



WORKING FOR A HEALTHY FUTURE

Research Report TM/08/05
May 2009

Occupational dermal exposure to heavy fuel oil

Part II

Yvette Christopher, Martie van Tongeren



WORLD HEALTH ORGANISATION
COLLABORATING CENTRE
FOR OCCUPATIONAL HEALTH

RESEARCH CONSULTING SERVICES

Multi-disciplinary specialists in Occupational and Environmental Health and Hygiene

www.iom-world.org

Occupational exposure to heavy fuel oil (Part II)

Yvette Christopher, Martie van Tongeren

Dermal exposure to heavy fuel oils (HFOs) was measured at two facilities in Finland using a newly developed method. This removal method for measuring dermal exposure to HFO is based on detecting specific PAHs in the oils as marker for total HFO exposure. In addition, an observational method for estimating dermal exposure (DREAM) was also applied. The two facilities were an oil refinery and a marine engine manufacturer. A total of 23 sets of dermal wipe samples were collected from 19 different workers in two different facilities during the performance of nine different tasks. Each sample set consisted of wipe samples from 4 anatomical locations: (palmar surfaces and forearms). The exposure levels appeared to be low, with approximately half the samples being below the limit of detection. The levels were generally higher in the marine engine building site with the geometric mean (GM) of 2.0 $\mu\text{g}/\text{cm}^2$ for the hand and 1.4 $\mu\text{g}/\text{cm}^2$ for the forearm, respectively. At the oil refinery site the GM was 0.2 $\mu\text{g}/\text{cm}^2$ for hand exposure and 0.7 $\mu\text{g}/\text{cm}^2$ for forearm exposure, respectively. There was no statistically significant correlation between average hand exposure measurements versus the DREAM estimates for hands.

This report and all IOM's research reports are available as PDF files, for free download from our website: <http://www.iom-world.org/research/libraryentry.php>

CONTENTS

SUMMARY	V
1 INTRODUCTION	1
1.1 Background	1
2 METHODOLOGY	3
2.1 Sampling strategy	3
2.2 Dermal sampling method	3
2.3 Analytical methods	4
2.4 Statistical analyses	4
2.5 SEMI-QUANTITATIVE EXPOSURE MEASUREMENTS	5
3 DESCRIPTION OF SITES	7
3.1 Oil refinery	7
3.2 Marine engine building and maintenance plant	8
4 RESULTS	11
5 DISCUSSION AND CONCLUSIONS	15
6 ACKNOWLEDGEMENTS	17
7 REFERENCES	19
APPENDIX 1 - DERMAL HAND AND FOREARM EXPOSURE AND SEMI-QUANTITATIVE ESTIMATES OF (ACTUAL) HAND EXPOSURE	21

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 amongst others as fuel for power stations and for heating of large industrial sites. The Institute of Occupational Medicine (IOM) has conducted a programme of research to investigate dermal exposures to HFO. This work is intended to provide information for CONCAWE (the oil companies' industry association) to undertake a risk assessment for the use of heavy fuel oils.

During the first phase of the project, a validated removal method for measuring dermal exposure to HFO was developed and used to collect exposure measurements. Dermal exposure surveys were undertaken in one refinery, two fuel terminals and two power stations. These data were compared with exposure estimates obtained using a semi-quantitative exposure assessment approach (DREAM). However, no association between the two methods was observed. Based on these data, the use of the semi-quantitative method to obtain exposure estimates could not be recommended. One possible reason for the lack of any association was the limited range of exposure levels that were observed. Subsequently, a follow-up study was carried out to collect further exposure data from a number of exposure scenarios that were not included in the first survey. The results of the follow up study are reported here.

Two surveys were carried out in Finland: one oil refinery and one marine engine manufacturer. A total of 23 sets of dermal wipe samples were collected from 19 different workers in two different facilities during the performance of nine different tasks. Each sample set consisted of wipe samples from 4 anatomical locations: (palmar surfaces and forearms).

The majority of forearm samples were below the limit of detection (LOD) while approximately half of the hand measurements had detectable levels of HFO. The exposure levels in the marine engine building site were generally higher than those in the oil refinery. In the oil refinery the Geometric Means (GM) for hand and forearm exposures were $0.2 \mu\text{g}/\text{cm}^2$ and $0.7 \mu\text{g}/\text{cm}^2$ respectively, while the GMs for hand and forearm exposures at the engine building site were $2.0 \mu\text{g}/\text{cm}^2$ and $1.4 \mu\text{g}/\text{cm}^2$, respectively. The highest hand exposure levels were $17.4 \mu\text{g}/\text{cm}^2$, observed during a 'filter changing' task and $9.5 \mu\text{g}/\text{cm}^2$ observed during a 'maintenance: cleaning nozzles' task within the marine engine building facility. The highest forearm exposure were $33.3 \mu\text{g}/\text{cm}^2$ and $6.6 \mu\text{g}/\text{cm}^2$, observed during a 'filter changing' and a 'cleaning: work area/machine' task, respectively.

Similar to the results from the first survey, no statistically significant correlation between measured dermal exposure and DREAM estimates was observed. Consequently, it is recommended that exposure estimates for these scenarios should be based on measurement data collected using the method for dermal exposure measurements of HFO which was developed and validated during this study.

1 INTRODUCTION

1.1 BACKGROUND

The Institute of Occupational Medicine (IOM) has conducted a programme of research to investigate dermal exposures to heavy fuel oils (HFO). This work is intended to provide information for CONCAWE (the oil companies' industry association) to undertake a risk assessment for the use of heavy fuel oils.

This programme had the following aims:

- 1) To develop a validated method for measuring dermal HFO exposure;
- 2) To collect exposure data in a limited number of surveys using the validated method;
- 3) To compare the exposure data with results from a semi-quantitative assessment of dermal exposure based on observations (van Wendel de Joode *et al*, 2003), and if necessary, modify the semi-quantitative method for HFO exposure; and
- 4) To apply the modified semi-quantitative method to obtain exposure information for a larger number of exposure scenarios.

During the first phase of the project, a validated removal method for measuring dermal exposure to HFO was developed. The method is based on measuring the level of certain polycyclic aromatic hydrocarbons (PAHs) as a marker of HFO exposure. Laboratory experiments using pig skin showed a good level of sampling efficiency, recovery and stability on the skin and during storage (Christopher *et al*, 2007). The sampling method was then applied in a small number of surveys at petrochemical sites and power stations. However, when comparing the results from the measurements with the semi-quantitative assessments, no association between the two methods was observed. Based on these results, the use of the semi-quantitative method to obtain exposure estimates from a larger number of exposure scenarios could not be recommended. One possible reason for the lack of any association was the limited range of exposure levels that were observed.

Subsequently, a follow-up study was carried out to collect further exposure data to widen the range of exposure scenarios. Two surveys were carried out in Finland: one in an oil refinery and one in a marine engine manufacturer. This report describes the results of the dermal exposure measurements collected at these two sites.

2 METHODOLOGY

2.1 SAMPLING STRATEGY

At the oil refinery site, the focus of the dermal monitoring survey was on workers who were employed within the refinery, the harbour area and the fuel distribution area. At the marine engine manufacturing site, the areas targeted included the test run unit and the repair shop. Relevant staff monitored within these areas were selected with the assistance of the companies' Health and Safety staff.

Prior to the measurement survey several tasks were identified as being relevant for HFO exposure. These are listed in Table 1. Task-based sampling was the most appropriate strategy given the nature of the activities carried out at these sites. An opportunistic approach was planned since it was not possible to determine exactly when certain tasks were undertaken during the period of the survey.

Table 1 Summary of tasks identified as having potential for HFO exposure in the oil refinery

Facility Type	Tasks
OIL REFINERY	Tank dipping in tank farm Sample collection in tank farm or pump house Sample collection/ullaging in shipping Loading HFO to ships at harbour (connecting/disconnecting hoses) Pump maintenance Spading Line (isolation of line for maintenance work) Cleaning fuel filter Cleaning up HFO spills or overflows Tank Cleaning Tank Inspection
SHIP AND POWER PLANT ENGINE BUILDING	Maintenance: engine parts Maintenance: fuel hoses and injectors Changing fuel filter Changing LFO filter Changing engine injectors in repair shop Changing pumps/uncoupling hoses Measuring fuel overflow Cleaning work area, equipment & machines Scale calibration & draining scale tank Sampling

2.2 DERMAL SAMPLING METHOD

The dermal sample method was identical to that described in the report by Christopher *et al* (2007) with the exception that the neck was not sampled. This was based on the fact that the exposure levels of 97% of the neck samples collected in the previous survey were less than

LOD. There was nothing to suggest that neck exposure in this second survey would differ significantly from the previous one. Dermal samples were obtained using a removal method using clinical wipes saturated with 70% isopropyl alcohol. The anatomical areas sampled were the hands and forearms. Wipe samples were collected from the entire palmar surface of each hand. An acetate template with an open aperture of 25 cm² was used to collect wipe samples from the inner surface of each forearm. Each sample comprised three sequential wipes from the same anatomical area and stored in a single container. In two cases where there were visibly high levels of contamination present on the skin, two sets of 3-wipe samples were collected (double samples). These two sets of samples were stored in separate sample bottles and laboratory analysis conducted separately for each sample.

To avoid cross contamination via transfer between anatomical sites and between workers, the researcher used a fresh pair of gloves after each sample set (i.e. after 3 sequential wipes from a single anatomical site). 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 (prior to cleaning of hands) and therefore were representative of the level of skin contamination immediately upon completion of the task. 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.

2.3 ANALYTICAL METHODS

The samples were analysed at the IOM analytical laboratory. 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-Mass Spectrometer (MS) capillary column which was programmed to heat from 60 to 310°C. The MS was set in selected ion monitoring (SIM) mode for the specific ions corresponding to phenanthrene. Specific calibration standards were prepared using relevant bulk samples and using phenanthrene as the marker for exposure to HFO.

2.4 STATISTICAL ANALYSES

The dermal exposure for each anatomical area was expressed in terms of mass per unit area (µg/cm²). The hand exposure was calculated using a palmar surface area of 210 cm². For calculating the exposure on the inner forearms the surface area defined by the acetate template (25 cm²) was used.

$$\text{Hand exposure } (\mu\text{g} / \text{cm}^2) = \frac{\text{mass on hand } (\mu\text{g})}{210 (\text{cm}^2)}$$

$$\text{Forearm exposure } (\mu\text{g} / \text{cm}^2) = \frac{\text{mass on forearm } (\mu\text{g})}{25 (\text{cm}^2)}$$

For each individual sample set the average HFO hand and forearm exposures were calculated.

$$\text{Average hand exposure } (\mu\text{g} / \text{cm}^2) = \frac{\text{mass on right hand } (\mu\text{g}) + \text{mass on left hand } (\mu\text{g})}{420 (\text{cm}^2)}$$

$$\text{Average forearm exposure } (\mu\text{g} / \text{cm}^2) = \frac{\text{mass on right forearm}(\mu\text{g}) + \text{mass on left forearm}(\mu\text{g})}{50 (\text{cm}^2)}$$

Sample results below the LOD were replaced by the LOD divided by the square root of 2 prior to the statistical analysis. The average HFO exposure on both hands and forearms was recorded as being greater than LOD when at least one sample (either left or right side) was greater than the LOD. For example, if the right hand exposure was >LOD but the corresponding left hand exposure was < LOD, then the average dermal surface load for both hands was recorded as being >LOD.

Exposure levels 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. None of the field blanks contained any detectable levels of HFO, and therefore no correction was required for the field samples.

2.5 SEMI-QUANTITATIVE EXPOSURE MEASUREMENTS

The DeRmal Exposure Assessment Method (DREAM) developed by van Wendel de Joode *et al* (2003) was used to obtain semi-quantitative estimates of exposure. The application of DREAM in this study is described in greater detail in Christopher *et al* (2007).

3 DESCRIPTION OF SITES

3.1 OIL REFINERY

In addition to the oil refinery, there is a large container area, a harbour and a technology centre at this site. The refinery has an annual capacity of approximately 11 million tonnes with 40% of this being exported. There are 2,000 workers employed at this site.

Most of the raw materials and products are transported via the harbour facilities that handle between 1,000 to 1,300 vessels a year. The annual cargo discharge and load is about 16-19 million tonnes. There is also a distribution centre which delivers to customers by road tankers and rail or by vessels to coastal storage facilities.

3.1.1 Tasks descriptions

Unfortunately, not all the tasks that were identified in advance took place during the survey. Consequently, no measurements for ship loading (harbour) and pump maintenance (fuel distribution) were collected. Dermal measurements were carried out for tasks within the refinery plant, the maintenance workshop and the analytical laboratory. The following section describes the tasks for which dermal measurements were collected. The basic personal protective equipment required in most areas of the site included safety helmets, safety glasses, overalls and safety boots. The areas where this differed are indicated under the task description.

Sample Collection

HFO samples for quality control are collected in several areas of the plant. At the tank farm, six one-litre samples are collected from each tank from three different levels, with two samples collected per level. These are called 'selling samples' and are collected twice per month. The worker collects the sample into narrow-necked one-litre bottles that fit snugly onto the hose of the sampling points. There is little or no spillage onto the bottle. However, the surfaces around these sampling points – hand rails, floor - were visibly contaminated with HFO.

At the catalytic cracking unit HFO samples at a temperature of 200°C are collected using a metal tin. This takes place about twice per week.

Samples at moderate temperature are also collected from other parts of the process. This is facilitated by sampling points similar to those found in the tank farm and using the same type of glass one-litre, narrow-necked bottles.

Operators wear basic personal protective equipment required on site in addition to leather safety gloves.

Cleaning

Tubes from tube-in-shell heat exchangers from the production lines are removed in order to clean the inner tubes. The system is firstly flushed with light fuel oil (LFO) to dilute the HFO, before removal of the tube caps and the rings holding the tubes in place. Hot water is used to loosen the HFO from the tube caps. Two workers were observed carrying out this cleaning task and they became heavily contaminated with petroleum residues.

Residual HFO-LFO mix from inside the tube caps is removed by shovelling. A solvent (kerosene) and hot water are sprayed onto the sticky residue to loosen it before shovelling.

This takes place in the process area where the heat exchangers are located. The inner tubes, with a diameter of approximately two metres and which contain several horizontal channels, are sent to a washing/repair area for clearing of the channels.

Maintenance

Miscellaneous maintenance activities, including washing of equipment, takes place in a special workshop/wash area. It comprises an outdoor and indoor area. For washing of large pieces of equipment, a high-power water jet spray equipment is used. For clearing the channels of the heat exchangers a special piece of equipment is used, consisting of a metal tube that releases a hot-water (55°C) jet spray. Workers may carry out repair work on this jet spray equipment, which may be contaminated with HFO, just prior to cleaning the heat exchanger tubes. The worker conducting the cleaning sits behind a Perspex screen at a small control panel from where he directs the metal tube cleaner with its jet spray to each separate channel of the tube. The action is similar to that of a syringe needle being directed at each channel and clearing residues of HFO in the channel along the way.

The workers in this area wear standard personal protective equipment with the exception of safety helmets. They also use leather gloves but on occasion were observed to take these off, especially when required to do fine repair work. The surface areas were contaminated with miscellaneous petroleum-based products.

Sample testing (laboratory)

Within the analytical laboratory, laboratory technicians conduct several standard test on HFO samples. These include tests to determine viscosity, sulphur content, flash point, density and metal content. These tests require considerable handling of samples, such as pouring, heating and other manipulation of HFO in vessels.

The surface areas were observed to be exceptionally clean. The workers wear long-sleeved, full-length laboratory coats over their regular clothing. They also use safety glasses and two pairs of gloves (cotton and nitrile) when conducting tests with HFO.

3.2 MARINE ENGINE BUILDING AND MAINTENANCE PLANT

The second survey took place at a company that manufactures marine engines and provides maintenance and reconditioning services for ship machinery and power plants. The company employs 2,500 workers.

3.2.1 Tasks descriptions

The following sections describe the tasks for which dermal measurements were collected from the ship and power plant engine building facility. The basic personal protective equipment required in most areas of the site consists of coveralls and safety boots. Gloves are worn when required during certain tasks. Where additional protective clothing is worn for different tasks, this is indicated under the tasks description.

Cleaning

Two different types of cleaning tasks were observed; cleaning injector nozzles and cleaning HFO overflow or drips from the floor tray under machinery. In the former tasks, the injector is firstly removed from the engine and taken to the repair shop where the nozzles are removed and placed in a small bath containing light fuel oil (LFO). They are allowed to soak for several

minutes after which the mechanic wipes each nozzle with a rag. Pressurized air is used to clear the nozzles of HFO. The nozzles are repeatedly soaked in the LFO and wiped with the rag until all the HFO is removed. The mechanic sometimes sprays the nozzle with a degreaser to dissolve the HFO prior to wiping clean. The entire procedure, from removal of the injector from the engine to replacing the injector with the cleaned nozzles, takes about two hours and is usually performed by two mechanics. However, during the survey only the nozzle cleaning part of the tasks was performed for about 10-15 minutes prior to collection of the dermal samples. The mechanic wears leather gloves in addition to the standard PPE when performing this task.

During the second cleaning task, two workers were observed cleaning HFO overflows from the floor tray under machinery and an HFO scale. A solvent is repeatedly sprayed onto the thick layer of HFO on the floor after which the HFO residues are removed using thick absorbent rags. When most of the HFO is removed, LFO is added to the dirty surface and the absorbent rags are once again used to wipe away any residual HFO. The workers wear vinyl gloves in addition of the standard PPE during performance of this task. This task can take up to 8 hours depending on the amount of HFO. However, during the survey this task was performed twice for approximately 10 minutes.

Filter cleaning/changing

Two workers were observed during filter cleaning or changing. The cover of the filter housing is removed using hand-held tools. Absorbent rags are used while lifting the cover. The inner lining of the filter housing and the filter are removed and placed into a bucket. These are sprayed with a solvent. To facilitate cleaning, LFO is used on the filter assembly. Absorbent sheets are laid over the floor and neighbouring machinery to capture any oil drippings. Following filter removal the floor, machinery and tools are cleaned and wiped down using clean absorbent sheets. The workers wear leather gloves in addition to the standard personal protective equipment. One worker was observed removing his gloves just prior to clean-up. This task takes 15-20 minutes.

Maintenance

Two different maintenance tasks were observed; pump dismantling and preparation for pipe disconnection. Pump dismantling takes place in the repair workshop and the worker uses various hand-held tools to dismantle the pump that has been sent for repair. A small volume of HFO mixed with LFO was observed dripping out of the pump during this activity.

In the second maintenance tasks that was observed, the worker uses a long-handled spanner to loosen the nut on a piece of machinery. HFO was observed dripping out of the joint. Absorbent sheets are placed on the neighbouring machinery and on the floor to catch any drip. These workers wear leather gloves, in addition to their standard personal protective equipment during performance of these tasks.

4 RESULTS

A total of 23 sets of dermal samples (excluding field blanks) were collected from 19 different workers. In total, 92 samples were analysed of which 58 (63%) were reported as below the limit of detection (LOD). The LOD varied from 0.57 to 0.07 $\mu\text{g}/\text{cm}^2$ depending on the anatomical location.

The results of the dermal measurements are given in Tables 2 to 4 and are reported as mass HFO per unit area. Table 2 presents the hand exposure by anatomical site and by industrial facility. In both facilities, the majority of forearm samples were below the LOD. For the hands, approximately half of the measurements had detectable levels of HFO. The exposure levels in the marine engine building site were generally higher than those in the oil refinery. The geometric mean (GM) for the hand and forearm exposures at the oil refinery site ranged from 0.1 to 0.7 $\mu\text{g}/\text{cm}^2$ while the GM exposure at the engine building site ranged from 0.9 to 1.7 $\mu\text{g}/\text{cm}^2$.

Table 2 Dermal HFO exposures in the oil refinery and the marine engine building and repair sites by anatomical site ($\mu\text{g}/\text{cm}^2$)

Facility Type	Bodypart	<LOD (%)	N _s	AM	GM	GSD	90th %tile	Range
OIL REFINERY	left hand	47	15	0.2	0.1	2.6	0.5	(0.1, 1.5)
	right hand	47	15	0.4	0.2	3.3	1.1	(0.0, 1.8)
	left forearm	93	15	0.6	0.6	1.0	0.6	(0.6, 0.6)
	right forearm	80	15	0.9	0.7	1.7	1.9	(0.6, 2.9)
SHIP AND POWER PLANT ENGINE BUILDING	left hand	25	8	4.4	1.0	10.3	18	0.1, 18
	right hand	25	8	7.0	1.7	9.6	33	0.1, 33
	left forearm	63	8	1.5	0.9	2.4	6.6	0.6, 6.6
	right forearm	63	8	9.4	1.4	5.8	65	0.6, 65

N_s: 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.

Table 3 summarises the results of the average hand exposure measurements by task. The highest exposures were observed within the marine engine building facility, with a GM for the combined hand exposure of 2.0 $\mu\text{g}/\text{cm}^2$, compared to 0.2 $\mu\text{g}/\text{cm}^2$ for the refinery site. The highest levels were measured during a 'filter changing' task (17.4 $\mu\text{g}/\text{cm}^2$) and 'maintenance: cleaning nozzles' task (9.5 $\mu\text{g}/\text{cm}^2$). The high exposure during the filter changing activity could be explained by the fact that he removed his gloves just prior to the cleaning up stage of this task of filter changing. This involved handling highly contaminated absorbent sheets that had been placed on the floor and other equipment in the area to collect oil drippings. During the maintenance tasks of cleaning nozzles the operator repeatedly immersed the contaminated nozzle into a bath of light fuel oil to soak following which he wiped the nozzle with a rag. The operator wore leather gloves during this task. However given the permeability of such gloves it is likely that these did not afford sufficient protection for an immersion type scenario such as this one. Also the light fuel oil may be a potential source of PAHs. Much lower levels (<LOD) were observed for 'laboratory analyses' at the oil refinery and a cleaning task that took place within the marine engine building plant.

Table 3 Average hand exposures in the oil refinery and the marine engine building and repair sites ($\mu\text{g}/\text{cm}^2$) by tasks

Tasks	N _s	<LOD (%)	AM	GM	GSD	Median	90th %tile	Range
Oil Refinery								
Cleaning heat exchangers	10	30	0.4	0.2	2.8	0.2	1.1	(0.1, 1.3)
Laboratory analyses	2	100	0.1	0.1	1.0	0.1	0.1	(0.1, 0.1)
Sampling	3	33	0.3	0.2	2.8	0.2	0.5	(0.1, 0.5)
All Oil Refinery	15	40	0.3	0.2	2.7	0.2	0.9	(0.1, 1.3)
Marine Engine Building								
Cleaning	1	100	0.1			0.1		
Cleaning: workarea/machines	1	0	2.8			2.8		
Filter changing	2	50	8.7	1.0	52.3	8.7	17.4	(0.1, 17.4)
Maintenance: cleaning nozzles	1	0	9.5			9.5		
Maintenance: dismantling pumps	1	0	4.9			4.9		
Preparing for uncoupling	1	0	5.7			5.7		
Sampling	1	0	5.0			5.0		
All Marine Engine Building	8	25	5.7	2.0	8.8	5.0	17.4	(0.1, 17.4)

N_s: 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.

Table 4 shows the results of average forearm exposures by tasks. Once again, exposure levels at the marine engine building site ($\text{GM} = 1.4 \mu\text{g}/\text{cm}^2$) were greater than those at the oil refinery site ($\text{GM} = 0.7 \mu\text{g}/\text{cm}^2$). However, the majority of forearm exposures were less than the LOD in both facilities with only one out of three tasks in the oil refinery and three out of seven tasks in the engine building site being greater than the LOD.

Table 4 Average forearm exposures in the oil refinery and the marine engine building and repair sites ($\mu\text{g}/\text{cm}^2$) by tasks

Tasks	N _s	<LOD (%)	AM	GM	GSD	Median	90th %tile	Range
Oil Refinery								
Cleaning heat exchangers	10	70	0.8	0.7	1.5	0.6	1.7	(0.6, 1.7)
Laboratory analyses	2	100	0.6	0.6	1.0	0.6	0.6	(0.6, 0.6)
Sampling	3	100	0.6	0.6	1.0	0.6	0.6	(0.6, 0.6)
ALL Oil Refinery	15	80	0.7	0.7	1.4	0.6	1.2	(0.6, 1.7)
Ship and Power Plant Engine Building								
Cleaning	1	100	0.6			0.6		
Cleaning: workarea/machines	1	0	6.6			6.6		
Filter changing	2	0	17.0	4.6	16.4	17.0	33.3	(0.6, 33.3)
Maintenance: cleaning nozzles	1	0	0.9			0.9		
Maintenance: dismantling pumps	1	100	0.6			0.6		
Preparing for uncoupling	1	100	0.6			0.6		
Sampling	1	100	0.6			0.6		
ALL Marine Engine Building	8	50	5.5	1.4	4.7	0.6	33.3	(0.6, 33.3)

N_s: 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.

Table 5 shows the summary results for the semi-quantitative exposure measurements using the DREAM methodology alongside the corresponding measured results. (The individual DREAM data are listed in Appendix 1). The semi-quantitative estimates were expressed as arbitrary Dream Units (DU) per cm^2 of skin surface. The geometric means of the potential exposure (i.e. exposure ignoring any protective effects from clothing and gloves) for hand and forearm exposures in both facilities were higher than actual exposure estimates (i.e. actual exposure on the skin taking into account the effect of gloves and clothing).

Table 5 Measured, potential and actual hand exposure by facility

Facility Type	N	Hand exposure GM (GSD)			Forearm exposure GM (GSD)		
		Actual (DU/cm ²)	Potential (DU/cm ²)	Measured (µg/cm ²)	Actual (DU/cm ²)	Potential (DU/cm ²)	Measured (µg/cm ²)
Oil Refinery	15	1.1 (28.3)	38 (20.9)	0.2 (2.7)	9 (22.7)	16 (28.8)	0.7 (1.4)
Engine Building & Repair	8	0.0 (61.8)	1.1 (25)	1.6 (7.5)	0.0 (109)	0.1 (17.7)	0.9 (2.4)

Figure 1 shows a scatter plot for the average hand exposure measurements versus the DREAM estimates for actual hand exposure plotted on a log scale. There was no statistically significant correlation between these measures (Pearson's correlation, $r = -0.13$; $p < 0.5$)

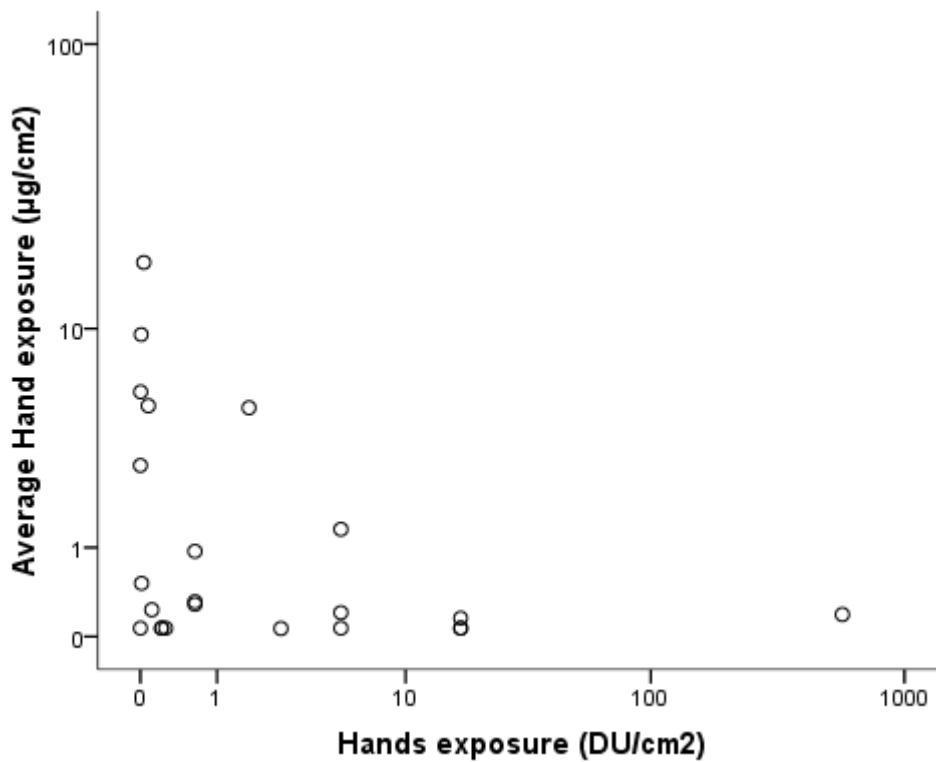


Figure 1 Scatter plot of measured HFO exposure against DREAM estimates for hand exposure (both on a log-scale)

5 DISCUSSION AND CONCLUSIONS

The aim of this follow-up study on the main HFO project was to collect additional exposure data to extend the evidence base of dermal exposure levels to HFO. Measurements were obtained from an oil refinery and a marine engine building facility in Finland. The results showed that the levels observed at the marine engine building facility tended to be much higher than those at the refinery site. Comparison of the quantitative dermal measurements from this study with the initial results reported by Christopher *et al.*, (2007), indicates that while the dermal exposure levels observed for the oil refinery fall within the overall exposure ranges of the initial study, the dermal hand exposure levels observed in the engine building facility were higher than found in other facilities. In the initial study, hand exposure levels were generally below $5 \mu\text{g}/\text{cm}^2$, while for the forearms the levels were generally below $15 \mu\text{g}/\text{cm}^2$. However, in the engine building facility, the hand and forearm exposure concentrations were below $9.5 \mu\text{g}/\text{cm}^2$ and $6.6 \mu\text{g}/\text{cm}^2$, respectively. Further, in the initial study most of the hand and forearm exposures were below the LOD with the proportion less than LOD ranging from 31 – 100% for hand exposure and 75 – 100% for forearm exposure. In the marine engine building plant only 25% of the hand exposure samples were less than LOD while 50% of the forearm samples were less than LOD. It should, however, be noted that while most of the tasks monitored in the marine engine building plant resulted in detectable levels of HFO exposure, these exposure levels still tended to be low with a maximum hand exposure concentration of $17.4 \mu\text{g}/\text{cm}^2$ being obtained for the task ‘filter changing’ and the maximum forearm exposure observed at $33.3 \mu\text{g}/\text{cm}^2$.

During the monitoring survey it was observed that some workers appeared to have high levels of HFO exposure based on visual inspection of their hands and in these cases a second set of wipe samples were collected. This occurred on two occasions at the marine engine building site where double samples were collected during cleaning (heat exchangers) and maintenance (filter changing). For the double samples collected during cleaning (heat exchangers), all samples (first and second sets) collected from the left hand and the left forearm were below the LOD. For the right hand, the first set of wipe samples for this task were $1.8 \mu\text{g}/\text{cm}^2$ and $2.9 \mu\text{g}/\text{cm}^2$, for the right hand and forearm, respectively, while the exposure levels on the second set of samples were $0.6 \mu\text{g}/\text{cm}^2$ and $2.4 \mu\text{g}/\text{cm}^2$, respectively. Taking these results into account would have increased the combined hand exposures from $0.9 \mu\text{g}/\text{cm}^2$ to $1.3 \mu\text{g}/\text{cm}^2$ and the combined forearm exposure from $1.3 \mu\text{g}/\text{cm}^2$ to $3.2 \mu\text{g}/\text{cm}^2$, respectively. For the double samples collected during maintenance (filter changing) the amount of HFO found on the second set of samples on the right hand ($32.6 \mu\text{g}/\text{cm}^2$) and right forearm ($65.4 \mu\text{g}/\text{cm}^2$) were much higher than that of the first set of samples where the concentrations were $6.4 \mu\text{g}/\text{cm}^2$ and $2.7 \mu\text{g}/\text{cm}^2$, respectively. This is counter-intuitive and after ascertaining that the analytical results were correct, it was assumed that there may have been a swap over of sample sets 1 and 2 at the sample collection stage or at the laboratory analysis stage. It was decided to take a cautionary approach so we have reported the results from the second set of wipe samples in Tables 2, 3 and 4 in the Results section.

The results of these double samples suggest that while the recovery efficiency of the method based on spiking pig skin was very good (>84%) (Christopher *et al.*, 2007), this could in some situation be further improved by conducting a second set of wipe sampling, especially in cases where there is a high level of visible contamination on the skin. The relationship between visible appearance of skin contamination with heavy fuel oils or other PAH-containing substances and the biological marker of exposure to PAH, 1-hydroxypyrene (1OHP) has been investigated by Nilsson *et al* (2003). They found that there was a clear association between 1OHP and exposure group where exposure groups were categorised based on self-reported visible contamination on the skin. Engine room personnel on ships who reported oil

contamination on the skin 24 hours prior to collecting the urinary sample had a higher mean concentration of 1OHP in their urine than unexposed controls and engine room personnel with no visible contamination on the skin. Therefore, we recommend that for employees with a high visible skin contamination, at least 2 samples sets will be collected for each anatomical location.

Complementary dermal exposure observations based on the methodology of van Wendel de Joode *et al.* (2003) were also collected during these measurement surveys. There was no statistically significant correlation between the exposure data based on DREAM estimates with measured data. This may be due to the small sample size and limited range of exposure levels. It is also possible that the DREAM methodology does not sufficiently account for substances with the particular properties of HFO. Consequently, it is advisable that 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 rather than rely on the DREAM model.

We believe that the results of this exposure assessment together with the results from the initial survey conducted by Christopher *et al.* (2007) provide a reliable picture of the levels of exposure to HFO in the workplace. The aim of this study, to investigate exposure to HFO in life cycle stages missed in the first monitoring survey, has been achieved, for the most part, by conducting a more thorough investigation in an oil refinery and an engine building and repair site. These have captured some of the higher exposure level scenarios such as cleaning and maintenance tasks including a major clean-up operation in the oil refinery where workers were cleaning heat exchangers. While most of the relevant regular occupational scenarios have been covered in these surveys, there are some tasks for which it was not possible to collect data. These include exposure during cleaning of HFO tanks and major oil spills as seen in the recent MSC Napoli incident in 2007¹ (BBC 2007). Such scenarios rarely occur and it is difficult to capture personal exposure data at these times. With the exception of these rare scenarios, the exposure assessment presented here, together with the initial survey conducted by Christopher *et al.* (2007) provide a comprehensive view of occupational exposure to HFO.

¹ BBC News 21 January 2007. Stricken cargo ship run aground.
<http://news.bbc.co.uk/1/hi/england/devon/6283455.stm>

6 ACKNOWLEDGEMENTS

We thank the companies that participated in the study and the employees who participated in the measurement surveys. The study was funded by CONCAWE.

7 REFERENCES

Christopher Y, van Tongeren M, Cowie H, Cherrie JW (2007) Occupational dermal exposure to heavy fuel oils. Research Report TM/07/05. Institute of Occupational Medicine.

Nilsson R, Nordlinder R, Moen BE, Øvrebø S, Bleie K, Skorve AH, Hollund BE, Tagesson C. (2004). Increased urinary excretion of 8-hydroxyguanoisine in engine room personnel exposed to polycyclic aromatic hydrocarbons. *Occup Environ Med*; 61: 692-696

van Wendel de Joode B, Brouwer DH, Vermeulen R, Van Hemmen JJ, Heederik D, Kromhout H. (2003). DREAM: a method for semi-quantitative dermal exposure assessment. *Annals of Occupational Hygiene*; 47: 71-87.

APPENDIX 1 - DERMAL HAND AND FOREARM EXPOSURE AND SEMI-QUANTITATIVE ESTIMATES OF (ACTUAL) HAND EXPOSURE

Worker Code	Type of Facility	Task	Task Group	Left hand*	Right hand	Hand ($\mu\text{g}/\text{cm}^2$)	Left forearm	Right forearm	Forearm ($\mu\text{g}/\text{cm}^2$)	Actual *(DU/cm ²)
914-01	Oil Refinery	sampling	sampling	0.1	1.0	0.5	0.6	0.6	0.6	0.01
914-04	Oil Refinery	sampling	sampling	0.1	0.3	0.2	0.6	0.6	0.6	0.1
914-10	Oil Refinery	sampling	sampling	0.1	0.1	0.1	0.6	0.6	0.6	0.001
914-12	Oil Refinery	laboratory analyses	sampling	0.1	0.1	0.1	0.6	0.6	0.6	0.2
914-13	Oil Refinery	laboratory analyses	sampling	0.1	0.1	0.1	0.6	0.6	0.6	0.2
914-02	Oil Refinery	cleaning heat exchangers	cleaning	0.1	0.1	0.1	0.6	0.6	0.6	17.1
914-08	Oil Refinery	cleaning heat exchangers	cleaning	0.1	0.1	0.1	0.6	0.6	0.6	5.1
914-03	Oil Refinery	cleaning heat exchangers	cleaning	0.3	0.0	0.2	0.6	0.6	0.6	17.1
914-09	Oil Refinery	cleaning heat exchangers	cleaning	0.1	0.1	0.1	0.6	0.6	0.6	17.1
914-05	Oil Refinery	cleaning heat exchangers	cleaning	1.5	1.1	1.3	0.6	0.6	0.6	501
914-06	Oil Refinery	cleaning heat exchangers	cleaning	0.1	0.3	0.2	0.6	1.8	1.2	501
914-07	Oil Refinery	cleaning heat exchangers	cleaning	0.1	0.2	0.2	0.6	1.9	1.2	570
914-11	Oil Refinery	cleaning heat exchangers	cleaning	0.3	0.3	0.3	0.6	0.6	0.6	0.6
914-14	Oil Refinery	cleaning heat exchangers	cleaning	0.1	1.8	0.9	0.6	2.9	1.7	0.6
914-16	Oil Refinery	cleaning heat exchangers	cleaning	0.5	0.1	0.3	0.6	0.6	0.6	0.6
914-17	Engine Building & Repair	maintenance:cleaning nozzles	cleaning	18.2	0.9	9.5	1.2	0.6	0.9	0.01

Worker Code	Type of Facility	Task	Task Group	Left hand [*]	Right hand	Hand ($\mu\text{g}/\text{cm}^2$)	Left forearm	Right forearm	Forearm ($\mu\text{g}/\text{cm}^2$)	Actual *(DU/cm ²)
914-18	Engine Building & Repair	Filter changing	cleaning	0.1	0.1	0.1	0.6	<i>0.7</i>	<i>0.6</i>	2.6
914-22	Engine Building & Repair	Filter changing	cleaning	<i>2.2</i>	<i>32.6</i>	<i>17.4</i>	<i>1.2</i>	<i>65.4</i>	<i>33.3</i>	0.03
914-19	Engine Building & Repair	cleaning	cleaning	0.1	0.1	0.1	0.6	0.6	0.6	0.3
914-20	Engine Building & Repair	sampling	sampling	<i>6.5</i>	<i>3.5</i>	<i>5.0</i>	0.6	0.6	0.6	0.1
914-21	Engine Building & Repair	cleaning:workarea/ machinery	cleaning	<i>2.0</i>	<i>3.6</i>	<i>2.8</i>	6.6	<i>6.6</i>	<i>6.6</i>	0
914-24	Engine Building & Repair	maintenance: dismantling pump	maintenance	<i>6.2</i>	<i>3.7</i>	<i>4.9</i>	0.6	0.6	0.6	1.7
914-25	Engine Building & Repair	preparing for uncoupling	maintenance	0.1	<i>11.4</i>	<i>5.7</i>	0.6	0.6	0.6	0.002

^vValues in *bold italics* are >LOD;

Left hand: Concentration on the left hand ($\mu\text{g}/\text{cm}^2$)

Right hand: Concentration on the right hand ($\mu\text{g}/\text{cm}^2$)

Left forearm: Concentration on the left forearm ($\mu\text{g}/\text{cm}^2$)

Right forearm: Concentration on the right forearm ($\mu\text{g}/\text{cm}^2$)

Hand: Average hand exposure

Forearm: Average forearm exposure

*Actual (DU/cm²): Semi-quantitative estimate of exposure using DREAM method expressed in arbitrary DREAM units per cm²

worker 914-06 \equiv worker 914-07, worker 914-02 \equiv worker 914-08,

worker 914-03 \equiv worker 914-09, worker 914-20 \equiv worker 914-21

HEAD OFFICE:

Research Avenue North,
Riccarton,
Edinburgh, EH14 4AP,
United Kingdom
Telephone: +44 (0)870 850 5131
Facsimile: +44 (0)870 850 5132

Tapton Park Innovation Centre,
Brimington Road, Tapton,
Chesterfield, Derbyshire, S41 0TZ,
United Kingdom
Telephone: +44 (0)1246 557866
Facsimile: +44 (0)1246 551212

Research House Business Centre,
Fraser Road,
Perivale, Middlesex, UB6 7AQ,
United Kingdom
Telephone: +44 (0)208 537 3491/2
Facsimile: +44 (0)208 537 3493

Brookside Business Park,
Cold Meece,
Stone, Staffs, ST15 0RZ,
United Kingdom
Telephone: +44 (0)1785 764810
Facsimile: +44 (0)1785 764811

Email: iom@iom-world.org