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Validation and Comparison of Two Sampling Methods to Assess Dermal Exposure to Drilling Fluids and Crude Oil

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ABSTRACT

Dermal exposure to drilling fluids and crude oil is an exposure route of concern. However, there have been no published studies describing sampling methods or reporting dermal exposure measurements. We describe a study that aimed to evaluate a wipe sampling method to assess dermal exposure to an oil-based drilling fluid and crude oil, as well as to investigate the feasibility of using an interception cotton glove sampler for exposure on the hands/wrists. A direct comparison of the wipe and interception methods was also completed using pigs' trotters as a surrogate for human skin and a direct surface contact exposure scenario. Overall, acceptable recovery and sampling efficiencies were reported for both methods, and both methods had satisfactory storage stability at 1 and 7 days, although there appeared to be some loss over 14 days. The methods' comparison study revealed significantly higher removal of both fluids from the metal surface with the glove samples compared with the wipe samples (on average 2.5 times higher). Both evaluated sampling methods were found to be suitable for assessing dermal exposure to oil-based drilling fluids and crude oil; however, the comparison study clearly illustrates that glove samplers may overestimate the amount of fluid transferred to the skin. Further comparison of the two dermal sampling methods using additional exposure situations such as immersion or deposition, as well as a field evaluation, is warranted to confirm their appropriateness and suitability in the working environment.

KEYWORDS: contact scenario; crude oil; dermal exposure; drilling fluids; offshore; sampling methods

INTRODUCTION

Drilling fluids are a complex mixture of solids and liquids, based on either oil or water, and are extensively used in the upstream oil industry (IPIECA/GPA, 2009; Searl and Galea, 2011). They have many roles during the drilling process including removing cuttings, cooling and lubricating the drill bit, and carrying various chemicals down the borehole. Workers can be exposed to drilling fluids and crude oil by various routes of exposure including skin contact. Searl and Galea (2011) reported that the main health effects that may arise from dermal exposure to drilling fluids included irritation of the skin, with long-term exposure potentially leading to dermatitis.

Searl and Galea (2011) also reported that a range of other serious health effects including allergic dermatitis are possible depending on the composition of the fluid and exposure levels. Crude oil may cause adverse dermal effects, including dryness, irritation, and hyperkeratosis (ATSDR, 1999). Dermal exposure to both drilling fluids and crude oil is therefore an exposure route of concern to workers. There have been no published studies describing sampling methods or reporting measurements for dermal exposure to drilling fluids and crude oil. The collection of samples to quantify dermal exposure in this sector would aid in the identification of exposure scenarios where dermal exposure to drilling fluids and crude oil is of particular concern, as well as assist in the evaluation of any risk management measures introduced to reduce exposure.

Dermal exposure is defined as the amount of a chemical in contact with the outer layer of the skin that is available for dermal uptake and/or for producing an effect in the skin (Rajan-Sithamparanadarajah *et al.*, 2004). Dermal exposure normally occurs by one of three pathways: (i) immersion or direct contact with the source material; (ii) deposition of aerosol to the skin or uptake of vapour through the skin; and (iii) surface contact with contaminated surfaces resulting in some residue transfer (Fenske, 1993). Different dermal exposure methods are available that measure different parameters and will therefore measure different aspects of exposure. Sampling methods generally fall into three categories:

1. Interception methods that involve placing a chemical collection medium on the skin, for example, whole body garments, cotton gloves, or patch samplers. This method quantifies what is deposited on the skin during a specific period of time.
2. Removal techniques that include skin washing, wiping, and skin stripping. These sample the mass of material retained on the skin at a particular point in time.
3. Fluorescent tracers where the amount of a contaminant deposited on the skin and the area of the skin/clothing at a particular time is measured (fluorescent tracer added to the chemical).

Various guidance documents discussing dermal exposure sampling methods are available (US EPA, 1986; OECD, 1997). The International Organization for Standardization (ISO) published a general guidance document in 2011 on the possible principles available to assess dermal exposure (ISO, 2011). This describes the advantages and limitations of the different dermal exposure methods; however, it is not intended to provide expert guidance such as in the case of method selection with respect to particular chemical agents.

This article describes a small study to evaluate a wipe sampling method trialled in earlier private contract by the project team (Sánchez Jiménez *et al.*, 2011) as well as to investigate the feasibility of using a cotton glove sampler interception method for the hands/wrists to assess dermal exposure to oil-based drilling fluids and crude oil.

The specific objectives of this laboratory-based exercise were to assess the sample stability, recovery efficiency of the two sampling methods, and the sampling efficiency of the wipe sampling method. Different methods may measure different aspects of dermal exposure for the same scenario, and there is currently no way to convert one measurement method to the other. A direct comparison of the wipe and interception methods was carried out as a small focused laboratory-based study using a surface contact exposure scenario with pigs' trotters as a surrogate for human skin.

Previous validations had identified that Hypaclean Clinical wipes (13 × 13 cm), moist in 70% mass percentage of isopropyl alcohol, were a suitable material to wipe heavy fuel oil contamination from the hands of workers (Christopher *et al.*, 2007) and, as a result, these were identified as being a reasonable standard material for the wipe sampling method in this study. Cotton forchette gloves were selected as the glove samplers. An oil-based drilling fluid and a crude oil (API Gravity, measure of how heavy or light the petroleum liquid is compared to water, between 30° and 40°) were supplied for use in the tests.

METHODOLOGY

Identification of suitable markers in the oil-based drilling fluid and crude oil

Suitable markers of the drilling fluid and the crude oil were identified to allow for calibration and

quantification of exposure. This preparatory work was carried out using gas chromatography–mass spectrometry (GC/MS) with both the drilling fluid and the crude oil samples.

Recovery efficiency

The recovery efficiency refers to the amount of compound recovered from the sampling medium divided by the total amount of compound deposited on the sampling medium. Spiked samples were prepared by accurately weighing aliquots of the drilling fluid or crude oil onto the sampling medium. Wipes and gloves were spiked (pipetted) at three different levels (overall spiking range for drilling fluid being 14–119 mg and 9–116 mg for crude oil); for each level, three sampling media were spiked. Spiked sampling medium was placed inside capped 30-ml (wipes) or 60-ml (cotton gloves) glass jars. The spikes were left for ~1 h then desorbed.

Storage stability

Spiked samples were prepared by pipetting known amounts of drilling fluid (range 36–89 mg) and crude oil (range 56–68 mg) onto the sampling media subsequently stored in 30-ml (wipes) or 60-ml (cotton gloves) glass jars with solvent suitable cone caps. These were sealed with parafilm. Three different spiking levels were used, and for each level, three of each of the sampling media were spiked. The jars were stored at room temperature for 1, 7, and 14 days prior to analysis. These storage durations were selected to reflect typical time periods between sample collection and analysis and identify whether storage duration impacts on recovery of drilling fluid and crude oil from the two sampling media.

Wipe sampling efficiency

Sampling or removal efficiency refers to how much of the contaminant deposited on the skin is actually sampled (removed) by the wipe. Pig trotters were used as a surrogate for human skin to determine the sampling efficiency. The pigs' trotters were spiked at two levels using the following procedure, with repeats (three tests) being completed on fresh pigs trotters for each loading used. The drilling fluid was placed in a glass vial, with a pasteur pipette being inserted through the septa in the cap and the vial placed in a 25-ml beaker. The initial weight of this was recorded. Crude oil was placed in a glass vial; a capillary tube, open at both ends, was inserted through the septa in the cap; and this initial weight was recorded. The pasteur pipette was used to dispense spots of the drilling fluid onto the trotter, with the capillary tube being used to dispense spots of the crude oil to the trotter. The pipette/capillary tube was then replaced and the vial/beaker reweighed (final weight). The amount spiked onto the trotter was calculated as the difference between the initial and the final weight.

A standardized wiping pattern was employed. This consisted of five horizontal and five vertical wipes across the spiked surface of the trotter, followed by a wipe in the clockwise direction. This procedure was repeated with two different wipes. Each wipe was analysed separately in order to evaluate the relative efficiency of each successive wipe.

There are no published data on potential workplace dermal exposure levels of drilling fluids, so we selected the mass range based on the limit of detection (LOD) of the analytical method, maximum fluid that could be spiked on the trotter without leaking along the trotter and also based on previous work by Sánchez Jiménez et al. (2011). The spike levels for the drilling fluid were in the range of 31–99 mg. For crude oil, the spiked levels were between 13 and 50 mg.

Known weights of the drilling fluid and crude oil were also spiked onto a watch glass to assess potential losses due to evaporation

Wipe and interception methods' comparison study

Due to the potential hazards associated with exposure to drilling fluids and crude oil, it was considered inappropriate to use human volunteers. Pig trotters were again used as a surrogate. A direct surface (galvanized steel) contact scenario was used.

Applying similar methodology as described in Gorman Ng *et al.* (2013), known quantities of drilling fluid and crude oil were loaded onto freshly cleaned surfaces as previously described. The masses applied were similar to those used in the validation exercises (loading range used was 24–132 mg for drilling fluid and 25–122 mg for crude oil, respectively), and all covered an area smaller than the surface of the trotter coming into contact with the metal plate. The metal plate was placed on a set of scales. Pigs' trotters were assigned into pairs with one trotter from each pair being randomly allocated the wipe sampling method,

the second as receiving the interception method. Similar loadings of drilling fluid and crude oil were applied to each trotter in the pair.

In instances when the wipe sampling method was used, the trotter was placed directly onto the metal plate, where the drilling fluid or crude oil had been loaded, with a weight of 5 kg being applied and held for 5 s. The standardized wiping pattern was then used. This procedure was repeated with two different wipes; these were immediately placed in the same glass jar and analysed as one sample. A further wipe was used to sample any drilling fluid left on the metal tray; this wipe was immediately placed in a glass jar and analysed as a separate sample.

In instances when the cotton glove sampler was used, the pig trotter was placed into a cotton glove. The trotter and glove were then placed onto the metal plate, where the drilling fluid or crude oil had been loaded, with a weight of 5 kg being applied for 5 s. The cotton glove was removed from the trotter and immediately placed in a 60-ml glass jar. In addition, a wipe was used to wipe the trotter to determine whether any fluid had passed through cotton sampling glove. This was analysed as a separate sample. A further wipe was used to sample any drilling fluid left on the metal tray, again analysed as a separate sample.

The samples obtained during the method comparison study were immediately prepared for analysis and analysed following collection.

Chromatographic conditions, sample preparation, and analysis

Each wipe was placed into an individual 30-ml glass jar, whereas the cotton gloves were placed into an individual 60-ml glass jar. Dichloromethane (12 ml) was pipetted into the wipe vial and 40 ml for the cotton glove jar, ensuring the wipe/glove was completely submersed. The solution was ultrasonicated for 10 min and allowed to stand for 1 h, before being agitated further with a pasteur pipette. The solution was then filtered into a 2-ml glass vial; glass inserts were used in the vial when filtering was difficult.

A Shimadzu GC/MS QP2010S using electron impact ionization in full scan mode was used for the analysis, fitted with a Restek Rxi-5ms 30 m, 0.25 mm id, 0.25 μm film thickness column. The run time was 29 min for the drilling fluid and 18.2 min for the crude oil samples. The column temperature programme for the samples was as follows: drilling fluid samples: 35°C for 4 min to 200°C at 10°C/min then to 300°C at 20°C/min hold for 3.5 min; crude oil samples: 35°C for 3 min to 300°C at 50°C/min then hold for 9.9 min.

Standard solutions of drilling fluid/crude oil were run, together with spiked samples and the instrument conditions adjusted to optimize results. Quality control included (i) the running of a standard repeat after every 10 samples to monitor any calibration drift during the analysis, (ii) preparation of a control sample by a separate analyst to check the calibration standards had been prepared correctly, and (iii) 1 in 10 samples being reanalysed.

The LOD for the drilling fluid from the wipes was 0.5 mg/sample and from the crude oil was 0.2 mg/sample. For the cotton gloves, the LOD of the drilling fluid was 0.7 mg/sample and 0.6 mg for the crude oil.

Data analysis

The amounts of compound recovered from the wipe and cotton glove sampling media from each of the tests were expressed as percentages. The distributions of percentages recovered were examined using histograms and Q-Q plots. Data appeared to be normally distributed.

Recovery efficiencies and stability efficiencies at different spike levels were compared for the cotton glove and wipe methods using analysis of variance (ANOVA) for the oil-based drilling fluid and crude oil separately. Sampling efficiencies for the wipe sampling method for the two time periods (15 min and 2 h) were compared using a two-sample *t*-test for the drilling fluid and crude oil separately. Finally for the comparison study tests, the cotton glove and wipe sampling methods were compared using a paired *t*-test.

RESULTS

Identification of suitable markers in the oil-based drilling fluid and crude oil

For the drilling fluid, the most significant peak at retention time 16.46 min was tentatively identified by GC/MS as tridecane (mass to charge [m/z] ratios = 57, 71, 85), and the results are presented using this peak. Results for other calibrations are reported in McGonagle *et al.* (2013). It was evident that crude oil is a complex mixture of hydrocarbons and contains a wider range of

hydrocarbons than the drilling fluid, with many of these being more volatile than those found in the drilling fluid. The wide variety of peaks makes choosing one as a marker almost impossible. Some changes were made to the GC/MS temperature programme in order to 'condense' the peak pattern into a more suitable shape for calibrating using the crude oil; 155 and 152 were chosen as suitable m/z (mass to charge) ratios and results reported as such.The calibration curves for both the drilling fluid and crude oil were considered acceptable (correlation coefficient [R^2] > 0.99).

Recovery efficiency

The recovery efficiencies for the drilling fluid and crude oil spiked directly onto the wipes and cotton gloves are reported in Table 1. Recovery efficiencies at different spike loadings were compared for glove and wipe methods using ANOVA for the fluids separately.

The average recovery efficiency for the drilling fluid from the wipes was 102%, whereas the average recovery efficiency from the wipes using crude oil as a calibration standard was 104%. For the cotton sampling gloves, mean recoveries of 110% were obtained when drilling fluid was spiked. The mean recovery for all the spiked loadings when crude oil was spiked directly onto the cotton gloves was 114%.

For the drilling fluid, there are statistically significant differences in recovery efficiencies for spike level and sampling method. There is also significant interaction between spiking level and method, suggesting that there are differences in recovery efficiencies by level and method. However, as only small numbers are involved, caution should be exercised when interpreting the results. From Table 1, it can be seen that recovery efficiencies are lower at the low spiking level for the wipe method, whereas for the glove sampling method, recovery efficiency is slightly lower at the higher level.

For crude oil, there are no significant differences in recovery efficiencies for spike level or sampling method or any significant interaction between level and method.

Storage stability

The storage stability was determined by calculating the recovery weights against the amount of drilling fluid or crude oil spiked onto the wipe.

For the drilling fluid, the average recovery efficiencies for the wipes were 102, 97, and 82% for the 1-day, 1-week, and 2-week stability tests, respectively (Table 2). The average recovery efficiencies for crude oil for the wipes were on average 98, 99, and 83% for the 1-day, 1-week, and 2-week storage stability tests, respectively. There is a statistically significant difference in storage stabilities over time, with stability being highest for the shortest storage time.

Average recoveries of 109% were obtained for 1-day sample storage; 91% for 1-week sample storage, and 89% for the 2-week sample storage tests of the drilling fluid on the cotton gloves, whereas the average recoveries for the storage tests for cotton gloves spiked

Table 1. Recovery efficiency by sampling method and spiking level (three repeats per test)

Method	%	Drilling fluid			Crude oil		
		Low	Medium	High	Low	Medium	High
Wipe	Mean	94	106	108	107	100	106
	SD	1.15	2.00	4.16	1.53	7.51	2.89
Glove	Mean	110	113	108	108	108	125
	SD	3.06	3.51	6.81	2.08	1.15	28.29
P value	Level			0.010			0.272
	Method			0.001			0.111
	Interaction level and method			0.013			0.429

Mean: arithmetic mean; SD: standard deviation.

Table 2. Storage stability by sampling method and time stored (three repeats per test)

Method	%	Drilling fluid			Crude oil		
		2 weeks	1 week	1 day	2 weeks	1 week	1 day
Wipe	Mean	82	97	102	83	99	98
	SD	4.93	2.65	7.37	2.31	2.31	2.65
Glove	Mean	89	91	109	88	108	109
	SD	1.53	2.00	10.15	1.73	1.53	4.51
P value	Method			0.286			<0.001
	Time			<0.001			<0.001
	Interaction method and level			0.100			0.192

Mean: arithmetic mean; SD: standard deviation.

with crude oil were 109, 108, and 99%, for 1 day, 1 week, and 2 weeks, respectively. There are statistically significant differences in storage stabilities over time (with stability being highest for the shortest storage time) and also between methods, with recovery efficiency being significantly higher for glove.

Sampling efficiency

The sampling efficiency for the drilling fluid and crude oil was determined by calculating the recovery weights from the wipes against the amount of fluid/oil spiked onto the trotter. Trotters were spiked with loadings ranging from 19 to 100 mg and left for either a 15-min or a 2-h period between spiking and wiping. Table 3 summarizes the results of the sampling efficiency tests.

The sampling efficiency for crude oil was significantly lower after 2 h than after 15 min (P value = 0.016). There are no significant differences in sampling efficiencies for the drilling fluid. This is likely due to the large standard deviation at 2 h, which itself is due to one value which is considerably lower than the rest; however, there was no justifiable reason for its exclusion so it is retained in the data set.

For the drilling fluid, the recoveries from the second wipe were all ≤2%, with the majority being <1%. For crude oil, the recoveries from the second wipe were all ≤6%, with the majority being 2% or less.

The watch glass tests showed average recoveries of 89% (15-min lag period) and 88% (2-h lag period) for the first wipe for the drilling fluid loadings. The watch glass tests using the crude oil showed average recoveries of 95% (15-min lag period) and 90% (2-h lag period) for the first wipe. Recovery from all second wipes was <1%.

Comparison of the dermal sampling methods using a surface contact scenario

A total of 32 paired pigs trotter tests were completed (16 using the drilling fluid and 16 using the crude oil). One trotter from each pair 'wore' a cotton glove; the second was wiped using the wipe sampling method. The transfer efficiency was determined by calculating the sampled masses against the amount of fluid loaded onto the metal tray. Table 4 summarizes the results of these tests, with the two sampling methods being compared using a paired *t*-test. The full results are presented in the study by McGonagle *et al.* (2013).

Not surprisingly, transfer efficiencies are highly significantly different for the glove and wipe methods for both the drilling fluid and crude oil. On average, recovery with the gloves was ~2.5 times the recovery using the wipe method. In some cases, there was some evidence of seepage of the drilling fluid and crude oil through the cotton glove onto the pig skin although this was generally found to be <1% of the mass loaded onto the steel surface. The high standard deviations observed for the glove methods was due to values that were considerably lower than the rest; however, there was no justifiable reason for their exclusion so they are retained in the dataset.

Table 3. Sampling efficiency of the wipes removing drilling fluid and crude oil from pigs' trotters (six repeats per test)

%	Drilling fluid		Crude oil	
	15 min	**2 h**	**15 min**	**2 h**
Mean	88	72	92	83
SD	6.06	18.88	5.99	4.02
Range	78–95	41–88	86–102	77–89
P value		0.095		0.016

Mean: arithmetic mean; SD: standard deviation.

Table 4. Comparison of the two sampling methods using drilling fluid and crude oil (16 repeats per test)

%	Drilling fluid		Crude oil	
	Glove	**Wipe**	**Glove**	**Wipe**
Mean	96	39	99	40
SD	12.81	4.13	16.90	3.35
Range	58–107	30–44	52–117	31–44
P value		<0.001		<0.001

Mean: arithmetic mean; SD: standard deviation.

The transfer from the plate to the trotter, assessed using the wipe method for both the drilling fluid and crude oil, was generally low (mean transfer for drilling fluid was 39%; mean transfer for crude oil was 40%). A large amount of the fluid was left on the metal tray after the test (mean recovery of drilling fluid from tray wipe results was 38%; mean recovery for crude oil was 35%). However, when both the trotter and tray wipes were added together, the recoveries for this method were generally ~80%, suggesting that there may have been some sample loss. Although previous validations showed that skin absorption of the drilling fluid tested was minimal (Sanchez-Jimenez et al., 2011), these had not used force when sampling.

To determine whether the force used to achieve contact between the trotter and the plate was causing skin absorption and therefore loss of sample, further spikes were prepared. Disposable nitrile gloves were placed on two trotters, and two trotters were also used without gloves. The trotters were pressed onto the loaded metal surfaces as previously described. The wipe sampling method was used to remove the fluid from the disposable gloves on the gloved trotters, the surface of the two trotters used without gloves, and the surface of the two gloved trotters following removal of the gloves. Finally, a wipe of the surface of the tray was collected. The wipes were analysed as previously described. Table 5 presents the results using the drilling fluid and crude oil. The total recoveries for this part of the validation were all within acceptable limits indicating that there does not seem to be any sample loss due to skin absorption; however, it is still not possible to explain where the sample loss arose.

DISCUSSION

There have been no published studies describing sampling methods or reporting measurements of dermal exposure to drilling fluids or crude oil. In this article, we describe a study that aimed to evaluate further the wipe sampling method developed in an earlier private contract by Sánchez Jiménez et al. (2011) as well as to investigate the feasibility of using a cotton glove interception method for the hands/wrists. These methods were chosen for evaluation as it was considered that both could be easily used to assess dermal exposure during offshore operations. There is currently no standard methods to convert one measurement method to be equivalent to another. A direct comparison of the wipe and interception methods was therefore undertaken. The study was completed using an oil-based drilling fluid and a sample of crude oil.

The wipes and cotton gloves selected for the study were found to be appropriate for the analysis. The recovery efficiencies from the wipes and cotton glove samplers using drilling fluid and crude oil were all deemed acceptable (within the IOM in-house criterion of 85–115%). The spiked samples for both the drilling fluid and crude oil show satisfactory storage stability for 1 day and 1 week; however, there appeared to be some loss over 2 weeks stored at room temperature. It is therefore recommended that samples are analysed promptly. It is likely that these longer term storage losses can be minimized through the refrigerated storage of samples; however, this has not been assessed.

In general, the majority of the results for both the 15-min and 2-h sampling efficiency time periods (the

Table 5. Assessment of possible sample losses using wipe method due to skin absorption

Trial	Description	Drilling fluid		Crude oil	
		Recovered (mg)	Recovery (%)	Recovered (mg)	Recovery (%)
1	Skin (2 wipes)	67	60	35	54
	Tray (1 wipe)	58	52	27	42
	Total recovery				96
2	Disposable glove (2 wipes)	42	44	29	48
	Under disposable glove (1 wipe)	<0.5	<1	<0.2	<1
	Tray (1 wipe)	53	55	37	60
	Total recovery				108
3	Skin (2 wipes)	31	44	44	52
	Tray (1 wipe)	31	45	42	50
	Total recovery				102
4	Disposable glove (2 wipes)	32	42	31	41
	Under disposable glove (1 wipe)	<0.5	<1	<0.2	<1
	Tray (1 wipe)	39	52	52	69
	Total recovery				110

time product left on the pigs' trotters before wiping) were within the acceptable criterion. The majority of the drilling fluid and oil were recovered on the first of the two wipes used. There appeared to be a slight decrease in sampling efficiency when the crude oil is left on the skin for 2 h. The watch glass recoveries were also slightly lower over the longer time period, suggesting that the decrease is due to evaporation rather than skin absorption of the crude oil. Tests with the drilling fluid indicated no losses due to evaporation or skin absorption over these times. Kezic *et al.* (2010) reported that studies on the dermal absorption of individual hydrocarbons in petroleum products have shown a reduction in absorption with increasing lipophilicity and molecular weight. This is reflected in the greater reported dermal absorption of aromatics than that of aliphatics, which includes tridecane the marker used in our study.

It is important to consider that this validation study has a number of limitations. The study involves a relatively small number of samples, which should be considered when interpreting the results. The drilling fluid used in our study contained petroleum distillate (30–60%), emulsifier (5–10%), calcium chloride (1–5%), and lime (1–3%). Many different drilling fluids are available for use, which may differ in composition to this. In addition, fluids used offshore may contain additional components that are added as necessary depending on the drilling process. This is likely to result in possible changes in the composition of the drilling fluid during the various circulations through the drill well. Also, the composition of the crude oil will differ depending on many factors, e.g. geological, geographic, etc. It should be considered that dermal samples collected from the working environment may require further sample preparation (i.e. filtering and dilution) prior to analysis. In addition, the sampling efficiency and analytical recovery from wipes contaminated with the studied drilling fluid and crude oil may differ from those estimated from dermal samples collected in the working environment due to the composition of the actual drilling fluids and crude oils being handled as well as any interferences present. Quantification of dermal exposure in the working

environment should be assessed using calibration standards derived from the actual drilling fluid being used or samples of the extracted crude oil.

The wipe and cotton glove interception sampling methods were compared using a surface contact scenario and pigs' trotters as a surrogate for human skin. The transfer efficiencies for the wipe method for both the drilling fluid and crude oil were generally low. A large amount of the fluid was left on the metal tray after sampling; however, when added together the transfers for this method were still slightly low, generally ~80%, suggesting that there had been some sample loss. Further tests indicated that this was not due to skin absorption, but it was not possible to identify how the losses occurred. The transfers for the interception method for both the drilling fluid and crude oil were generally within acceptable limits. In some cases, there was some evidence of seepage of the drilling fluid/crude oil through the cotton glove onto the pig skin although this was minimal.

Much higher transfers of both fluids were measured on the glove samples than on wipe samples, on average 2.5 times higher. Fenske *et al.* (1999) reported mean exposure rates of 6.48 mg/h for a glove sampling method and 0.28 mg/h for a wipe sampling method used to determine hand exposure to a pesticide during apple thinning (23 times difference). Gorman Ng *et al.* (2013) report that during an experiment studying deposition of 87% glycerol, the dermal exposure estimate from the glove sample was 42 times higher than the wipe estimate (3.81 μg/cm^2 versus 0.09 μg/cm^2). In our experiment, it was evident that the cotton glove sampler 'captured' most of the drilling fluid and crude oil loaded onto the metal surface, whereas the skin was less efficient at capturing the surface contamination. The methods were compared using only one exposure situation, and it is likely that the performance of the samplers may differ depending on the exposure situation being assessed. For example, Gorman Ng *et al.* (2013) reported glove:wipe ratios ranging from 10.4 to 1.4 for an immersion task, whereas for the deposition task, the ratios ranged from 24.5 to 42.3 times difference. In addition, Gorman Ng *et al.* (2013) reported that the relative performance of the glove and wipe sampling methods may differ depending on the level of exposure being experienced, with the difference between the two approaches appearing to decrease with increasing exposure.

Both the wipe and cotton glove interception sampling methods were found to be suitable for use in assessing dermal exposure to oil-based drilling fluids and crude oil although both have their respective advantages and disadvantages. Wipe, or removal techniques, quantifies the contaminant present on the skin surface at the time of removal and will not quantify any contaminant that has penetrated through the skin or otherwise been removed, e.g. by washing or from contact with clean surfaces, or not retained by the skin. Cotton gloves, an interception sampling technique, will retain and capture the contaminant which lands on the sampler (until saturation is reached) although because of the absorbent nature of the glove, they generally appear to collect and retain more contaminant than skin. When selecting an appropriate dermal sampling method, consideration must be given to several factors including the main exposure pathway and the sampling objective.

Further comparison of the two dermal sampling methods using additional exposure situations such as immersion or deposition (both exposure pathways encountered during drilling operations) and a greater range of exposures typically encountered in the working environment, as well as a field evaluation, is warranted to confirm their appropriateness and suitability to assess dermal exposure to drilling fluids and crude oil in the working environment.

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contribution to the execution of the sampler comparison study and was responsible for the statistical analysis of the data. A.S.J. had significant contribution to the experimental set-up for the sampler validation study. All authors assisted with the drafting and revision of the manuscript and have read and approved the final version. There are no conflicts of interest arising from this work.

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