (petroleum) hydrotreated vacuum	64741-59-2
Residues (petroleum), hydrodesulfurized atmospheric tower	64742-78-5
Gas oils (petroleum), hydordesulfurize heavy vacuum	64742-86-5
Residues (petroleum), steam-cracked	64742-90-1
Residues (petroleum)	68333-22-2
Clarified oils (petroleum) hydrodesulfurized catalytic cracked	68333-26-6
Distillates (petroleum), hydrodesulfurized intermediate cataclytic cracked	68333-27-7
Distillates (petroleum), hydrodesulfurized heavy catalytic cracked	68333-28-8
Fuel oil, residues-straight-run gas oils, high sulphur	68476-32-4
Fuel-oil, residual	68476-33-5
Residues (petroleum), catalytic reformer fractionator residue distillation	68478-13-7
Residues (petroleum), heavy coker gas oil and vacuum gas oil	68478-17-1
Residues (petroleum), heavy coker and light vacuum	68512-61-8
Residues (petroleum), light vacuum	68512-62-9
Residues (petroleum), steam-cracked light	68513-69-9
Fuel oil, no 6	68553-00-4
Residues (petroleum), topping plant, low sulfur	68607-30-7

HFO or component	CAS No
Gas oil (petroleum), heavy atmospheric	68783-08-4
Residues (petroleum), coker scrubber, condensed-ring-aromatic contg.	68783-13-1
Distillates (petroleum), petroleum residues vacuum	68955-27-1
Residues (petroleum), steam-cracked, resinous	68955-36-2
Distillates (petroleum), intermediate vacuum	70592-76-6
Distillates (petroleum), light vacuum	70592-77-7
Distillates (petroleum), vacuum	70592-78-8
Gas oil (petroleum), hydrodesulfurized coker heavy vacuum	85117-03-9
Residues (petroleum), steam-cracked, distillates	90669-75-3
Residues (petroleum), vacuum, light	90669-76-4
Fuel oil, heavy, high-sulfur	92045-14-2
Residues (petroleum), catalytic-cracking	92061-97-7
Distillates (petroleum), intermediate catalytic cracked, thermally degraded	92201-59-7
Residues oil (petroleum),	93821-66-0
Residues, steam-cracked, thermally treated	98219-64-8
Distillates (petroleum), hydrodesulfurized full-range middle	101316-57-8

APPENDIX II – ANALYTICAL METHOD VALIDATION FOR DERMAL EXPOSURE TO HEAVY FUEL OIL

Analytical Method Validation For Dermal Exposure to Heavy Fuel Oil

An interim report for CONCAWE

Report No. 891-00200

Report Date.

Report prepared by: Neil Gatward

Contents:

Analytical Method Validation for Dermal Exposure to Heavy Fuel Oil

Introduction

As part of a research project the IOM was requested by CONCAWE to develop and validate an analytical method to determine the occupational dermal exposure to heavy fuel oil. Preliminary work had identified that steret wipes were a reasonable candidate material to wipe heavy fuel oil contamination form the hands of workers. A simple holder was developed to enable the wipe sample to be collected without direct handling, so minimising the potential for contamination.

Scope

This analytical method was designed to determine the mass of specific polyaromatic hydrocarbons (PAHs) on sterets in order to facilitate the measurement of dermal exposure to fuel oil in the workplace. The aims of the validation work were to establish the limit of quantification (LOQ), the Detection Limit (DL), the desorption efficiency from sterets and from skin, and storage stability losses. This report describes the method used to validate the analysis and discusses the results of the IOM's investigation.

Procedure

Analyses were carried out using a Shimadzu QP2010S gas chromatograph/mass spectrometer. The instrument was initially set up using conditions that had previously been used for determining the 16 priority PAHs on air samples. Standard solutions of heavy fuel oil were run, together with spiked samples and the instrument conditions adjusted to optimise results. A quality control method was developed in-house.

Reagents

Dichloromethane – HPLC Grade
Calcium chloride fused anhydrous – ACS reagent
Sterets (Pre-injection swabs Isopropyl alcohol)
Heavy Fuel Oil TK624-check EC No 270-675-6 (supplied by client)

Standard Preparation
Stock Solutions

Approximately 0.25g of heavy fuel oil was weighed accurately and dissolved in 10ml of dichloromethane.

From these stock solutions, working standards were prepared to cover the analytical range of interest. Standards were prepared for each instrument run by adding microliters of the stock solution to 1ml aliquots of dichloromethane. An example is tabulated on the following page.

Table 1 Example of Standard Preparation

Stock Solution (µg/µl)	µl added to 1 ml of mobile phase	Final concentration (µg/ml)
28.92	1	28.9
28.92	5	144.6
28.92	10	289.2
28.92	30	867.2
28.92	50	1446.0

Chromatographic Conditions

Instrument: Shimadzu GCMS QP2010S using electron impact (EI) ionization in selected ion mode (SIM).

Column:	J&W DB-5MS 30m, 0.25mm id, 0.25µm film thickness
Run Time :	25.3 Minutes
Column Temperature:	60°C for 1 min to 170°C at 10°C/min then to 310°C at 15°C/min
Injection Temperature:	310°C splitless injection
Carrier gas:	Helium at 2.00 ml/min
Injection Volume :	1µL
Interface Temperature :	310°C
Ion Source Temperature:	200°C
Ion monitored (m/z) :	128.1, 127.1, 129.1 (for naphthalene) 178.1, 76.0, 89.0 (for phenanthrene) 252.1, 126.1, 250.1 (for benzo(a)pyrene)

Scan interval : 0.2sec

Preparation of Spiked Samples

Desorption Efficiency

Spiked samples were prepared at two different levels by injection of stock standard solutions of fuel oil onto sterets and allowing these to dry for approximately 20 minutes. The samples were then transferred into individual vials and analysed immediately. The recoveries were calculated by subtracting the average concentrations (µg/ml) found in the blank sterets from the concentrations detected on each spiked sample, the recoveries are reported as a percentage of the "true" concentrations.

Desorption efficiency from skin was assessed in a similar manner. We have judged that because of the PAH content in the heavy fuel oils, it would not be ethical to use human volunteers for this work, so we have used pigskin (pigs trotters). Three different levels of fuel oil were spiked from stock standard solutions onto the skin of a pig's trotter. This was allowed to dry for approximately 10 minutes then removed with steret wipes. Two sterets were used when 14.5 and 289.2µg were spiked onto skin. Three sterets were used when 1449µg were spiked onto skin. The sterets were then placed into individual vials and analysed immediately. Each level of fuel oil was analysed four times. Spikes were also made to a glass slide to assess what effect the skin was having on recovery, i.e. was there any permeation into the skin.

Storage Stability

Spiked samples were prepared by injecting a known amount of fuel oil onto sterets as above. Control spikes were also prepared by injecting known amounts of fuel oil directly into a 4mL glass vial. The sterets and control spikes were stored at room temperature for 1, 3, 7 and 14 days before analysis.

Stability on skin

Fuel oil was spiked from stock standard solutions onto the skin of a pig's trotter. This was allowed to dry for approximately 20 minutes, 2 hours and 4 hours before removal with two sterets. The sterets were then placed into individual vials and analysed immediately.

Preparation of Sample for Analysis

The following procedure was used to prepare the sample for analysis:

Each steret was placed into an individual 4ml glass vial using tweezers.
2mls of dichloromethane was pipetted into the vial.
The solution was ultrasonicated for 30 mins.
2 spatula tips of calcium chloride was added to the vial and left for 1 hour.
The solution was then filtered through further calcium chloride into a clean 2mL vial.
2 microspatula tips of calcium chloride was added to this vial.

Limit of Quantification and Detection Limit

Ten blank sterets were prepared as in section 3.5 and analysed using the chromatographic conditions described in section 3.3. Any peaks with the same retention time as phenanthrene or benzo(a)pyrene were measured, the standard deviation of these measurements was then determined.

The estimated LOQ was calculated by multiplying the standard deviation (SD) of the ten measurements by three.

PAH Levels in oils

Oils were prepared in a similar fashion to the standards in section 3.2. Stock solutions were diluted with dichloromethane to give final concentrations of oil of between 500 and 600µg/ml. The solutions were then analysed against a calibration of the 16 priority PAHs. Calibration standards were prepared by diluting a proprietary mixed standard at 2000µg/ml with dichloromethane. The chromatographic conditions were the same as used in section 3.3. However, further ions were monitored for the other PAH compounds. The three major ions for each PAH were monitored in each case.

RESULTS

The peak area on the chromatogram of fuel oil was plotted against the weight of fuel oil per millilitre of preparation solution and the correlation coefficient calculated. All correlation coefficients (r^2) for the calibrations used during this validation were greater than 0.995.

Desorption Efficiency

The percentage recoveries for the spikes were determined by calculating the recovery weights against the amount of fuel oil used to spike the sterets (Table 2.). The percentage recoveries for the amount of fuel oil used to spike the pig skin and then removed by sterets can be seen Tables 3, 4 and 5. The averaged percentage recoveries are shown in Table 6.

Table 2 Desorption Efficiency from Sterets

Blank Corrected Concentration Fuel oil (µg/ml)		True Concentration fuel oil (µg/ml)	% Recovery	% Recovery
As Phenanthrene	As Benzo(a)pyrene		As Phenanthrene	As Benzo(a)pyrene
139.8	130.1	131.85	106.0	98.7
261.2	250.2	263.70	99.1	94.9

Table 3 Collection Efficiency from pig skin with 14.5µg fuel oil spikes

Blank Corrected Concentration Fuel oil (µg/ml)			True Concentration fuel oil (µg/ml)	% Recovery	% Recovery
Sample	Phenanthrene	Benzo(a) pyrene		Phenanthrene	Benzo(a) pyrene
Skin 1–1 Steret 1	19.5	10.5	14.46	134.9	72.6
Skin 1–1 Steret 2	-	-	14.46	-	-
Skin 1–2 Steret 1	16.0	13.2	14.46	110.3	91.4
Skin 1–2 Steret 2	-	-	14.46	-	-
Skin 1–3 Steret 1	12.1	8.0	14.46	83.7	55.3
Skin 1–3 Steret 2	-	5.5	14.46	-	38.0
Skin 1–4 Steret 1	15.6	13.2	14.46	107.9	91.3
Skin 1–4 Steret 2	-	-	14.46	-	-
Glass1 steret 1	19.5	12.7	14.46	134.9	87.8
Glass1 steret 2	-	-	14.46	-	-

Table 4 Desorption Efficiency from pig skin with 289.2µg fuel oil spikes

Blank Corrected Concentration Fuel oil (µg/ml)			True Concentration fuel oil (µg/ml)	% Recovery	% Recovery
Sample	Phenanthrene	Benzo(a) pyrene		Phenanthrene	Benzo(a) pyrene
Skin 2–1 Steret 1	234.0	226.1	289.23	80.9	78.2
Skin 2–1 Steret 2	11.9	-	289.23	4.1	-
Skin 2–2 Steret 1	238.0	234.1	289.23	82.3	81.0
Skin 2–2 Steret 2	10.6	-	289.23	3.7	-
Skin 2–3 Steret 1	187.2	173.8	289.23	64.7	60.1
Skin 2–3 Steret 2	63.4	48.8	289.23	21.9	16.9
Skin 2–4 Steret 1	188.0	192.8	289.23	65.0	66.7
Skin 2–4 Steret 2	111.6	117.9	289.23	38.6	40.8
Glass2 steret 1	238.2	256.4	289.23	82.4	88.7
Glass2 steret 2	15.1	-	289.23	5.2	-

Table 5 Desorption Efficiency from pig skin with 1446µg fuel oil spikes

Blank Corrected Concentration Fuel oil (µg/ml) Sample	Phenanthrene	Benzo(a) pyrene	True Concentration fuel oil (µg/ml)	% Recovery Phenanthrene	% Recovery Benzo(a) pyrene
Skin 3–1 Steret 1	1163.3	1148.7	1446.0	80.4	79.4
Skin 3–1 Steret 2	387.7	385.0	1446.0	26.8	26.6
Skin 3-1 Steret 3	67.8	61.7	1446.0	4.6	4.2
Skin 3–2 Steret 1	894.5	968.0	1446.0	61.9	66.9
Skin 3–2 Steret 2	183.1	157.5	1446.0	12.7	10.9
Skin 3–2 Steret 3	40.0	21.2	1446.0	2.8	1.5
Skin 3–3 Steret 1	1407.8	1316.3	1446.0	97.4	91.0
Skin 3–3 Steret 2	29.2	21.0	1446.0	2.0	1.5
Skin 3–3 Steret 3	14.3	-	1446.0	1.0	-
Skin 3–4 Steret 1	1325.2	1246.5	1446.0	91.6	86.2
Skin 3–4 Steret 2	100.4	82.8	1446.0	6.9	5.7
Skin 3–4 Steret 3	21.6	11.7	1446.0	1.5	1.0
Glass3 steret 1	1142.6	1099.7	1446.0	79.0	76.1
Glass3 steret 2	142.9	161.9	1446.0	9.9	11.2

Table 6 Average Desorption Efficiency from pig skin with fuel oil spikes

True Concentration of Fuel Oil Spiked onto pig skin (µg/ml)	Average and Standard Deviation (%) Recovery as Phenanthrene		Average and Standard Deviation (%) Recovery as Benzo(a)pyrene	
14.5	109.2	18.1	87.2	8.4
289.2	90.3	7.7	85.9	12.5
1446.0	97.4	12.5	93.7	11.0

Limit of Quantification

The concentrations detected in the blank filters are tabulated below.

Table7 Limit of Quantification (LOQ)

Phenanthrene Concentration (µg/ml)		Benzo(a)pyrene Concentration (µg/ml)	
6.52		Not detected	
5.51		Not detected	
2.67		Not detected	
4.06		Not detected	
4.01		Not detected	
4.54		Not detected	
3.64		Not detected	
3.64		Not detected	
4.49		Not detected	
3.42		Not detected	
Mean	4.25	**Mean**	N/A
3 * SD (LOQ)	3.132	**3 * SD (LOQ)**	N/A*

* - See section 5.3

Storage Stability

The percentage recoveries for the 1, 3, 7 and 14 day spikes were determined by calculating the recovery weights against the amount of fuel oil used to spike the filters. The percentage recoveries for the control spikes into glass vials were determined in the same manner.

Table 8 Storage Stability

Blank Corrected Concentration Fuel oil (µg/ml)			True Concentration fuel oil (µg/ml)	% Recovery	% Recovery
Sample	As Phenanthrene	As Benzo(a) pyrene		As Phenanthrene	As Benzo(a) pyrene
Day 1 spike	272.1	240.3	287.6	94.6	83.6
Day 1 control	285.1	279.6	287.6	99.1	97.2
Day 3 spike	242.9	265.4	287.6	84.5	92.3
Day 3 control	288.8	302.8	287.6	100.4	105.3
Day 7 spike	289.5	286.7	287.6	100.7	99.7
Day 7 control	341.2	365.8	287.6	118.6*	127.2*
Day 14 spike	262.8	270.2	287.6	91.3	93.9
Day 14 control	276.2	287.9	287.6	96.0	100.1

* - incorrect spiking of control suspected – sample rejected

Stability on skin

Table 9 Stability of fuel oil on skin

Blank Corrected Concentration Fuel oil (µg/ml)			True Concentration fuel oil (µg/ml)	% Recovery	% Recovery
Sample	**Phenanthrene**	**Benzo(a) pyrene**		**Phenanthrene**	**Benzo(a) pyrene**
On skin 20mins Steret 1	306.6	297.2	320.8	95.6	92.6
On skin 20mins Steret 2	16.2	-	320.8	5.0	-
On skin 2hours Steret 1	304.3	306.4	320.8	94.8	95.5
On skin 2hours Steret 2	22.2	14.7	320.8	6.9	4.9
On skin 4hours Steret 1	302.4	303.0	320.8	94.3	94.4
On skin 4hours Steret 2	17.9	11.2	320.8	5.6	3.5

4.5 PAH Levels in Oils

Table 10 PAH levels in oil samples provided to IOM

PAH Compound	PAH Concentrations in Oil (mg/kg)								
	Oil 1	Oil 2	Oil 3	Oil 4	Oil 5	Oil 6	Oil 7	Oil 8	Oil 9
Naphthalene	160	3390	51850	<2	<2	716	56	107	221
Acenaphthalene	<2	43	3340	<2	<2	30	3	11	<2
Acenaphthene	35	310	44	<2	<2	293	8	77	34
Fluorene	48	327	4240	<2	<2	515	39	306	45
Phenanthrene	95	650	5315	20	<2	2840	84	943	266
Anthracene	93	92	984	22	<2	515	83	74	18
Fluoranthene	13	28	431	17	<2	307	<2	31	11
Pyrene	48	77	771	25	<2	1630	24	119	250
Benz(a)anthracene	43	8	200	<2	<2	635	<2	<2	111
Chrysene	43	11	200	<2	<2	1240	<2	<2	95
Benzo(b)fluroanthene	14	5	27	15	<2	140	11	<2	16
Benzo(k)fluroanthene	6	3	<2	15	<2	17	9	<2	<2
Benzo(a)pyrene	46	7	39	27	<2	371	15	<2	71
Indeno(1,2,3-cd)fluoranthene	<2	<2	<2	<2	<2	<2	<2	<2	<2
Dibenz(a,h)anthracene	<2	<2	<2	<2	<2	<2	<2	<2	<2
Benzo(ghi)perylene	<2	<2	<2	32	<2	190	<2	<2	97

Oil 1 = Heavy fuel oil TK-624 (EC No 270-675-6) used in validation
Oil 2 = Bunker fuel oil TK-225 (EC No 270-675-6)
Oil 3 = PFO TK-339 (Cas No 64742-90-1)
Oil 4 = Wax job 66 (Cas No 64741-87-7)
Oil 5 = Residue job 66 (Cas No 68955-27-1)
Oil 6 = HCO job 67 (Cas No 64741-61-3)
Oil 7 = HGO job 63 (Cas No 68783-08-4)
Oil 8 = VGO job 66 (Cas No 70592-77-7)
Oil 9 = Heavy Fuel Oil S502 (EC No 270-675-6)

DISCUSSION

5.1 Linearity

The IOM judges that a calibration curve is acceptable if the correlation coefficient is >0.990. All calibration curves in the validation study met this criterion.

5.2 Desorption Efficiency

The validation criteria applied by IOM for spiked samples is a mean recovery of 85% to 110%. The mean recoveries met this criterion. However, it should be noted that individual recoveries, especially at lower level spikes, were outwith these limits. The results of this exercise suggest that the analytical method is likely to be suitable for samples containing more than 20μg of fuel oil on skin.

5.3 Limit of quantification and Detection Limit

The limit of quantification using blank sterets for benzo(a)pyrene was theoretically calculated as 0μg/ml, the samples were desorbed in 2 ml, this equates to an LOQ of 0 μg per sample. However, an analytical detection limit of 10μg/ml for this method is probably more appropriate, this equates to a detection limit of 20μg per steret. The limit of quantification using blank sterets for phenanthrene was theoretically calculated as 3.1μg/ml, the samples were desorbed in 2 ml, this equates to an LOQ of 6.2μg per sample. However, an analytical detection limit of 10μg/ml for this method is probably more appropriate, this equates to a detection limit of 20μg per steret.

5.4 Storage Stability and stability on skin

The spiked samples show storage stability at room temperature for 1, 3, 7 and 14 days. The fuel oil appears to be stable on the skin when using the PAH markers. There is acceptable recovery of the oil when the oil is left on the skin for up to 4 hours.

5.5 Use of PAH Markers

Phenanthrene and benzo(a)pyrene were shown to be the most useful PAH markers in the fuel oil (TK-624) used for the validation. Naphthalene was also considered as a marker in the fuel oil. The recoveries from spikes directly onto sterets were found to be close to 100%. However, when the fuel oil was spiked onto the pig skin, the recoveries of naphthalene were variable. The fuel oil was spiked onto pig skin dissolved in solvent. It is thought that naphthalene levels may be being affected by the evaporation of the solvent on the skin. This evaporation effect would not take place when fuel oil was being spiked directly onto sterets, due to the high levels of isopropyl alcohol present on the sterets.

Phenanthrene was present in seven out of the eight oils analysed. Benzo(a)pyrene was present in six out of the eight oils analysed. However, it should be noted that not all the oils analysed were heavy fuel oils. We conclude that phenanthrene and benzo(a)pyrene are likely to be appropriate markers for use in this study.

Report prepared by: **Authorised by:**

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Carolyn McGonagle
Senior Chemist

APPENDIX III – DERMAL EXPOSURE ASSESSMENT METHOD (ADJUSTED VERSION)

DERMAL EXPOSURE ASSESSMENT METHOD (DREAM) – QUESTIONNAIRE PART 1: COMPANY

Observer (fill in your name):	
Date (dd-mm-yyyy):	
Company code[2]:	
Company name:	
Company address:	
Contact person's name	
Sector:	
Main activity of company:	
Total number of workers:	

[2] Fill in a specific code for this company [e.g. date (yy-mm-dd) followed by your initials and company code]

DERMAL EXPOSURE ASSESSMENT METHOD (DREAM) – QUESTIONNAIRE PART 4: JOBTITLE

Observer (fill in your name):						
Company code:						
Department:						
Job title:						
	QUESTION			**ANSWERS**		
1	Total number of workers with this job title:					
2	Number of workers per duty / shift:					
3	Mark covered[3,4] body parts			Description of outer layer of clothing		
		No	Yes	Woven[5]	Non-woven[6]	Non-permeable[7]
	Head / neck	O	O	O	O	O
	Upper arms	O	O	O	O	O
	Forearms	O	O	O	O	O
	Wrists / hands	O	O	O	O	O
	Torso (front)	O	O	O	O	O
	Torso (back)	O	O	O	O	O
	Lower abdomen and upper legs	O	O	O	O	O
	Lower legs	O	O	O	O	O
	Feet	O	O	Open shoes O	Closed shoes O	Rubber boots O

[3] A body part is defined as covered when more than <u>90%</u> of a body part is covered. Do not include TASK SPECIFIC personal protective equipment (PPE). Task specific protective devices are filled in at task level
[4] If workers differ regarding clothing, indicate less covered worker.
[5] Such as cotton / linen / polyester, agent may penetrate.
[6] Such as tyvek / leather, agent may permeate.
[7] Non-woven and non-permeable, agents do not permeate

<table>
<tr><td>4</td><td colspan="3">Are work clothes immediately changed after work?</td><td colspan="5">O no
O some workers
O yes</td></tr>
<tr><td>5</td><td colspan="3">How often are work clothes replaced by clean ones?</td><td colspan="5">O daily
O more times a week
O once a week</td></tr>
<tr><td>6</td><td colspan="3">Are workers responsible for washing their own work clothes?</td><td colspan="5">O no
O yes</td></tr>
<tr><td>7</td><td colspan="3">Workers wash their hands during work?</td><td colspan="5">O no → 8
O yes</td></tr>
<tr><td>7.1</td><td colspan="3">Specify how hands are normally washed:</td><td colspan="5"></td></tr>
<tr><td></td><td></td><td>No</td><td>Yes</td><td>1 / shift end of day</td><td>1 / shift during day</td><td>2-4 / shift</td><td>5-10 / shift</td><td>11-20 / shift</td></tr>
<tr><td></td><td>O only water
O general soap
O scrub soap
O solvents
O other (specify)
______________________</td><td>O
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O</td></tr>
<tr><td>8</td><td colspan="3">Do workers shower at work?</td><td colspan="5">O no
O some workers
O yes</td></tr>
</table>

DERMAL EXPOSURE ASSESSMENT METHOD (DREAM) – QUESTIONNAIRE PART 5: TASK

Observer (fill in your name):		
Company code:		
Department:		
Job title:		
Task:		
Agent:		
	QUESTION	**ANSWERS**
1	Number of months per year task is performed?	
2	How many workers perform this task?[8]	
3	How many workers perform this task at the same moment?[10]	
4	Task performance [Estimated for **one** general worker with this job title and task]	O daily → 4.1 O weekly O monthly O yearly
4.1	Task frequency per day (Estimated for **one** worker)	***O 1 time*** ***O 2 – 10 times*** ***O > 10 times***

[8] Workers with this job title, within this department

		Per day	Per week (Hours)	Per month (Hours)	Per year (Hours)
5	Total time of task performance **(frequency * duration)** *Estimated for one worker*	**O ≤ 10 min** **O 11-60 min** **O >1 – 4 h** **O > 4 – 8 h**	**O 0 – 1** **O >1 – 4** **O >4 – 20** **O >20**	**O 0 – 4** **O > 4 – 16** **O > 16 – 80** **O > 80**	**O 0 – 40** **O > 40 – 160** **O > 160 – 800** **O > 800**
6	***Total time of task performance (absolute)*** **Estimated for one worker**	____ Minutes per day ____ Hours per week / month / year[9]			
7	You observed the task?	O no O yes → 7.1			
7.1	How often did you observe?	O one person, once O one person, repeatedly O several persons, once O several persons, repeatedly			

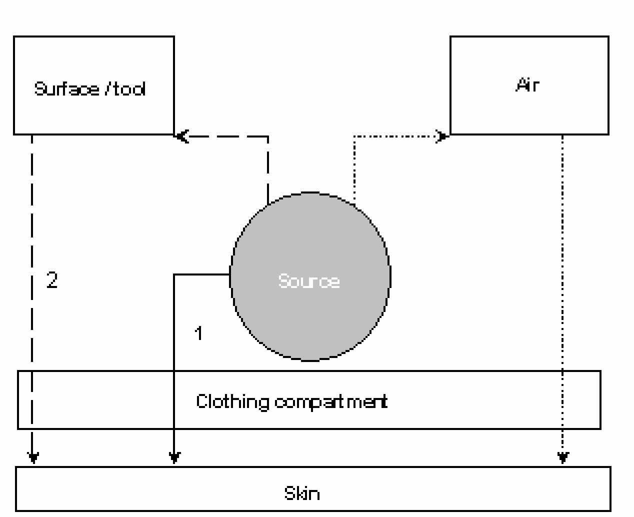
[9] Strike out whichever not applicable

INSTRUCTIONS

- Choose always the answer closest to your opinion.
- Read footnotes carefully.
- Assess exposure to HEAVY FUEL OIL.
- The questions consider POTENTIAL dermal exposure, which is defined as dermal exposure on clothing and uncovered skin; if body parts are covered exposure to the covered body parts is assessed. The evaluation part of DREAM takes into account the protective effects of clothing and personal protections devices like gloves etc.
- The questions of DREAM are based on the conceptual model for dermal exposure according to Schneider et al., 1999. This model considers, amongst others, the following exposure routes for dermal exposure (see also figure 1):

1. **Emission:** direct release from a source onto skin or clothing, such as exposure by splashes, or immersion of hands into a liquid or powder; droplets and powder particles have an aerodynamic diameter of ≥ 100 micrometer.
2. **Transfer:** contact with surfaces or working tools that have been previously contaminated with agent.

Figure 1: exposure routes for dermal exposure (1= emission; 2=transfer).



- ***After filling in, check whether you marked the body parts you consider to be exposed.***
- ***Please continue***

Observer (fill in your name):	
Company Code:	
Department:	
Job title:	
Task:	
Exposure to (fill in agent):	
Date:	
ID of observed worker:	

1	**Emission.**[10] (Covered) hands are exposed by direct release of agent from a source or by immersion?	O no, unlikely → 2 O yes, occasionally[11] O yes, repeatedly[12] O yes, almost constantly[13]
1.1	Specify amount	O small amount (<10% hands) O medium amount (10 – 50% hands) O large amount (> 50% hands)
2	**Emission.** Other (covered) body parts are exposed by direct release of agent from a source, or by immersion?	O no → 3 O yes, occasionally[13] O yes, repeatedly[14] O yes, almost constantly[15]
2.1	Specify amount	O small amount (<10% of body part) O medium amount (10 – 50% of body part) O large amount (> 50% of body part)
2.2	Indicate which body parts are exposed due to emission	(see body part table below)

Body part	Exposed?	
	No	Yes
Head / neck	O	O
Upper arms	O	O
Forearms	O	O
Torso (front)	O	O
Torso (back)	O	O
Lower abdomen and upper legs	O	O
Lower legs	O	O
Feet	O	O

[10] **Emission:** direct release from a source onto skin or clothing, such as immersion of hands into a liquid or powder, or exposure by splashes; droplets and powder particles have an aerodynamic diameter of ≥ 100 micrometer.
[11] <10% of task duration
[12] 10-50% of task duration
[13] >50% of task duration

3	*Transfer of agent to (covered) hands.*[14] ***When performing this task…***								
3.1		**Hands have contact with surfaces or tools?**				**Estimated contamination level of <u>contact surface</u>?**			
	Surfaces[15,16]:	**No, unlikely**	**Occasionally[17]**	**Repeatedly[18]**	**Almost constantly[19]**	**Not Contaminated**	**Possibly contaminated**	**< 50% of contact surface**	**> 50% of contact surface**
	Floor	O	O	O	O	O	O	O	O
	Worktables	O	O	O	O	O	O	O	O
	Machines	O	O	O	O	O	O	O	O
	Working tools	O	O	O	O	O	O	O	O
	Other surfaces,	O	O	O	O	O	O	O	O
	3.1.a Other surfaces specification:								

[14] **Transfer:** contact with surfaces or working tools that have been <u>previously</u> contaminated with agent
[15] In case surfaces are not present (e.g. work tables), tick 'unlikely'.
[16] In case 'surfaces' of one category have different contact frequencies or contamination levels, indicate then the surface with the highest product of contact frequency and contamination level in that category.
[17] <10% of task duration
[18] 10-50% of task duration
[19] >50% of task duration

4	**Transfer of agent to other (covered) body parts.** [20] When performing this task[21]**…**								
4.1		**Other body parts have contact with surfaces, tools or hands?**				**Estimated contamination level of contact surface?**			
	Surfaces:[22,23]	**No, unlikely**	**Occasionally**[24]	**Repeatedly**[25]	**Almost constantly**[26]	**Not Contaminated**	**Possibly contaminated**	**< 50% of contact surface**	**> 50% of contact surface**
	Floor	O	O	O	O	O	O	O	O
	Worktables	O	O	O	O	O	O	O	O
	Machines	O	O	O	O	O	O	O	O
	Working tools	O	O	O	O	O	O	O	O
	Hands	O	O	O	O	O	O	O	O
	Other surfaces	O	O	O	O	O	O	O	O
	5.1a Other surfaces specification:								

4.2	Indicate which body parts have contact with contaminated surfaces, tools or hands:	Body part:	Contact?	
			No	Yes
		Head / neck	O	O
		Upper arms	O	O
		Forearms	O	O
		Torso (front)	O	O
		Torso (back)	O	O
		Lower abdomen and upper legs	O	O
		Lower legs	O	O
		Feet	O	O

[20] **Transfer:** contact with surfaces or working tools that may have been previously contaminated with agent
[21] Do not consider contact of feet with contaminated floor if footwear is supposed to provide proper protection
[22] In case surfaces are not present (e.g. work tables), tick 'unlikely'.
[23] In case 'surfaces' of one category have different contact frequencies or contamination levels, indicate then the surface with the highest product of contact frequency and contamination level in that category.
[24] <10% of task duration
[25] 10-50% of task duration
[26] >50% of task duration

5	**Contamination.** Indicate how surfaces get contaminated with agent during task.					
5.1		**Contaminated during task?**			**Indicate main route only**	
	Surfaces:	**No**	**Possibly**	**Yes**	**Emission**[27]	**Transfer**[28]
	Floor	O	O	O	O	O
	Worktables	O	O	O	O	O
	Machines	O	O	O	O	O
	Working tools	O	O	O	O	O
	Hands	O	O	O	O	O
	Other surfaces	O	O	O	O	O
	6.1a Other surfaces specification:					

[27] **Emission:** direct release from source onto surfaces, such as immersion of surfaces into a liquid or powder, exposure by splashes. Droplets and powder particles have an aerodynamic diameter of ≥100 micrometer.

[28] **Transfer:** contact of surfaces with surfaces or working tools that have been previously contaminated with agent

7	Does worker use gloves when performing task?	O no → 13 O yes
7.1 **ASK**	Specify glove type	O Latex / natural rubber, disposable O Latex / natural rubber, non disposable O Vinyl disposable O Polychloroprene O Nitrile rubber O Neoprene rubber O Butyl rubber O Fluorocarbon rubber (e.g. Viton tm) O Laminated, impregnated, coated (e.g. cloth with rubber or leather) O Cotton/linen (cloth) O Plastic disposable O Leather O Other: ____________________
8	Gloves connect well to clothing of arms?	O no O yes
9	When performing task gloves are worn during:	O 0 – 10 % of task duration O 10 – 50% of task duration O 50 – 100% of task duration
10	Are gloves taken off correctly (skin does not have contact with outer surface gloves)?	O No O Not observed O Yes
11 ASK	How often are gloves replaced	O after having used them once O daily O weekly O monthly
12	Does worker wear a second pair of gloves under outer gloves?	O no O yes
12.1	How often are these inner gloves replaced?	O after having used them once O daily O weekly O monthly
13	Is barrier creme used?	O no O yes
14	Does worker use personal protective clothing **in addition to** clothing indicated at job title level?	O no → 16 O yes

15	Mark covered body parts[29]								
	Covered?		***Material outer layer clothing***			***How often replaced?*** *(Ask)*			
	No	Yes	**Woven[30]**	**Non-woven[31]**	**Imper-meable [32]**	**After 1 time**	**Daily**	**Week-ly**	**Month ly, yearly**
Head / neck	O	O	O	O	O	O	O	O	O
Upper arms	O	O	O	O	O	O	O	O	O
Forearms	O	O	O	O	O	O	O	O	O
Torso (front)	O	O	O	O	O	O	O	O	O
Torso (back)	O	O	O	O	O	O	O	O	O
Lower abdomen and upper legs	O	O	O	O	O	O	O	O	O
Lower legs	O	O	O	O	O	O	O	O	O
Feet	O	O	Open shoes O	Closed shoes O	Rubber boots O	Daily O	Weekl y O	Month ly O	Yearly O
16	Total amount of agent handled by the worker during total time of task performance[33]		O _____ O mg O mL O g O L O kg O m3 O not applicable						

[29] A body part is defined as covered when >90% is covered.
[30] Such as cotton, linen, polyester
[31] Such as tyvek, plastic, rubber, leather
[32] Both non-woven and non-permeable, which is agent specific, search information if you are not sure!
[33] In case of performing measurements task performance is equal to measurement time.

APPENDIX IV - RAW DATA FROM DERMAL MEASUREMENTS

									DERMAL EXPOSURE	
	Date	Worker number	Site Code	Type of Facility[1]	Analyte[2]	Task	Anatomical location[3]	Sample status	Sample Amount (µg)	Sample Concentration (µg cm^{2})[4]
1	22-Jan-2007	1	1	EP	N	pre-task	LFA	<LOD	7.07	0.28
2	22-Jan-2007	1	1	EP	N	pre-task	LH	<LOD	7.07	0.03
3	22-Jan-2007	1	1	EP	N	pre-task	NK	<LOD	7.07	0.28
4	22-Jan-2007	1	1	EP	N	pre-task	RFA	<LOD	7.07	0.28
5	22-Jan-2007	1	1	EP	N	pre-task	RH	<LOD	7.07	0.03
6	25-Jan-2007	3	1	EP	N	pre-task	LFA	<LOD	14.14	0.57
7	25-Jan-2007	3	1	EP	N	pre-task	LH	<LOD	14.14	0.07
8	25-Jan-2007	3	1	EP	N	pre-task	NK	<LOD	14.14	0.57
9	25-Jan-2007	3	1	EP	N	pre-task	RFA	<LOD	14.14	0.57
10	25-Jan-2007	3	1	EP	N	pre-task	RH	<LOD	14.14	0.07
11	02-Apr-2007	14	4	D	P	bottom unloading	LFA	<LOD	14.14	0.57
12	02-Apr-2007	14	4	D	P	bottom unloading	LH	<LOD	14.14	0.07
13	02-Apr-2007	14	4	D	P	bottom unloading	NK	<LOD	14.14	0.57
14	02-Apr-2007	14	4	D	P	bottom unloading	RFA	<LOD	14.14	0.57
15	02-Apr-2007	14	4	D	P	bottom unloading	RH	<LOD	14.14	0.07
16	03-Apr-2007	15	4	D	P	bottom unloading	LFA	<LOD	14.14	0.57
17	03-Apr-2007	15	4	D	P	bottom unloading	LH	<LOD	14.14	0.07
18	03-Apr-2007	15	4	D	P	bottom unloading	NK	<LOD	14.14	0.57
19	03-Apr-2007	15	4	D	P	bottom unloading	RFA	<LOD	14.14	0.57
20	03-Apr-2007	15	4	D	P	bottom unloading	RH	<LOD	14.14	0.07
21	03-Apr-2007	16	4	D	P	bottom unloading	LFA	<LOD	14.14	0.57

[1] Type of Facility: EP – Energy provider; D – Fuel distribution; OR – Oil refinery
[2] Analyte: N – Naphthalene; P – Phenanthrene
[3] Anatomical location: LFA – left forearm; LH – left hand; NK – neck; RFA – right forearm; RH – right hand
[4] Exposure areas used to calculate concentration: LFA, NK, RFA: area = 25 cm^2. LH, RH: area = 210 cm^2

	Date	Worker number	Site Code	Type of Facility[1]	Analyte[2]	Task	Anatomical location[3]	Sample status	Sample Amount (µg)	Sample Concentration (µg cm^2)[4]
22	03-Apr-2007	16	4	D	P	bottom unloading	LH	<LOD	14.14	0.07
23	03-Apr-2007	16	4	D	P	bottom unloading	NK	<LOD	14.14	0.57
24	03-Apr-2007	16	4	D	P	bottom unloading	RFA	<LOD	14.14	0.57
25	03-Apr-2007	16	4	D	P	bottom unloading	RH	<LOD	14.14	0.07
26	03-Apr-2007	17	4	D	P	bottom unloading	LFA	<LOD	14.14	0.57
27	03-Apr-2007	17	4	D	P	bottom unloading	LH	<LOD	14.14	0.07
28	03-Apr-2007	17	4	D	P	bottom unloading	NK	<LOD	14.14	0.57
29	03-Apr-2007	17	4	D	P	bottom unloading	RFA	<LOD	14.14	0.57
30	03-Apr-2007	17	4	D	P	bottom unloading	RH	<LOD	14.14	0.07
31	04-Apr-2007	18	4	D	P	bottom unloading	LFA	<LOD	14.14	0.57
32	04-Apr-2007	18	4	D	P	bottom unloading	LH	<LOD	14.14	0.07
33	04-Apr-2007	18	4	D	P	bottom unloading	NK	<LOD	14.14	0.57
34	04-Apr-2007	18	4	D	P	bottom unloading	RFA	<LOD	14.14	0.57
35	04-Apr-2007	18	4	D	P	bottom unloading	RH	<LOD	14.14	0.07
36	15-Mar-2007	10	3	EP	P	cleaning (bay)	LFA	<LOD	10.61	0.42
37	15-Mar-2007	10	3	EP	P	cleaning (bay)	LH	>LOD	560.00	2.67
38	15-Mar-2007	10	3	EP	P	cleaning (bay)	NK	<LOD	10.61	0.42
39	15-Mar-2007	10	3	EP	P	cleaning (bay)	RFA	<LOD	10.61	0.42
40	15-Mar-2007	10	3	EP	P	cleaning (bay)	RH	<LOD	10.61	0.05
41	25-Jan-2007	3	1	EP	N	cleaning (filter)	LFA	>LOD	33.00	1.32
42	25-Jan-2007	3	1	EP	N	cleaning (filter)	LH	>LOD	53.00	0.25
43	25-Jan-2007	3	1	EP	N	cleaning (filter)	NK	>LOD	32.00	1.28
44	25-Jan-2007	3	1	EP	N	cleaning (filter)	RFA	>LOD	36.00	1.44
45	25-Jan-2007	3	1	EP	N	cleaning (filter)	RH	>LOD	42.00	0.20
46	30-Jan-2007	4	2	D	P	top loading	LFA	<LOD	7.07	0.28
47	30-Jan-2007	4	2	D	P	top loading	LH	>LOD	40.00	0.19
48	30-Jan-2007	4	2	D	P	top loading	NK	<LOD	7.07	0.28
49	30-Jan-2007	4	2	D	P	top loading	RFA	<LOD	7.07	0.28

	Date	Worker number	Site Code	Type of Facility[1]	Analyte[2]	Task	Anatomical location[3]	Sample status	Sample Amount (µg)	Sample Concentration (µg cm^2)[4]
50	30-Jan-2007	4	2	D	P	top loading	RH	>LOD	20.00	0.10
51	30-Jan-2007	4	2	D	P	top loading	LFA	<LOD	7.07	0.28
52	30-Jan-2007	4	2	D	P	top loading	LH	>LOD	13.00	0.06
53	30-Jan-2007	4	2	D	P	top loading	NK	<LOD	7.07	0.28
54	30-Jan-2007	4	2	D	P	top loading	RFA	<LOD	7.07	0.28
55	30-Jan-2007	4	2	D	P	top loading	RH	<LOD	7.07	0.03
56	30-Jan-2007	5	2	D	P	top loading	LFA	<LOD	7.07	0.28
57	30-Jan-2007	5	2	D	P	top loading	LH	>LOD	19.00	0.09
58	30-Jan-2007	5	2	D	P	top loading	NK	<LOD	7.07	0.28
59	30-Jan-2007	5	2	D	P	top loading	RFA	<LOD	7.07	0.28
60	30-Jan-2007	5	2	D	P	top loading	RH	>LOD	19.00	0.09
61	30-Jan-2007	5	2	D	P	top loading	LFA	<LOD	7.07	0.28
62	30-Jan-2007	5	2	D	P	top loading	LH	>LOD	39.00	0.19
63	30-Jan-2007	5	2	D	P	top loading	NK	<LOD	7.07	0.28
64	30-Jan-2007	5	2	D	P	top loading	RFA	<LOD	7.07	0.28
65	30-Jan-2007	5	2	D	P	top loading	RH	>LOD	131.00	0.62
66	30-Jan-2007	6	2	D	P	top loading	LFA	<LOD	7.07	0.28
67	30-Jan-2007	6	2	D	P	top loading	LH	>LOD	40.00	0.19
68	30-Jan-2007	6	2	D	P	top loading	NK	<LOD	7.07	0.28
69	30-Jan-2007	6	2	D	P	top loading	RFA	<LOD	7.07	0.28
70	30-Jan-2007	6	2	D	P	top loading	RH	>LOD	22.00	0.10
71	30-Jan-2007	7	2	D	P	top loading	LFA	<LOD	7.07	0.28
72	30-Jan-2007	7	2	D	P	top loading	LH	>LOD	34.00	0.16
73	30-Jan-2007	7	2	D	P	top loading	NK	<LOD	7.07	0.28
74	30-Jan-2007	7	2	D	P	top loading	RFA	<LOD	7.07	0.28
75	30-Jan-2007	7	2	D	P	top loading	RH	>LOD	70.00	0.33
76	30-Jan-2007	5	2	D	P	top loading	LFA	<LOD	7.07	0.28
77	30-Jan-2007	5	2	D	P	top loading	LH	>LOD	24.00	0.11

	Date	Worker number	Site Code	Type of Facility[1]	Analyte[2]	Task	Anatomical location[3]	Sample status	Sample Amount (µg)	Sample Concentration (µg cm^2)[4]
78	30-Jan-2007	5	2	D	P	top loading	NK	<LOD	7.07	0.28
79	30-Jan-2007	5	2	D	P	top loading	RFA	<LOD	7.07	0.28
80	30-Jan-2007	5	2	D	P	top loading	RH	>LOD	34.00	0.16
81	30-Jan-2007	5	2	D	P	top loading	LFA	<LOD	7.07	0.28
82	30-Jan-2007	5	2	D	P	top loading	LH	>LOD	19.00	0.09
83	30-Jan-2007	5	2	D	P	top loading	NK	<LOD	7.07	0.28
84	30-Jan-2007	5	2	D	P	top loading	RFA	<LOD	7.07	0.28
85	30-Jan-2007	5	2	D	P	top loading	RH	>LOD	21.00	0.10
86	31-Jan-2007	4	2	D	P	top loading	LFA	<LOD	7.07	0.28
87	31-Jan-2007	4	2	D	P	top loading	LH	>LOD	14.00	0.07
88	31-Jan-2007	4	2	D	P	top loading	NK	<LOD	7.07	0.28
89	31-Jan-2007	4	2	D	P	top loading	RFA	<LOD	7.07	0.28
90	31-Jan-2007	4	2	D	P	top loading	RH	<LOD	7.07	0.03
91	31-Jan-2007	4	2	D	P	top loading	LFA	<LOD	7.07	0.28
92	31-Jan-2007	4	2	D	P	top loading	LH	<LOD	7.07	0.03
93	31-Jan-2007	4	2	D	P	top loading	NK	<LOD	7.07	0.28
94	31-Jan-2007	4	2	D	P	top loading	RFA	<LOD	7.07	0.28
95	31-Jan-2007	4	2	D	P	top loading	RH	>LOD	19.00	0.09
96	31-Jan-2007	8	2	D	P	top loading	LFA	<LOD	7.07	0.28
97	31-Jan-2007	8	2	D	P	top loading	LH	>LOD	21.00	0.10
98	31-Jan-2007	8	2	D	P	top loading	NK	<LOD	7.07	0.28
99	31-Jan-2007	8	2	D	P	top loading	RFA	<LOD	7.07	0.28
100	31-Jan-2007	8	2	D	P	top loading	RH	>LOD	72.00	0.34
101	31-Jan-2007	6	2	D	P	top loading	LFA	<LOD	7.07	0.28
102	31-Jan-2007	6	2	D	P	top loading	LH	>LOD	188.00	0.90
103	31-Jan-2007	6	2	D	P	top loading	NK	<LOD	7.07	0.28
104	31-Jan-2007	6	2	D	P	top loading	RFA	<LOD	7.07	0.28
105	31-Jan-2007	6	2	D	P	top loading	RH	>LOD	261.00	1.24

	Date	Worker number	Site Code	Type of Facility[1]	Analyte[2]	Task	Anatomical location[3]	Sample status	Sample Amount (µg)	Sample Concentration (µg cm^2)[4]
106	31-Jan-2007	9	2	D	P	top loading	LFA	<LOD	7.07	0.28
107	31-Jan-2007	9	2	D	P	top loading	LH	>LOD	315.00	1.50
108	31-Jan-2007	9	2	D	P	top loading	NK	<LOD	7.07	0.28
109	31-Jan-2007	9	2	D	P	top loading	RFA	<LOD	7.07	0.28
110	31-Jan-2007	9	2	D	P	top loading	RH	>LOD	176.00	0.84
111	02-Apr-2007	13	4	D	P	top loading	LFA	<LOD	14.14	0.57
112	02-Apr-2007	13	4	D	P	top loading	LH	<LOD	14.14	0.07
113	02-Apr-2007	13	4	D	P	top loading	NK	<LOD	14.14	0.57
114	02-Apr-2007	13	4	D	P	top loading	RFA	<LOD	14.14	0.57
115	02-Apr-2007	13	4	D	P	top loading	RH	<LOD	14.14	0.07
116	02-Apr-2007	14	4	D	P	top loading	LFA	<LOD	14.14	0.57
117	02-Apr-2007	14	4	D	P	top loading	LH	<LOD	14.14	0.07
118	02-Apr-2007	14	4	D	P	top loading	NK	<LOD	14.14	0.57
119	02-Apr-2007	14	4	D	P	top loading	RFA	<LOD	14.14	0.57
120	02-Apr-2007	14	4	D	P	top loading	RH	<LOD	14.14	0.07
121	03-Apr-2007	16	4	D	P	top loading	LFA	<LOD	14.14	0.57
122	03-Apr-2007	16	4	D	P	top loading	LH	<LOD	14.14	0.07
123	03-Apr-2007	16	4	D	P	top loading	NK	<LOD	14.14	0.57
124	03-Apr-2007	16	4	D	P	top loading	RFA	<LOD	14.14	0.57
125	03-Apr-2007	16	4	D	P	top loading	RH	<LOD	14.14	0.07
126	03-Apr-2007	17	4	D	P	top loading	LFA	<LOD	14.14	0.57
127	03-Apr-2007	17	4	D	P	top loading	LH	<LOD	14.14	0.07
128	03-Apr-2007	17	4	D	P	top loading	NK	<LOD	14.14	0.57
129	03-Apr-2007	17	4	D	P	top loading	RFA	<LOD	14.14	0.57
130	03-Apr-2007	17	4	D	P	top loading	RH	<LOD	14.14	0.07
131	04-Apr-2007	18	4	D	P	top loading	LFA	<LOD	14.14	0.57
132	04-Apr-2007	18	4	D	P	top loading	LH	>LOD	361.00	1.72
133	04-Apr-2007	18	4	D	P	top loading	NK	<LOD	14.14	0.57

	Date	Worker number	Site Code	Type of Facility[1]	Analyte[2]	Task	Anatomical location[3]	Sample status	Sample Amount (µg)	Sample Concentration (µg cm^2)[4]
134	04-Apr-2007	18	4	D	P	top loading	RFA	<LOD	14.14	0.57
135	04-Apr-2007	18	4	D	P	top loading	RH	<LOD	14.14	0.07
136	23-Jan-2007	2	1	OR	N	spading line	LFA	<LOD	14.14	0.57
137	23-Jan-2007	2	1	OR	N	spading line	LH	<LOD	14.14	0.07
138	23-Jan-2007	2	1	OR	N	spading line	NK	<LOD	14.14	0.57
139	23-Jan-2007	2	1	OR	N	spading line	RFA	<LOD	14.14	0.57
140	23-Jan-2007	2	1	OR	N	spading line	RH	<LOD	14.14	0.07
141	22-Jan-2007	1	1	EP	N	tank dipping	LFA	<LOD	7.07	0.28
142	22-Jan-2007	1	1	EP	N	tank dipping	LH	<LOD	7.07	0.03
143	22-Jan-2007	1	1	EP	N	tank dipping	NK	<LOD	7.07	0.28
144	22-Jan-2007	1	1	EP	N	tank dipping	RFA	<LOD	7.07	0.28
145	22-Jan-2007	1	1	EP	N	tank dipping	RH	<LOD	7.07	0.03
146	25-Jan-2007	3	1	EP	N	general duties	LFA	<LOD	14.14	0.57
147	25-Jan-2007	3	1	EP	N	general duties	LH	<LOD	14.14	0.07
148	25-Jan-2007	3	1	EP	N	general duties	NK	<LOD	14.14	0.57
149	25-Jan-2007	3	1	EP	N	general duties	RFA	<LOD	14.14	0.57
150	25-Jan-2007	3	1	EP	N	general duties	RH	<LOD	14.14	0.07
151	15-Mar-2007	10	3	EP	P	cleaning (spillage/equipment)	LFA	<LOD	10.61	0.42
152	15-Mar-2007	10	3	EP	P	cleaning (spillage/equipment)	LH	>LOD	108.00	0.51
153	15-Mar-2007	10	3	EP	P	cleaning (spillage/equipment)	NK	<LOD	10.61	0.42
154	15-Mar-2007	10	3	EP	P	cleaning (spillage/equipment)	RFA	<LOD	10.61	0.42
155	15-Mar-2007	10	3	EP	P	cleaning (spillage/equipment)	RH	<LOD	10.61	0.05
156	15-Mar-2007	11	3	EP	P	sample collection (pumphouse)	LFA	<LOD	10.61	0.42
157	15-Mar-2007	11	3	EP	P	sample collection (pumphouse)	LH	<LOD	10.61	0.05
158	15-Mar-2007	11	3	EP	P	sample collection (pumphouse)	NK	<LOD	10.61	0.42
159	15-Mar-2007	11	3	EP	P	sample collection (pumphouse)	RFA	>LOD	99.00	3.96
160	15-Mar-2007	11	3	EP	P	sample collection (pumphouse)	RH	<LOD	10.61	0.05
161	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	LFA	<LOD	14.14	0.57

	Date	Worker number	Site Code	Type of Facility[1]	Analyte[2]	Task	Anatomical location[3]	Sample status	Sample Amount (µg)	Sample Concentration (µg cm^{2})[4]
162	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	LH	>LOD	1187.00	5.65
163	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	NK	<LOD	14.14	0.57
164	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	RFA	<LOD	14.14	0.57
165	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	RH	>LOD	277.00	1.32
166	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	LFA	>LOD	385.00	15.40
167	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	LH	>LOD	545.00	2.60
168	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	NK	<LOD	14.14	0.57
169	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	RFA	>LOD	271.00	10.84
170	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	RH	>LOD	174.00	0.83
171	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	LFA	>LOD	185.00	7.40
172	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	LH	>LOD	1177.00	5.60
173	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	NK	<LOD	14.14	0.57
174	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	RFA	>LOD	184.00	7.36
175	02-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	RH	>LOD	659.00	3.14
176	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	LFA	>LOD	103.00	4.12
177	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	LH	>LOD	395.00	1.88
178	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	NK	<LOD	14.14	0.57
179	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	RFA	>LOD	266.00	10.64
180	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	RH	>LOD	941.00	4.48
181	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	LFA	>LOD	56.00	2.24
182	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	LH	>LOD	606.00	2.89
183	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	NK	<LOD	14.14	0.57
184	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	RFA	>LOD	322.00	12.88
185	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	RH	>LOD	525.00	2.50
186	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	LFA	>LOD	292.00	11.68
187	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	LH	>LOD	997.00	4.75
188	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	NK	<LOD	14.14	0.57
189	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	RFA	>LOD	449.00	17.96

	Date	Worker number	Site Code	Type of Facility[1]	Analyte[2]	Task	Anatomical location[3]	Sample status	Sample Amount (µg)	Sample Concentration (µg cm^2)[4]
190	03-Apr-2007	12	4	D	P	cleaning (sample points)/gantry maintenance	RH	>LOD	1145.00	5.45

[1]Type of Facility: EP – Energy provider; D – Fuel distribution; OR – Oil refinery
[2] Analyte: N – Naphthalene; P – Phenanthrene
[3] Anatomical location: LFA – left forearm; LH – left hand; NK – neck; RFA – right forearm; RH – right hand
[4] Exposure areas used to calculate concentration: LFA, NK, RFA: area = 25 cm^2. LH, RH: area = 210 cm^2

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