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**Investigation of Oil Based Drilling Mud Phase 2:
Evaluation of Methods for Measuring Drilling
Mud Mist**

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EXECUTIVE SUMMARY

Objectives

The specific objective of this work was to establish the best method for measuring exposure to drilling mud vapours and mist.

Information on personal exposures to oil based drilling muds generated during this work will also go towards the development of an occupational exposure limit.

Main Findings

Traditional filter sampling for drilling mud aerosol formed from current formulations is inappropriate due to evaporation of volatile oil components.

Exposure to total airborne oil from the drilling muds (mist and vapour) can be measured by sampling using a combined filter and sorbent tube sampler. Analysis of both filter and sorbent can be performed by Fourier Transform Infra-Red (FTIR) spectroscopy. There were however unresolved problems with filter analysis during this work which impacted on the sensitivity and accuracy of the analyses, especially the FTIR analysis. The cause is suspected as being interaction between the perchloroethylene solvent and the PTFE lined bottle caps.

Measurement of vapour as a marker for total exposure was considered. Comparisons with the total airborne oil measurement were mixed, but suggested that although pumped sampling gave inconsistent results when compared with either total airborne oil or diffusive vapour measurements, diffusive sampling of the vapour was representative of total oil.

Personal exposure measurements for vapour suggest that although none of the six samples exceeded the UK industry OEL of 350 mg/m³, exposures in excess of 50 mg/m³ (the Norwegian Labour Inspection Authority 8 h TWA OEL) are not unusual. Limited real time personal exposure data showed relatively small peak exposures (roughly twice the average concentration).

Recommendations

Measurement of the oil vapour present, using diffusive tube sampling and analysis by GC should be used to demonstrate control of exposure to drilling mud mist and vapour.

A small survey of personal exposure to oil vapour should be performed, and the data used to help set a potential exposure standard or guidance value.

Filter sampling should be used for measurement of airborne dust only, using solvent extraction (e.g. cyclohexane) to remove any traces of oil. If filter sampling were to be used as part of the measurement of total airborne oil, then the problems experienced with FTIR analysis, should be investigated, and analysis by gas chromatography (GC) using pentane considered.

1 INTRODUCTION

One of the essential elements of drilling a well for the extraction of oil and gas is the drilling fluid, known as the 'mud' system. The mud is pumped down the drill pipe to flood from the neck of the drill bit. It is then returned to the surface around the outside of the drill pipe. The main functions of drilling mud are: cooling and lubrication; removal of cuttings; and maintaining the well under pressure to control ingress of liquid and gas.

Drilling muds are complex chemical mixtures containing a wide range of additives and are either oil or water based. This report is concerned solely with oil based muds, which are water in oil emulsions. The water used is brine and the oils are refined mineral base oils or synthetic oils. The other major components are clay and barite (barium sulphate), but there are also a large number of minor additives likely to be present. Traditional technology allows aerosols (mist) and vapours to be generated during the use of drilling muds and these have been linked to a number of ill health effects including eye and respiratory tract irritation. Skin contact with the mud and some individual components has been associated with dermatitis.

Because of the potential for occupational exposure, it is necessary to review the existing strategies for assessing exposure to drilling muds. In the past, the favoured methodology for assessing airborne exposure was simple gravimetry after sampling on to preweighed filters, assuming all collected matter to be oil with no contribution from particulate dust. Samples were usually background samples, not personal samples. Many oil mist studies have included sampling for hydrocarbon vapour, but rarely in parallel with the filter samples.

In earlier work in phase one of this study (Simpson et al, 2002), the composition of the mud during use was considered, and it was concluded that methods measuring total particulate or total oil were preferable to those for individual toxic components. It also revealed that the oil component in current formulations contained a significant proportion of semivolatile compounds, meaning that the aerosol would be composed of particles that would readily lose material by evaporation. This behaviour was investigated in follow up work, reproduced here in Appendix A. A filter spiked with drilling mud lost 58% of the sample after two hours aspiration (presumably the oil and water components). In a similar experiment, a filter spiked with just the neat oil lost 96%. Therefore there is a distinct possibility that filter samples of a drilling mud mist may contain very little oil after completion of sampling. The airborne mist particles may lose oil before or after they are trapped on the filter. Consequently traditional filter sampling and gravimetric analysis for oil mist appears to be inappropriate and likely to underestimate exposure. This approach also does not distinguish between oil and other particulate matter present.

Hydrocarbon vapour sampling is also carried out during drilling mud operations to determine 'total hydrocarbon vapours'. This involves sampling onto sorbent tubes and analysing by gas chromatography (GC). The most frequently cited exposure standards for this approach are 350mg/m³ or 60ppm (8-hr TWA) and 250mg/m³ (12-hr TWA), which have been derived by the industry from OES's for synthetic hydrocarbon mixtures such as white spirit. This approach has the disadvantage that pumped sampling is known to collect a portion of the particulate component. However if the vapour concentration is significantly high and can be shown to be representative of mist exposure then it may be possible to use this instead of particulate sampling to demonstrate control.

An alternative to the current methodologies used would be to use a two-stage sampler incorporating a filter with a backup sorbent tube. The inhalable fraction of the aerosol could be sampled, and any oil evaporated from the filter would be trapped on the sorbent tube. The filter

could be analysed by gravimetry to determine total inhalable particulate matter, and then be extracted with the sorbent and analysed to give an estimate of total oil aerosol.

The objective of this phase of the work was to compare methods for measuring operator exposure to oil based drilling muds. Once the best method for estimating exposure to airborne drilling mud has been established then it is intended to develop potential control limits by collecting further exposure data.

2 EXPERIMENTAL

2.1 SAMPLING

To make comparisons between the different methods considered, a number of parallel air samples were taken during visits to three different oil platforms, and included both personal and static background samples. At each sampling point was positioned one sampler for each method to be evaluated: i.e. one two-stage sampler (filter/sorbent tube combination), one pumped sorbent tube and one diffusive tube (with one empty diffusive control tube). Details of the rigs visited and samples taken are listed in Appendix C.

Bulk samples (~100 ml) of the returning mud and of the neat oil component were taken in HFL (Highly Flammable Liquid) tins that were then securely capped and double bagged for transportation and storage to prevent cross-contamination with the air samples. Material Safety Data Sheets were also obtained.

Whilst sampling was taking place, notes were taken of work patterns, operating conditions, engineering controls, personal protective equipment (PPE), and the prevailing weather conditions.

2.1.1 Samplers

The Gesamtsstaub-Gas-Probenahme (GGP) sampler, a commercially available sampler comprising of a conical inhalable filter sampler with a built in sorbent cartridge was used to collect the total oil sample. It was loaded with a pre-weighed 37 mm GF/A filter, and 3 g of charcoal sorbent. The samplers were fitted with sampling cones which allowed a flow rate of 1 litre/min, rather than the standard 3.5 litres/min. This was to prevent the sorbent becoming overloaded with too much sample. It also provided more shielding for the filter from splashing.

Standard Perkin Elmer Automated Thermal Desorption (ATD) tubes packed with Tenax TA sorbent were used to collect pumped and diffusive samples. The pumped samples were collected at a flowrate of 5-10 ml/min. The diffusive tubes were fitted with diffusion caps and orientated downwards. Empty ATD tubes were used as controls for diffusive sampling, and were handled identically. These were to estimate the impact of splashing on the diffusive tubes.

Upon completion of sampling, the samplers were inspected for any evidence of splashing likely to invalidate the measurements. The filter samples were placed in cold storage until they could be shipped ashore.

2.1.2 Sampler Positions

The personal samplers and pumps were mounted on a harness. The samplers were positioned high on the harness strap (workers 'lapel' area) and close to the breathing zone (Figure 1). Where possible all four samplers were mounted on the same strap, with the sampler inlets grouped together as closely as possible. At each static sampling point the sampler inlets were also grouped close together, and placed at a height of >1 m off the floor at a location safe from splashing (Figure2).

Sampling during this work was restricted to the shale shaker and mud tank areas. The drill floor was avoided because airborne concentrations are typically lower, and activity here can result in a high degree of splashing, which could contaminate the samplers.

2.1.3 Other Measurements

In addition to the equipment described above, one ToxiRae direct reading photo-ionisation detector (PID) was also used to monitor real-time vapour levels. This small instrument was used both for spot measurements and also as a personal monitor, and was capable of logging data points every 15 seconds. It was calibrated with isobutylene. On visit 3 the PID was supplemented by a Draeger CMS colour stain tube reader for spot measurements.



Figure 1. Arrangement of Samplers During Personal Sampling

Key: 1 = GGP, 2 = Pumped ATD Tube, 3 = Diffusive ATD Tube, 4 = PID

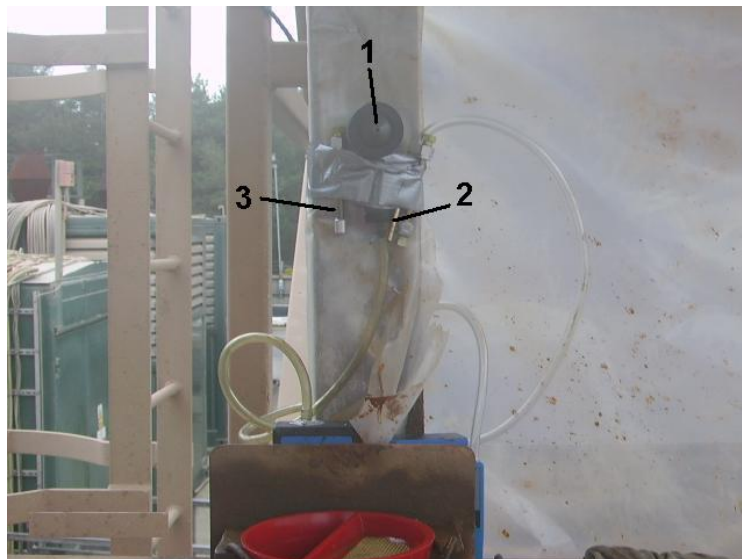


Figure 2. Arrangement of Samplers During Static Sampling

2.2 ANALYSIS

2.2.1 Gravimetric Analysis of Filters

The filter samples were placed in cold storage until they could be shipped ashore. Gravimetric analysis was then performed as soon as possible (no more than four days after collection) so that evaporative losses of oil sample could be minimised.

The filters were allowed 30 minutes equilibration time, and the blank filters were weighed before the sample filters and then reweighed afterwards to determine if there had been any change in weight caused by the short acclimatisation period. Once analysed, the filters were immediately deposited into extraction bottles containing 10 ml perchloroethylene.

2.2.2 Infra Red Spectroscopic Analysis of GGP Sample Extracts

The filters and charcoal cartridges from the GGP sampler were analysed separately by Fourier Transform Infra-Red (FTIR) spectroscopy for hydrocarbons. The charcoal was extracted overnight in 30 ml perchloroethylene (the filters had already been extracted after the gravimetric analysis).

The extracts were analysed using the conditions in Table B1 in Appendix B, measuring the absorbance band area associated with the Carbon – Hydrogen bond stretch at 2926 cm^{-1} . The sample of neat oil used in the mud was used for calibration.

2.2.3 Gas Chromatographic Analysis of GGP Sample Extracts

The perchloroethylene filter and sorbent extracts were also analysed by gas chromatography – flame ionisation detection (GC-FID) using the conditions in Table B2 in Appendix B. This was to identify any compositional differences with the oil from the drilling mud. The calibration standards used in the FTIR analysis were used for the GC-FID analysis. Integration was of the whole chromatographic envelope of hydrocarbon oil peaks to measure concentration.

2.2.4 Gas Chromatographic Analysis of Perkin Elmer ATD Tubes

Both diffusive and pumped ATD tubes were analysed by ATD-GC-FID, calibration was carried out using a single alkane, initially tridecane for the first visit, and then dodecane for the second and third visits. Dodecane was a major component of the vapour, and would be representative of average volatility and detector response. The results obtained using tridecane are equally valid. The analytical conditions can be found in Table B3 in Appendix B. The oil vapour was quantified by integrating the whole chromatographic envelope of hydrocarbon oil peaks together, however a number of volatile organic compounds (VOCs) were also often present, eluting before the oil components, and were integrated separately. The VOC results were calculated using the dodecane calibration, and so should be considered to be semi-quantitative.

The diffusive tube sample concentrations were calculated using an uptake rate of 0.318 ml/min , derived from experimentally determined uptake rates for C11 to C14 n-alkanes (Simpson 2000). The uptake rate was applied to all oil compounds.

3 RESULTS

3.1 QUANTITATIVE RESULTS

Details of the drilling rigs visited and the samples taken can be found in Appendix C. The aerosol results are presented in Table 1, and the vapour results in Table 2. The vapour results are also presented in the form of parts per million volume (calculated as tridecane at 20°C) in Table 3.

All the personal results have been summarised and presented as eight-hour time weighted averages in Table 4, and the real-time monitoring data of personal exposure are presented graphically in Figure 3. The PID results are in the form of the raw data from the instrument (i.e. in terms of ppm isobutylene).

Table 1. GGP Aerosol Sample Results

Sample Type and Number	Sampling Duration (mins)	Gravimetry (particulate) (mg/m ³)	FTIR (hydrocarbon) (mg/m ³)	GC-FID (oil) (mg/m ³)
Personal				
Shale Shaker Op (#1.1)	105	<0.17	<0.28	<1.0
Shale Shaker Op (#1.5)	210	0.21	<0.14	<0.5
Static				
Shale Shaker (#1.2)	155	0.42	<0.19	<0.7
Shale Shaker (#1.4)	600	0.03	<0.05	<0.2
Mud Tank (#1.3)	645	0.03	<0.04	<0.2
Personal				
Derrickman (#2.1)	300	2.15	<0.01	<0.4
Rough Neck (#2.2)	310	0.38	<0.01	<0.4
Static				
Shale Shaker (#2.3)	180 ^P / 600 ^D	No sample	No sample	No sample
Shale Shaker (#2.4)	180 ^P / 600 ^D	No sample	No sample	No sample
Shale Shaker (#2.5)	570 ^D	No sample	No sample	No sample
Shale Shaker (#2.7)	180 ^G / 570 ^D	~0.18	<0.02	<0.6
Personal				
Derrickman (#3.3)	452	0.70	0.15	0.16
Derrickman (#3.4)	420	0.70	0.06	0.16
Static				
Shale Shaker (#3.2)	428	0.65	<0.33	0.27
Shale Shaker (#3.6)	415	2.99	1.81	0.53
Mud Tank (#3.1)	437	3.96	2.12	0.74
Mud Tank (#3.5)	429	<0.07	<0.10	0.10

G – GGP sample, P – Pumped Tenax ATD tube, D – Diffusive Tenax ATD tube.

Table 2. Oil Vapour Sample Results (mg/m³)

Sample Type and Number	GGP (Back up sorbent tube)		Pumped ATD Tube		Diffusive ATD Tube
	FTIR (hydrocarbon)	GC-FID (oil)	ATD-GC-FID (oil)	ATD-GC-FID (VOC)*	ATD-GC-FID (oil)
Personal					
Shale Shaker Op (#1.1)	56	45	43	1	15
Shale Shaker Op (#1.5)	8	12	9	1	3
Static					
Shale Shaker (#1.2)	125	114	112	2	40
Shale Shaker (#1.4)	122	105	85	3	30
Mud Tank (#1.3)	84	70	57	1	31
Personal					
Derrickman (#2.1)	38	23	73	2	47
Rough Neck (#2.2)	7	4	15 [†]	<1	23 [†]
Static					
Shale Shaker (#2.3)	No sample	No sample	Not analysed	Not analysed	1591 [†]
Shale Shaker (#2.4)	No sample	No sample	Not analysed	Not analysed	1673 [†]
Shale Shaker (#2.5)	No sample	No sample	No sample	No sample	67
Shale Shaker (#2.7)	272	166	No sample	No sample	139 [†]
Personal					
Derrickman (#3.3)	75	72	135	14	73
Derrickman (#3.4)	76	73	196	1	77
Static					
Shale Shaker (#3.2)	85	79	364	4	274
Shale Shaker (#3.6)	146	68	890	8	129
Mud Tank (#3.1)	152	131	64	1	103
Mud Tank (#3.5)	89	83	65	2	91
*Estimate based on C12 or C13 calibration.					
[†] Sample includes non-oil peaks.					

Table 3. Oil Vapour Sample Results (ppm*)

Sample Type and Number	GGP (Back up sorbent tube)		Pumped ATD Tube	Diffusive ATD Tube
	FTIR (Hydrocarbon)	GC-FID (Oil)	ATD-GC-FID (Oil)	ATD-GC-FID (Oil)
Personal				
Shale Shaker Op (#1.1)	7	6	6	2
Shale Shaker Op (#1.5)	1.0	1.5	1.2	0.4
Static				
Shale Shaker (#1.2)	16	15	15	5
Shale Shaker (#1.4)	16	14	11	4
Mud Tank (#1.3)	11	9	8	4
Personal				
Derrickman (#2.1)	5	3	10	6
Rough Neck (#2.2)	0.9	0.5	1.9 [†]	3.0 [†]
Static				
Shale Shaker (#2.3)	No sample	No sample	Not analysed	208 [†]
Shale Shaker (#2.4)	No sample	No sample	Not analysed	219 [†]
Shale Shaker (#2.5)	No sample	No sample	No sample	9
Shale Shaker (#2.7)	36	22	No sample	18 [†]
Personal				
Derrickman (#3.3)	10	9	18	10
Derrickman (#3.4)	10	10	26	10
Static				
Shale Shaker (#3.2)	11	10	48	36
Shale Shaker (#3.6)	19	9	116	17
Mud Tank (#3.1)	20	17	8	13
Mud Tank (#3.5)	12	11	9	12
*Calculated as nC13 at 20°C				
†Sample includes non-oil peaks.				

Table 4. Drilling Mud Mist and Vapour Results as Eight Hour Time Weighted Averages

Sample Type and Number	GGP		Pumped ATD tube (oil) (mg/m ³)	Diffusive ATD tube (oil) (mg/m ³)
	Filter (particulate) (mg/m ³)	Sorbent (hydrocarbon) (mg/m ³)		
Visit 1*				
Shale Shaker Op (#1.1)	<0.04	14	11	4
Shale Shaker Op (#1.5)	0.05	2	2	0.8
Visit 2[†]				
Derrickman (#2.1)	3	57	110	71
Rough Neck (#2.2)	0.6	11	23	35
Visit 3[†]				
Derrickman (#3.3)	1	113	203	110
Derrickman (#3.4)	1	114	294	116
* Operatives spend no more than two hours at the shakers.				
† Operatives spend twelve hours in the shale shaker and mud tank areas.				

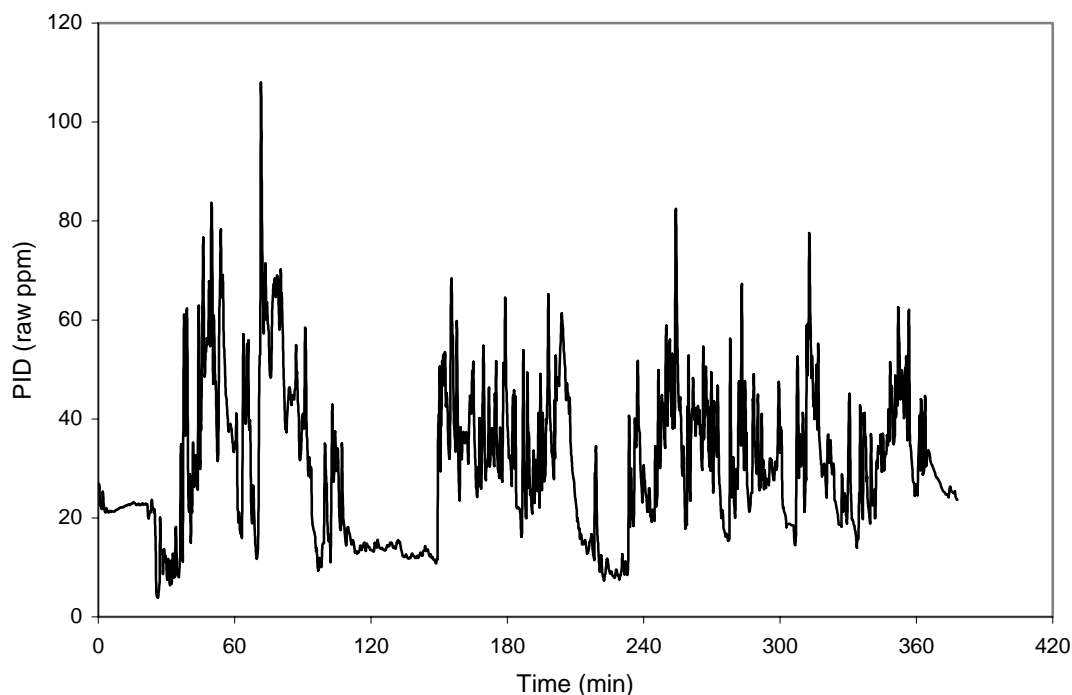


Figure 3 Real-time Personal Monitoring Using ToxiRae Photoionisation Detector

3.2 QUALITATIVE RESULTS

3.2.1 GGP Sampler

Analysis of the filter and charcoal extracts by GC was not ideal. The perchloroethylene solvent has a relatively high boiling point (121°C) and consequently the solvent peak obscured any volatile components present in the samples. Additionally, the perchlorethylene reacted with the PTFE lined septa of the glass vials used, producing a number of artefact peaks in the chromatogram. Nevertheless useful information could be obtained on the sample composition.

Only trace amounts of n-alkanes (C12 to C19) were detected in the filter extracts from visits 1 and 2. The peaks detected were at such a low level that the pattern of peaks characteristic of a paraffinic oil could not be distinguished (Figure 4), and it was uncertain whether they originated from the oil mist. The filter extracts from visit 3 however did have a definite pattern of oil peaks (C12 to C17). The charcoal extracts from the back-up tube contained oil vapour ranging up to C15 for visits 1 and 2, and up to C17 for visit 3 (Figure 5). For comparison, the base oil from visit 1 is presented in Figure 6.

3.2.2 Tenax ATD Tubes

The chromatograms from the thermally desorbed pumped Tenax tube samples were more useful in examining the vapour composition as there was no solvent peak. The oil vapour in all three visits was mainly C10 to C16 alkanes.

Generally the visit 1 and 3 sample chromatograms were relatively consistent with other sample chromatograms from the same visit, containing C10 to C16 and C10 to C17 alkanes respectively. The visit 2 samples were generally between C9 and C16, however sample sets 2.2,

2.3, 2.4 and 2.7 contained an additional ten unidentified peaks that eluted after hexadecane (C16), present on both the diffusive and pumped samples. These were most prominent in samples 2.2 (personal) and 2.7 (static in front of the shale shakers). The contaminant is presumably from some work activity not recorded during the visit. Any potential measurement method however would preferably be capable of accommodating such incidents. (Sample set 2.2 also contained additional unknown volatile components in the diffusive sample, which were considered to be contamination due to their concentration and absence from other samples.)

Low levels of VOCs were found in samples from all three visits. Many of the VOCs identified were found on all three visits: C5-C9 alkanes, C5-C7 naphthenes, benzene, toluene and xylene.

Visit 1 vapour samples also contained 2-butoxyethanol (one use of which is as a solvent for soluble oils), and the visit 3 samples also contained comparatively larger quantities of pentane, xylene and ethyl benzene (especially the diffusive sample from set 3.6).

3.2.3 Bulk Mud Analysis

Headspace analysis of the bulk mud sample revealed predominantly C10 to C14 alkanes. The visit 1 mud contained 2-butoxyethanol, but the visit 3 mud did not contain the larger quantities of pentane, xylene and ethyl benzene. The low level VOCs detected in the vapour samples were also detected in the headspaces at low concentration. The VOCs are likely to have had little impact on the FTIR results.

Although the oil in the visit 3 mud contained C10 to C19 alkanes, the top up oil supplied contained only C12 to C15 alkanes. Presumably this difference is due to the history of the mud and changes in the oil type used. These differences in composition are unlikely to affect the FTIR calibration.

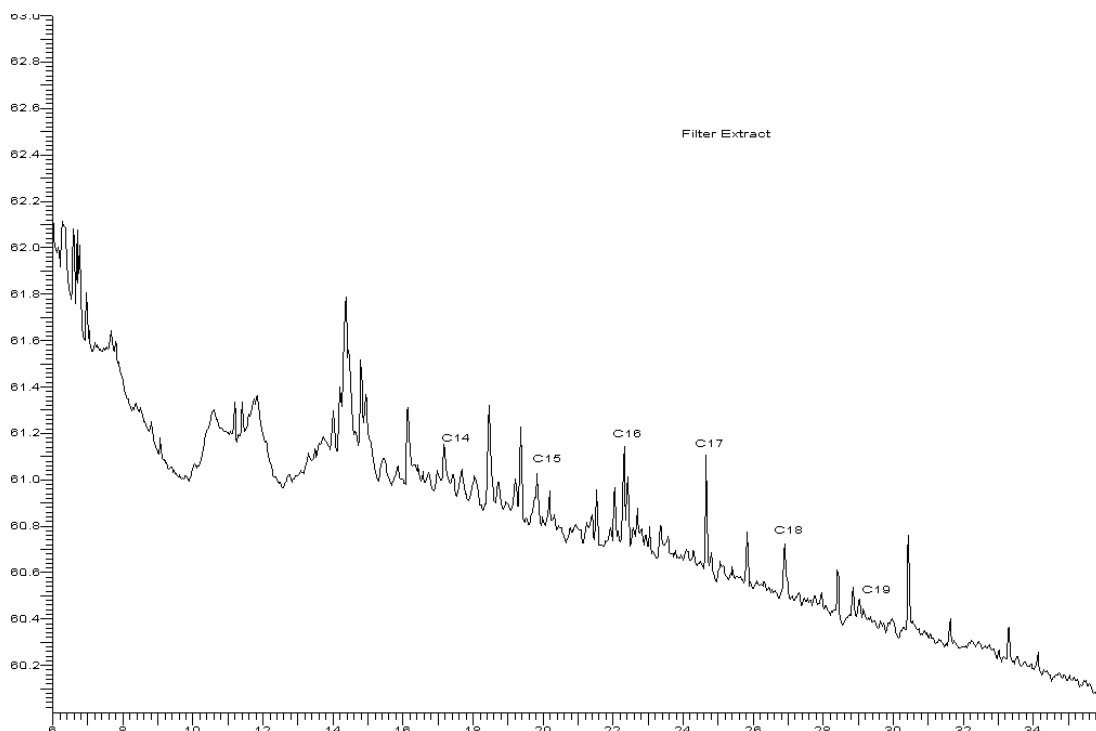


Figure 4. GC Chromatogram of a GGP Sampler Filter Extract (Visit 1)

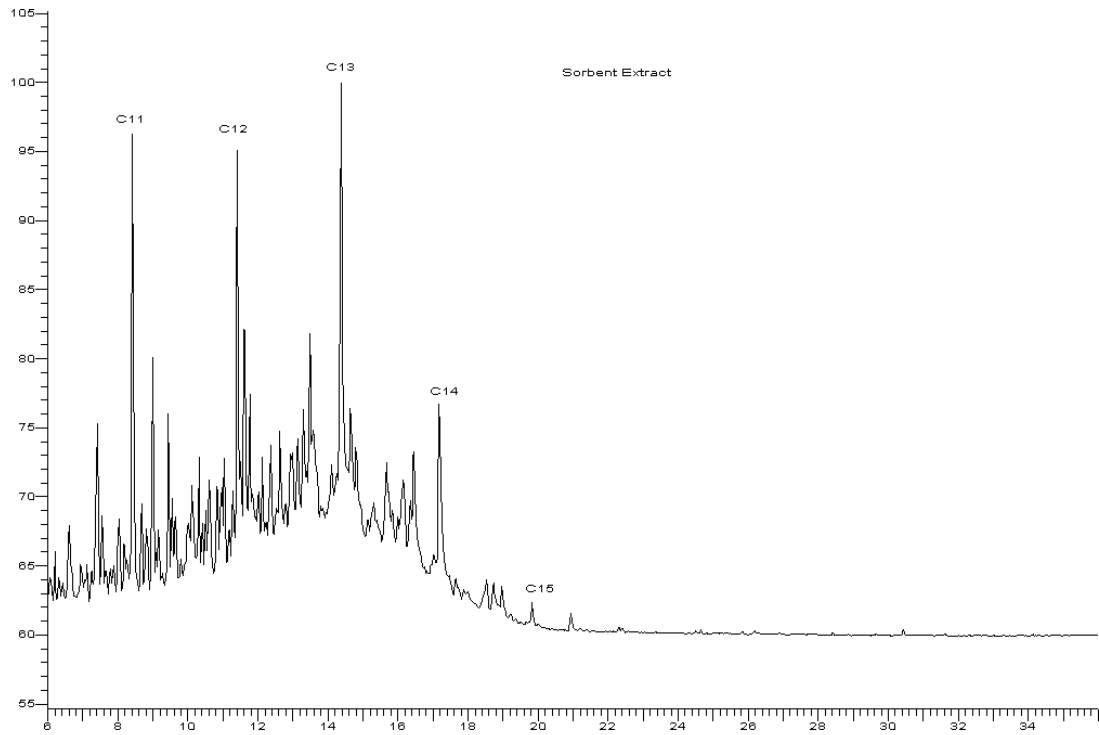


Figure 5. GC Chromatogram of a GGP Sampler Sorbent Tube Extract (Visit 1)

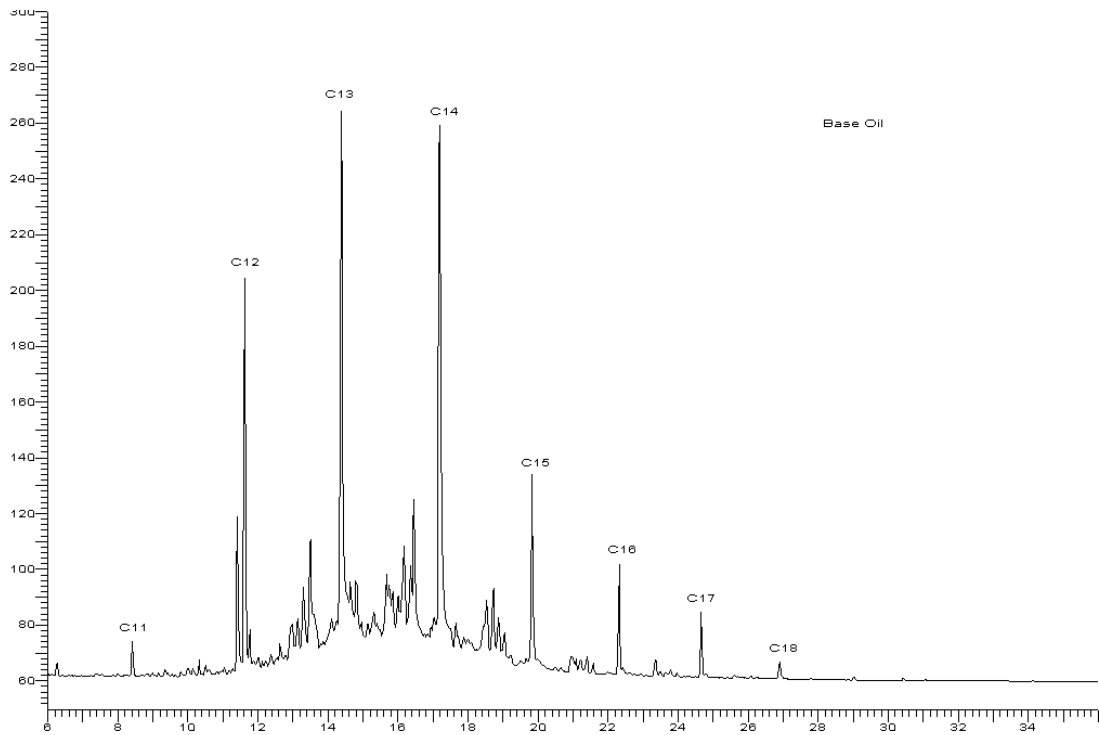


Figure 6. GC Chromatogram of the Drilling Mud Base Oil (Visit 1)

4 DISCUSSION

4.1 COMPARISON OF METHODS

4.1.1 Aerosol Measurements

Sample Loadings

Both the FTIR and GC analyses found very little evidence of the presence of oil in the filter extracts from visits 1 and 2. The FTIR showed no C-H absorption bands, and the limited alkane peaks detected by GC were at the limit of detection. The low levels of particulate material detected gravimetrically therefore were either background dust or the non-volatile remains of mud particles (e.g. clay and barite). Oil vapour was detected alongside the filter samples and some oil aerosol condensate would have certainly been expected during visit 2, as the mud return temperature was reported as 106°C whereas ambient temperature was only 6°C. There were however identifiable and measurable quantities of oil on the visit 3 sample filters. The aerosol results show the presence of non-oil material on the filter samples taken in both the shale shaker and mud tank areas.

Storage

Some oil could have been lost from the filters during storage, the filters were placed in cold storage and solvent desorbed as soon as possible to minimise losses. On visit 1, the filters were extracted after 2 and 5 days, and on visit 2 after 8 days. For comparison, during storage trials on oil mist filter samples from a metalworking fluid (C11 to C22 alkanes), less than 10% of the sample (mean loading 1 mg, n = 6) was lost when filters were stored under refrigeration for seven days (Simpson 2003). If there had been no gravimetric analysis prior to desorption then the storage times could have been reduced.

FTIR Analysis

There were a number of problems encountered during FTIR analysis of the filter extracts. On each of the three visits there was a small amount of solvent lost by evaporation from the bottles, but this was overcome by measuring the volume of solvent gravimetrically. The spectra obtained for both blank and sample filters had poor baselines that would have obscured any smaller oil absorption bands present. Spectral subtraction to clean up the spectra enabled any absorption bands to be identified, but would have decreased measurement accuracy somewhat for samples with low concentrations of oil. This baseline problem has not been observed during similar analyses of filter samples for metalworking fluid mist. The main difference between the drilling mud and metalworking fluid mist analyses was the long storage time. On both occasions storage was in glass bottles with a PTFE lined cap. This problem requires further investigation.

GC Analysis

The GC analysis of the perchlorethylene extracts was included as a qualitative analysis to confirm and characterise the composition of any oil present, and was quantified only to support the FTIR data. The perchloroethylene solvent caused some problems to accurate GC quantification, as it obscured any volatile components present and reacted with the PTFE liner in the bottle cap producing artefact peaks in the chromatogram. The analytical conditions used were better suited to the levels of oil found in the vapour samples than the much lower levels found on the filters.

The FTIR results were higher than the GC results, but due to the problems outlined above, this is not unexpected. If GC was to be used for quantitative rather than qualitative analysis of filter extracts then a different solvent would be needed, and the conditions changed to improve sensitivity. The oil represented 9 and 21% of the aerosol for the personal samples and between <50 and 61% for the static samples. The static samples are likely to have been constantly collecting air containing oil vapour, which would have slowed down any evaporation of aerosol trapped on the filters. The personal samples however, are likely to have had periods sampling air with lower levels of oil vapour, thus producing a higher evaporation rate. The proportion of oil originally sampled by the filters is likely to be higher in both cases, and hence the actual aerosol concentration is also likely to be higher.

Alternative Methods

For comparison, in Norway the industry standard is achieved by sampling mist and vapour together via glass fibre filters in closed face cassettes coupled with 'jumbo' charcoal back up tubes (Steinsvag et al 2006). The filters are analysed as per NIOSH method 5026 (Oil Mist, Mineral). This analysis is by FTIR using carbon tetrachloride as solvent. Sampling is typically at 1.5 litres/min for 2 h. This approach will not sample the inhalable fraction of the aerosol, and is likely to collect smaller masses of oil. Some companies however no longer use FTIR and have changed to GC-FID for analysis using pentane as solvent.

4.1.2 Vapour Measurements

Sample Loadings

Measurable quantities of oil were found on all the vapour samplers on each of the visits. Concentrations ranged from around 1 mg/m³ to over 1500 mg/m³. In fact the concentration determined from two of the diffusive samples (from sets 2.3 and 2.4) suggested that the corresponding pumped samples would overload the ATD-GC-FID instrument and they were omitted from the analysis. The estimated maximum sample loading for pumped Tenax TA tubes was 1 mg of oil. All the samples that were analysed were below 1 mg apart from sample set 3.6 (1.8 mg); three of the peaks went off-scale (n-alkanes C12, C13 and C14), but the majority of the sample remained on-scale throughout the chromatogram.

One of the sets of samplers (3.2) was reported to be wet, however it was uncertain whether this was due to splashing during cleaning of the shaker screens with the spray gun, or due to general impaction of airborne mist droplets. Comparing the concentrations found with those from set 3.6 suggests any contamination present was likely to be relatively low.

The empty control samples were not exposed during visits 1 and 3, but those from visit 2 did not indicate contamination of any of the diffusive tubes by impaction of mist particles.

Temperature and humidity can affect sampling. However the low temperatures encountered on visits 2 and 3 should not have significantly affected the samplers. There were reports of high humidity on visits 2 and 3. Tenax TA sorbent is unaffected by water vapour, but charcoal can reversibly adsorb water. There were reports of condensing water behind the shale shakers on visit 2, but sample sets 2.3 and 2.4 did not include any GGP samplers. There were also reports of water condensation on the roof above the mud tanks during visit 3. At the static sample locations the relative humidities were variable and were typically around 70%, but peaked at around 90%. By comparison with similar experimental data, this means that at times there may have been over 1 g of water on the 3 g of sorbent in the cartridge (Simpson 2000). The capacity of 3 g of charcoal for oil is reported to be 450 mg oil per gram of charcoal i.e. 1350 mg total, (Breuer and Pfeiffer 1989) however the highest loading encountered during visit 3 was only 66 mg.

Storage

Charcoal and Tenax TA both strongly adsorb compounds such as those found here, so there should have been no storage problems associated with the vapour samples.

Volatile Organic Compounds

VOCs were found on both the pumped and diffusive Tenax tubes, and so were likely to be present on the GGP sorbent back up tubes. These are the same range of compounds that were identified in one of the eight drilling mud headspace samples analysed during phase 1 of this work (Simpson et al, 2002). It has been speculated that these VOCs may have originated from pockets of natural gas encountered during drilling, but there is also the possibility that they are breakdown products from the mud.

Analysis by FTIR would not have distinguished the VOCs from the oil, and they would have been undetected by GC analysis of the extracts (due to the solvent peak). The quantities present were estimated from the pumped Tenax tube samples using the oil calibration data. The VOCs in the diffusive samples were not quantified. VOC amounted to very little of the total sample, generally accounting for less than 3%. However two samples comprised of approximately 10% VOC. Both were from personal samples, but from different visits. One of the samples (from set 1.5) was at very low oil concentration; the other however had higher concentrations (set 3.3). There is no record from the visit on why this sample should have such high levels.

Reference Method

Ideally when comparing methods, it is preferable to have an accepted reference method as a standard. In this case, of the three methods considered, the pumped sorbent tube method is probably the most widely used by the industry, but it is known to sample the vapour plus an uncharacterised fraction of the aerosol (Hamlin et al, 1988). Diffusive sampling, to a lesser degree has also been used for sampling oil vapour, and should be relatively unaffected by the presence of aerosol. Little data however could be found on sampler types or of uptake rates used. The GGP sampler collects the inhalable fraction of the mist but has not been used for drilling muds.

The vapour sample from the GGP sampler was analysed by two different methods, and in most cases the GC-FID results supported the FTIR results (Figure 7), despite the problems with the GC analytical conditions. The GC results are marginally lower than the FTIR results in most cases presumably due to underestimation caused by the perchloroethylene solvent peak. The GC results validate the FTIR analytical results, but this does not necessarily mean that the sampling was unbiased. Although the front filter sampler collects the inhalable fraction of the oil mist, it is not completely certain that the high humidity encountered during visit 3 may not have had some effect on the capacity of the charcoal to trap all the oil vapour. When planning this work, charcoal was chosen over the sorbent XAD-2 because some high concentrations were expected. Although XAD-2 is unaffected by water, it has a much lower capacity for oil (120 mg oil per 3 g of sorbent compared to 1350 mg for charcoal). Despite this reservation, the GGP would be the most suitable candidate to adopt as a reference method.

Comparison of Results

When compared graphically (Figures 8, 9 and 10), it is clear that the full data set does not give good correlations between any of the three methods. Some data points are very clearly outliers, but it is very difficult to determine why. Two points at very high concentrations (points 3.2 and 3.6) have been omitted from some of the graphs to maintain clarity of the remaining data.

Figure 7. Comparison of GGP Charcoal Extract Analytical Results

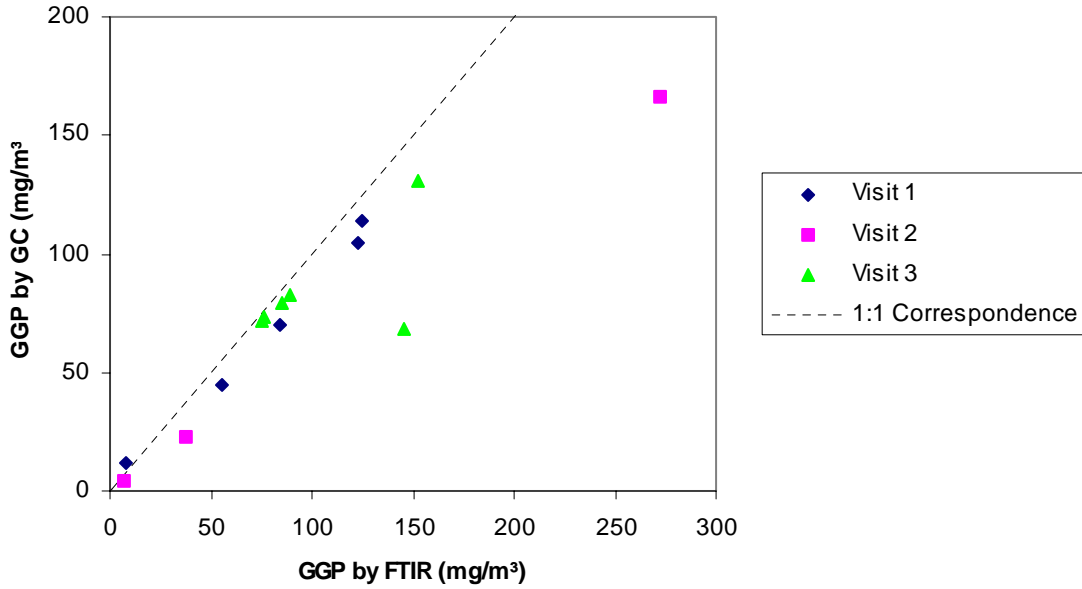
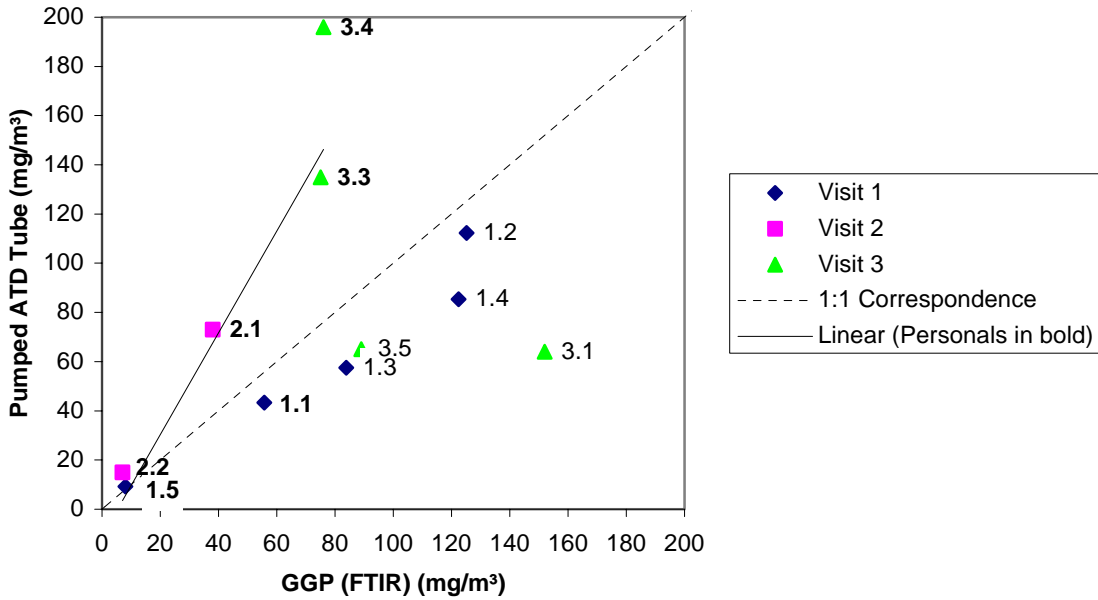


Figure 8. Comparison of Pumped ATD Tube and GGP (FTIR) Results



GGP and Pumped ATD Tube

When comparing the two pumped methods (Figure 8) there is only a very tenuous positive correlation present. When the visit 3 samples are ignored the correlation is improved.

The visit 1 and 2 samples together show a trend whereby the GGP samples give higher results than the pumped ATD tube samples. This is what would be expected based on knowledge of the particle sampling characteristics of the two samplers. The GGP sampler collects the inhalable portion of the mist, whereas the pumped ATD tube would be expected to under-sample the aerosol, especially the larger particles. The mist is likely to have been formed by both condensation of evaporated oil and atomisation (e.g. from the shale shaker). An atomised mist particle is likely to be larger and possibly contain solids. Changes in temperature and ventilation could also affect the ratio of mist to vapour as they are in dynamic equilibrium. Consequently the degree of this bias is likely to be highly variable.

When considered alone, the visit 3 samples do not show any pattern. The two samples with the greatest disagreement of all between results (samples 3.2 and 3.6) both originated from the static samples taken by the shale shakers. Sample set 3.2 has a wide spread of results over all three methods, whereas set 3.6 has one very high sample (the pumped ATD tube) and two other results which are of similar magnitude. The personal samples from visit 3 also gave high pumped ATD tubes results and similar GGP and diffusive sample results. The derrickmen would have received most exposure in the shale shaker area, perhaps explaining why they follow a similar trend to the static samples. This raises some doubt over the pumped ATD tube samples taken in the shale shaker area. There were reports of possible splashing on set 3.2, but nothing noticeably wrong with the other sets. The composition and size characteristics of the mist may have varied between the shale shaker and mud tank areas, but there is no obvious reason why the pumped ATD tubes should have given such high results.

Furthermore, when just the personal samples are considered (from all three visits), five of the six samples fit a linear correlation also indicating higher pumped tube results (samples 1.5, 2.2, 2.1, 3.3 and 3.4 in Figure 8).

The relative positioning of the orifices of the two samplers may have had some effect (Figure 1). The GGP samples are at a higher position than the pumped ATD tube, and also are orientated perpendicularly. The two samplers also appear to have been worn on opposite 'lapels' due to space limitations on at least two of the visits (visits 1 and 3). It can be speculated that when leaning over the shale shakers the lower entrance orifice of the pumped ATD tube may have been in closer proximity to higher concentrations of the mist cloud, but this would seem a less likely explanation of the similar results obtained from static samples 3.2 and 3.6. The diffusive tubes, placed in close proximity, did not show good correspondence with the pumped tubes, but did show some correspondence with the more remote GGP samplers.

The accuracy of an airborne concentration depends upon the accuracy of the calculated sample volume. The very low flowrates used for the pumped ATD tubes may not have been as accurate as those for the GGP samplers, but could not have caused the large differences observed for sets 3.2 and 3.6. Even a 20 % error on a 5 ml/min flowrate measurement would not cause a six-fold difference in concentration.

From the data available, the cause of the unexpectedly higher pumped ATD tube results could not be determined.

Diffusive Tubes

When comparing the diffusive tube results with those from the GGP (Figure 9) it can be seen that seven of the nine data points from visits 2 and 3 show good agreement. All the points from visit 1 however, although showing a linear relationship, have diffusive results somewhat lower than the corresponding GGP result. This is also the case when the diffusive ATD tube samples are compared to the pumped ATD tubes (Figure 10), however this time the other samples from visits 2 and 3 do not fit any apparent pattern. The entrance orifices of both the pumped and diffusive ATD tubes were positioned close together.

Although both pumped methods might be expected to give higher results than the diffusive method because of the bias caused by sampling aerosol particles, the amount of oil sampled as mist is likely to be somewhat smaller than the amount sampled as vapour. If the higher pumped tube results were caused by the presence of a large proportion of mist particles, then from the lines of best fit in Figures 9 and 10, it could be estimated that 60 to 70% of the total airborne oil was in the form of mist. However this seems unlikely given that very little oil was found on the visit 1 filters, the samples covered a wide range of durations (105 to 600 minutes) and locations (personal and static samples from both the shale shaker and mud tank areas), and the fact that there was a linear relationship across all the samples.

Another reason for the difference may have been the instrumental settings chosen during analysis of the visit 1 samples. ATD analysis is a one-shot analysis that requires only a set portion of the sample to be sent to the detector. On this occasion the amount of sample split to the detector was relatively small and consequently many of the smaller isomeric alkane peaks were close to or below the limit of detection, causing underestimation of the vapour concentration.

No evidence was collected on the possible interference from particle impaction on the diffusive samplers. Continued use of control tubes would provide reassurance in following work.

Alternative Methods

The Norwegian industry standard referred to in Section 4.1.1 collects the vapour on a large sorbent back-up tube containing 1 g of charcoal, and analysed as per NIOSH method 1500 (Hydrocarbons, BP 36-216°C). This analysis is by GC-FID using carbon disulphide as solvent and base oil as calibrant. Sample volumes are typically 0.18 m³, so the method should be able to sample atmospheres of over 500 mg/m³. Although FTIR analysis was originally recommended, the industry has preferred GC analysis of the vapour. NIOSH method 1500 could have been used to measure the VOCs identified in the vapour during this work.

NIOSH method 1500 has also been used to measure the vapour alone, excluding the filter cassette from the sampling train. This will inevitably sample some aerosol particles if present.

Figure 9. Comparison of GGP (FTIR) and Diffusive ATD Tube Results

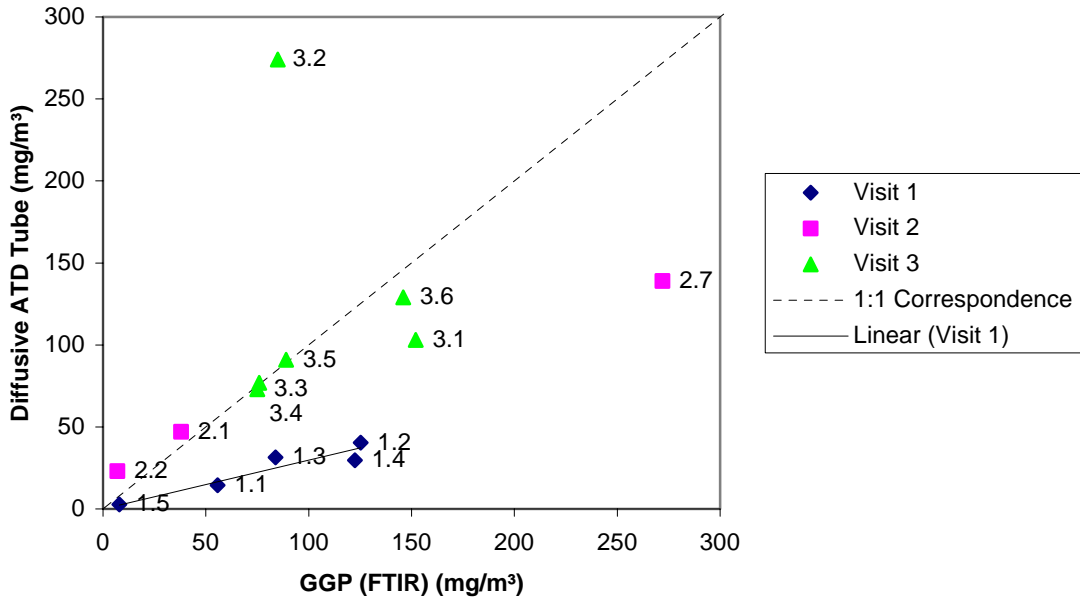
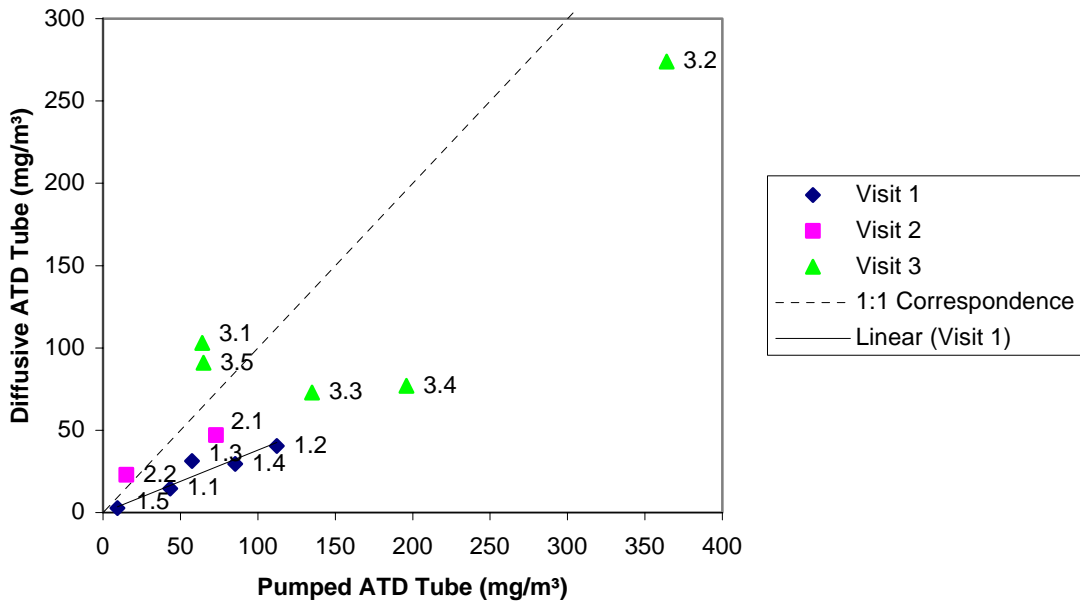


Figure 10. Comparison of Pumped and Diffusive ATD Tube Results



4.1.3 Choice of Method for Exposure Development Survey

There is little point in trying to measure the mist from current mud formulations by traditional filter sampling due to the huge errors caused by evaporation of the sample from the filter. Traditional filter sampling could still be used to measure the non-volatile part of the mist if required (e.g. the solids such as clay and barite). Any residual oil could be washed from the filter with cyclohexane. Measurement of non-volatile mud components would not necessarily be representative of the total aerosol concentration.

Alternative methods for assessing exposure to the mist are either by measuring total airborne oil (mist and vapour) or measuring just the vapour as a substitute measurement to demonstrate control. Because the vapour and aerosol are in equilibrium, the two are inextricably linked. Measuring total oil involves sampling the mist through a filter sampler followed by a sorbent trap. Ideally the filter sampler would be an inhalable sampler incorporated with a sorbent trap (e.g. the GGP sampler), but it is possible to use two independent samplers connected together (Simpson 2003, Steinsvag et al 2006).

Because they incorporate filters, there will be the same problems in sample storage as outlined for traditional filter sampling. Extraction offshore is not ideal because of the need to transport and use potentially dangerous solvents off-shore. Pentane, as used in Norway, is a relatively innocuous solvent compared to the others used (carbon disulphide, carbon tetrachloride and perchloroethylene). Alternatively it may be possible to store the filter with a portion of sorbent, so that any oil losses from the filter are trapped on the sorbent. Baseline problems with FTIR analysis of the filter extracts were encountered during this work which were not fully resolved. The GGP filters and sorbent were both analysed by FTIR during this work, but optional methods such as GC using a different solvent could be used (e.g. carbon disulphide). FTIR is very labour intensive and so more expensive than GC analysis. GC would also give compositional information, identify the presence of other components (e.g. VOCs or other contaminants) and also quantify them separately (i.e. introduce more accuracy).

Pumped sorbent tubes are the most popular samplers used by the industry for measuring vapour, but these are known to sample some of the mist as well. They do not sample the inhalable fraction of the aerosol so they are not equivalent to the GGP sampler. There are no standard sampling orifice dimensions or flowrates so the aerosol sampling characteristics will vary. Diffusive tubes should be relatively unaffected by the mist particles but diffusive badges would be unsuitable due to their vulnerability to splashing.

With current formulations, it is predicted that the mist particles are likely to represent a small fraction of the total amount of airborne oil. Very little oil was found on the filters during this work in comparison to the vapour, but the actual amount of oil mist sampled is unknown. The close correlation between the GGP and diffusive samplers on visits 2 and 3 suggests that the proportion of mist was low. It is therefore impossible to say whether a vapour only measurement accurately represents the exposure to just the mist, but because the two are in equilibrium and vapour concentrations are much higher, a pragmatic vapour only measurement appears to be an adequate substitute to show control. Vapour measurements have probably already been instrumental in monitoring /controlling mist levels. They are already established and allow VOCs to be measured as well. There is also historical data with which to make comparisons (but with some acknowledged bias for pumped method data).

The findings from this work indicate that the results obtained from pumped ATD tubes do not reflect either the GGP total oil results or the diffusive ATD tube sampler vapour results. The reasons for these discrepancies were not identified. The diffusive tubes did give results in line with the GGP sampler for samples from two of the visits.

Diffusive sampling would be the most practical method of sampling. There are no problems with sample pumps and flowrate measurements associated with the other two methods, nor are there any problems with storage or humidity. Diffusive tubes are unobtrusive and so would cause fewer objections to their use by workers. They are also simple to use so they could possibly be used by off-shore staff unsupervised. This would be an advantage when exposure measurements were required at short notice, but there may be some loss in quality in the hygiene context of the report.

One problem identified with the diffusive tube method during this work was the low concentrations determined during visit 1. If this was caused by the ATD instrumental settings (as seems likely), then this could be easily overcome by taking duplicate samples. The problem of using the correct split on the ATD is also equally applicable to the pumped ATD tube samples, but taking a second parallel pumped sample would be difficult. Modern ATD instruments now have a facility to re-catch the unused desorbed sample allowing a second chance for analysis.

4.2 OCCUPATIONAL HYGIENE REPORT

4.2.1 Personal Exposure Measurements

During this work there was disagreement observed between the results from the different methods employed, and only six personal samples were taken at three sites. These limitations mean that conclusions regarding the overall picture of exposure across the offshore drilling industry should not be drawn from this work. Some observations and limited conclusions can be made regarding the visits made.

This section of the report will focus on oil vapour measurements made with pumped ATD tubes, because this has been the most common method used of the three methods considered. The accuracy of the results by this method must be borne in mind when considering the conclusions made within this section of the report.

There are three main areas on a drilling rig where there is the potential for operator exposure to airborne oil based drilling muds: the drill floor, around the shale shakers and in the mud tank area. In general, airborne concentrations of drilling muds are highest around the shale shakers and in the mud tank areas, since the muds are at elevated temperatures in these areas (having just returned from the bore hole), and there is an increased rate of evaporation. Evaporated oil may subsequently condense on cooling into a mist. Agitation of the mud, especially as it passes over the vibrating screens of the shale shaker will also form mists by mechanical action. Airborne concentrations on the drill floor are typically somewhat lower. Activities on the drill floor can result in a high degree of splashing, which can make the taking of air samples difficult since splashes can contaminate the sampler and lead to false positive results. For these reasons sampling during this work was restricted to the shale shaker and mud tank areas.

Although it is not explicitly stated in the visit report, it is assumed that the exposure measurements provided for site 1 are task specific, for shaker house operation. The information supplied for this site indicated that individuals would typically spend 2 hours in the shaker house on a 12 hour shift, on a rota basis, i.e. time segregation is being used as an exposure control. There is no indication in the visit report as to whether exposure control is a significant reason for working in this manner. Two task specific exposure measurements were taken at this site, these yielded results for oil vapour of 43 mg/m³ (105 minute sample) and 9 mg/m³ (210 minute sample). Taking the higher of these results, and assuming 2 hours exposure on a typical shift, would result in an 8 hour TWA exposure of around 11 mg/m³. The ventilation rate in the shaker house at this site was exceptionally high.

Two longer duration personal samples were obtained from site 2 (300 and 310 minutes). The two individuals at this site worked the full 12 hour shift in the shaker and mud pit areas. Hence the measured values (73 mg/m^3 and 15 mg/m^3) can be assumed to represent full shift exposure, and 8 hour TWA may be calculated by multiplying these values by 1.5. This results in 8 hour TWA oil vapour exposures of 110 mg/m^3 and 22.5 mg/m^3 for the two exposed individuals. Information on LEV systems at this site is patchy, although the visit report indicates that some form of LEV was present on both the shale shakers and the mud pits. The mud pits were reported to be 90% covered.

Two personal samples were obtained from site 3. Sampling durations were the longest of the study, at 452 and 420 minutes. The amount of time an individual spent per shift in the shaker and mud pit areas is unclear, but would appear to be between 6 and 12 hours per 12 hour shift. Oil vapour concentrations at this site were 135 mg/m^3 and 196 mg/m^3 . This would result in 8 hour TWAs ranging from 101 mg/m^3 (assuming 6 hours exposure at the lower value) to 295 mg/m^3 (assuming 12 hour exposure at the higher value). The shakers and mud pit at this site are outdoors, with no LEV, hence ventilation is entirely dependant upon prevailing weather conditions.

As already stated above, the uncertainties associated with the measurement method, plus the very small number of data points, means that there are very large uncertainties associated with the exposure results discussed above. None of the six exposures exceeds the industry OEL of 350 mg/m^3 , although sample 2 at site 3 approached this value.

Inhalation exposure to drilling mud aerosol and vapour is dependant upon a number of factors. These include the physiochemical composition of the mud, the mud return temperature, the degree of enclosure around the shale shakers and mud pits, ventilation conditions, local site working patterns and the use of respiratory protection.

The OEL of 350 mg/m^3 (8 hour TWA) for hydrocarbon vapour used by the industry was derived from OELs for synthetic hydrocarbon mixtures such as white spirit. In 2003, the Norwegian Labour Inspection Authority set a health based 8 hour TWA OEL for oil vapour of 50 mg/m^3 (Steinsvag et al 2005). This was based on the possible increased prevalence of chronic, irreversible lung disease (lung fibrosis and lung cancer) at exposures in excess of this.

The very limited data set gathered during this survey (six personal samples from three locations) suggest that oil vapour exposures in excess of 50 mg/m^3 are not unusual, with three of the six personal samples yielding results in excess of this value. Of the three sites visited, two have produced at least one 8 hour TWA oil vapour exposure in excess of 50 mg/m^3 . Only at site 1 were both results below this value, and this would appear to be due to a combination of exceptionally high ventilation rates and time segregation of shaker and mud pit operations. A recent study (Steinsvag et al 2005) concludes that, although exposures have fallen over the period 1979 to 2004, oil vapour exposures in Norwegian offshore drilling operations may still exceed 50 mg/m^3 . This indicates that a wider survey, studying current exposures and associated controls, would be justified.

4.2.2 Real Time Measurements

The ToxiRae PID cannot differentiate between different chemical species. It is calibrated using isobutylene, but it has a different response to each vapour. The manufacturers give correction factors (CF) for a number of compounds, including n-alkanes up to decane (nC10), however the vapour encountered during monitoring was predominantly aliphatic hydrocarbons between C10 and C17. It is estimated that the straight chain n-alkanes in this range will have a CF of approximately 1.3 (i.e. the true concentration will be 30% higher than the PID reading). However the presence of cyclic and branched alkanes could have reduced this value, and the

presence of VOC would also have had an effect (e.g. CF for ethyl benzene is 0.52, and for pentane is 8.4).

The average concentration measured by the PID over 378 minutes was 30 ppm, whereas the other samplers (GGP and ATD tubes) worn gave results between 9 and 18 ppm oil vapour (over 452 minutes), and also contained VOCs (~10%). Therefore the results are presented here as raw data, and are presumed to give a rough estimate for the actual concentrations encountered, and an accurate representation of the pattern of exposure through the shift. Similarly, without validation data for the Draeger CMS, the results noted in Table C6 should also be interpreted with a degree of caution.

In Figure 3 it can be seen that although breaks in the work can be seen where exposure dropped to a baseline of around 10 to 20 ppm, the peak exposures during work activity are only around 40 to 80 ppm, approximately double the average concentration of 30 ppm. The highest single peak exposure was 107 ppm.

The vapour map created by the ToxiRae in Figure C1 in Appendix C gives a good impression of the relative vapour levels in the shale shaker and mud pit areas. The area around the shale shakers, and particularly to the rear have higher concentrations of vapour than the mud tank area (up to ten times). The shale shakers did not have enclosed sides, but the mud tanks were 90% covered by deck plates. A concentration gradient can be seen across the mud tank area caused by the natural ventilation at one end.

5 CONCLUSIONS

Traditional filter sampling for drilling mud aerosol formed from current formulations is inappropriate due to evaporation of volatile oil components. It may still be used for estimation of the solid components of the mud by solvent extracting any remaining oil.

Exposure to the airborne oil from the drilling muds can be measured by sampling both aerosol and vapour using a combined filter and sorbent tube sampler. The filter sampler should collect the inhalable fraction of the aerosol. The filter sample should be kept in cold storage and desorbed as soon as possible. Analysis of both filter and sorbent can be performed by FTIR spectroscopy.

Analysis of the sample extracts is also possible by GC. It would provide compositional data and would be more cost effective. Any contaminating hydrocarbons (e.g. solvents) could be identified and excluded, which would not be the case for FTIR analysis. The filter samples could be desorbed in pentane immediately after sampling, rather than other more toxic solvents such as perchloroethylene.

However there were unresolved problems with filter analysis during this work which impacted on the sensitivity and accuracy of the analyses. The cause is suspected as being interaction between the perchloroethylene solvent and the PTFE lined bottle caps.

Analysis of vapour only samples to demonstrate control was investigated. Comparisons with the total airborne oil measurement were not conclusive, but suggested that diffusive sampling of the vapour was representative of total oil. Vapour measurements using pumped sampling gave inconsistent results when compared with either total airborne oil or diffusive vapour measurements.

Both vapour methods considered (pumped and diffusive sampling) allow the simultaneous analysis of coincident VOCs. Pumped sampling has been commonly used for oil vapour for many years, but is also likely to sample some aerosol particles. At present diffusive sampling of semi-volatile hydrocarbons on thermal desorption tubes is not widely used, however here it was found to be the better option. Diffusive sampling should be the method used to collect further exposure data.

The very limited data set of personal exposures gathered during this work (six samples) suggests that although none of the samples exceeded the industry OEL of 350 mg/m³, three samples did exceed 50 mg/m³ (the Norwegian Labour Inspection Authority 8 h TWA OEL).

The one real time personal profile measurement made had peak exposures that were approximately twice the average concentration (approximately 30 ppm), although the highest single peak exposure was over three times the average (~107 ppm).

6 APPENDIX A: ADDITIONAL WORK ON FILTER SAMPLE LOSS

Introduction

Drilling mud sample 3, from the phase 1 work was selected to investigate the potential for sample loss by evaporation from a glass fibre filter. The mud was obtained February / March 2002. It contained no detectable amounts of any artifacts. It had a headspace concentration that could be described as middle of the range (relative to those of other mud samples from phase 1). It had a 65:35 oil : water ratio.

Evaporative Loss Analysis

This experiment was designed to give an indication of the potential for the sample to evaporate during sampling. Pre-weighed 25 mm GF/A filters were spiked with approximately 5 µl of homogenised drilling mud 3B (mean 4.37 mg, cv 3.4%). The raised mud globule was smeared across the filter, and the filter was re-weighed to determine the amount of mud added. Six spiked filters and three blank filters were placed in Gelman open-faced samplers and aspirated with laboratory air at 1 litre/min. A guard filter was positioned in a second Gelman sampler fastened face to face with the first to prevent collection of airborne dust. Air temperature was approximately 21°C, and relative humidity 22 %. The filters were periodically reweighed to monitor the rate of sample loss.

The experiment was repeated using the supernatant oil floating on top of drilling mud 3A (mean 3.95 mg, cv 4.5%). The oil pipetted onto the filter immediately soaked into the filter, and so no smearing was required. Air temperature was approximately 21°C, relative humidity 35%.

Results are presented in Table A1 and Figures A1 and A2. Error bars on the figures represent +/- one standard deviation.

Table A1. Drilling Mud Evaporative Sample Loss Results

Time (mins)	30	60	120	180	240
Mud					
Mean Loss (%)	45	54	58	59	59
Standard Deviation (%)	1	1	1	1	1
Oil					
Mean Loss (%)	56	81	96	97	97
Standard Deviation (%)	4	5	2	1	1

Figure A1. Drilling Mud Filter Sample Loss

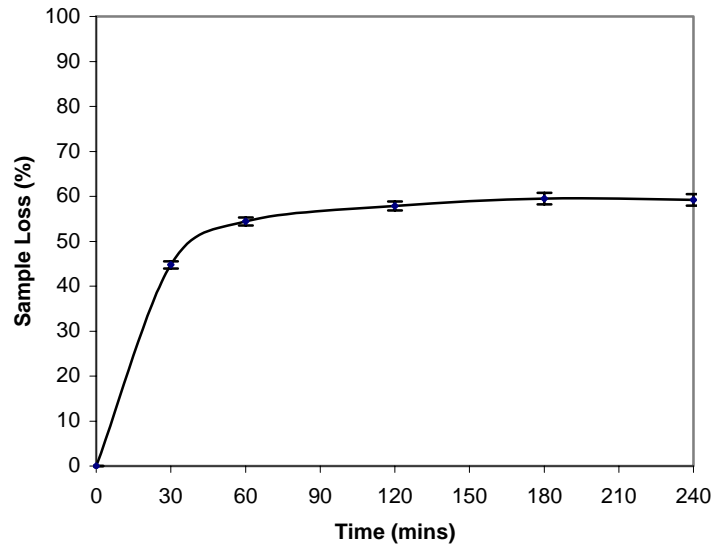
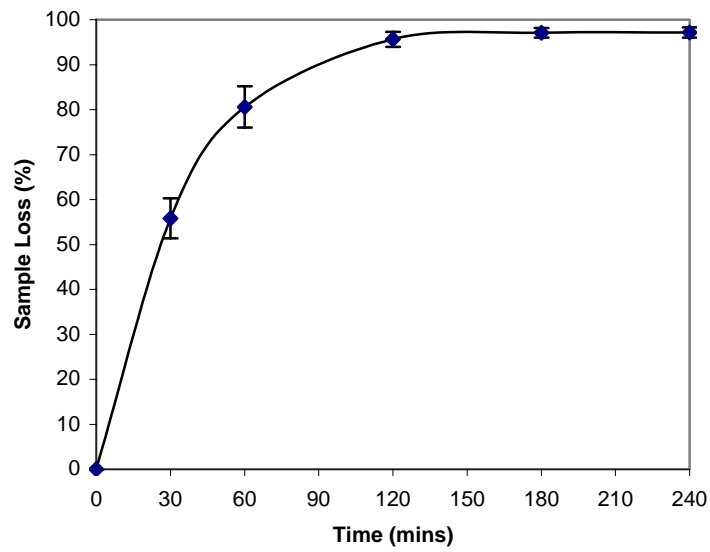


Figure A2. Supernatant Oil Filter Sample Loss



Discussion

The experimental design was not ideal, because real sampled mud aerosol particles would have a larger surface area than the spiked filters, thus increasing the rate of evaporation. On the other hand the presence of large quantities of vapour in the air passing through the filter would have reduced the rate of evaporation. Also, water and volatile oil components in the drilling mud mist would have already been evaporating from the mist particles before they were sampled. It is assumed that the mist particles are formed by atomisation rather than vaporisation-condensation, and so will contain clay particles etc.

The rate of sample loss from the mud spiked filters started to level off after two hours aspiration, with a loss of 58%. The material lost would be expected to compose of water and hydrocarbons from the oil. Actual sample loss from real samples would be likely to be less than this because of losses from the particles before capture on the filter. In previous work done by HSL on filters spiked with neat water based metalworking fluid concentrates, water was lost rapidly during the first period of the experiment, and subsequent sample loss was thought to be evaporation of oil. MWF concentrate contains homogenous water and oil, whilst drilling muds are water in oil emulsions containing large quantities of particulate clay and salts. Although these differences in composition would be expected to have some effect on the evaporative process, water would still be expected to evaporate relatively quickly, and oil somewhat slower.

Assuming that practically all the water and oil had been lost from the mud, then from the oil : water ratio data supplied it can be estimated that approximately one third of the sample loss was water and the remaining two thirds was due to the oil. Without formulation data or further practical work, it cannot be certain that all the water and oil has been removed.

When the neat supernatant oil was considered, most of the sample (96%) disappeared after two hours aspiration (at 1 litre/min). In the phase 1 work, the composition of the oil in the mud was determined to be C10 to C16 hydrocarbons. For comparison, similar work has been done in the past on kerosene (also C10 to C16) and 98% of the sample was lost after 30 minutes aspiration (at 2 litres/min). Similarly, mineral seal oil (C11 to C23) lost 57% after six hours (also 2 litres/min). Drilling muds based on a heavier oil would have lost material at a slower rate.

This work indicates that there is a possibility that filter samples may contain very little oil. This would bias the infrared analysis quantifying the 'oil' (hydrocarbon) on the filter. During development work (i.e. phase 2), quantitative analysis by GC could be used to determine whether this was the case.

Conclusion

The neat oil behaved as predicted from the compositional data obtained in phase 1, and highly significant quantities of material were lost rapidly.

Without further data on composition, it is difficult to fully interpret the sample loss profile of the filters spiked with mud. Actual sample loss from such a drilling mud mist would be likely to be less than the 59% found here, due to prior loss of some of the volatiles.

In both cases, material was rapidly lost over a short period of time. There is a possibility that real sample filters may contain little oil after sampling.

7 APPENDIX B: INSTRUMENTAL ANALYTICAL CONDITIONS

Table B1. FTIR Instrumental Conditions (Oil Extracts in Perchloroethylene)

Gain	1
Resolution	2 cm ⁻¹
Data Interval	0.5 cm ⁻¹
No. of Scans	16
Path Length	10 mm
Cell Material	Quartz
Scan Range	3500 to 2500 cm ⁻¹
Background Subtraction	neat Perchloroethylene

Table B2. GC-FID Instrumental Conditions (Oil Extracts in Perchloroethylene)

Programmable Split-Splitless Injector			
Volume	1 µl	Initial Temperature	90°C
Split	off	On Time	4.25 mins
Temperature Hold	0.25 mins	Final Temperature	280°C
GC			
Column	30 m BP1	Head Pressure	16 psi
Initial Temperature	70°C	Hold	5 mins
Ramp Rate	5°C/min	Final Temperature	280°C

Table B3. ATD Instrumental Conditions (ATD Tubes)

Oven Temperature	300°C
Trap Low	-30°C
Desorption Time	5 mins
Trap High	350°C
Trap Hold	5 mins
Split	0.5 / 4 %

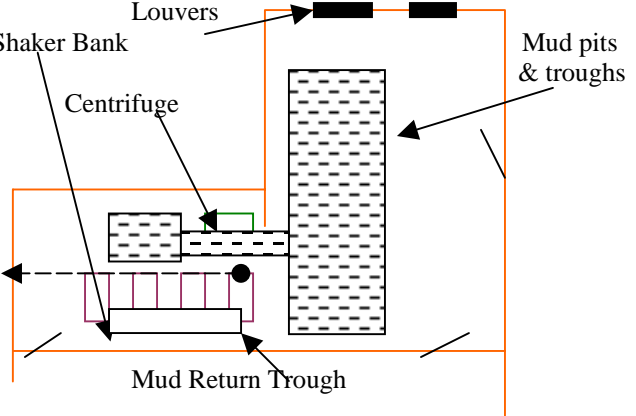
8 APPENDIX C: SAMPLING VISIT DETAILS

Table C1. Visit 1, September 2003 Site Details

Number of workers potentially exposed to drilling mud vapour/aerosol	In total approximately 30 (drill crew, mud engineer & mud loggers), but generally only one person present at any one time in shaker & mud tank areas for prolonged periods (2 h out of a 12 h shift).
Description of sampling area	<p>Shaker House Four shale shaker units in a row, with two units per LEV hood (one LEV fan out of action at the time of sampling).</p> <p>Air flow (face velocity):- Front edge of LEV capture hood: ~0.2 –0.5 m/s Mid LEV capture hood: ~0.5-1 m/s Ops Bench: 0.6 m/s (also natural air flow from adjacent to module door which was open)</p> <p>Mud Tank Module Half of the deck above the mud tanks is open grating. LEV extract slots are positioned over the tank access hatches, (face velocity = 0.12 m/s).</p> <p>Both areas are enclosed within interior modules with both forced and natural ventilation (via louvers & doors). The approximate volume of the modules was c200 m³</p>
Weather conditions	Temperature = 22.7°C, Humidity = 43% Wind speed/direction = 20-38 degrees SW
Engineering controls (if exhaust ventilation is used please include hood shape, size, face velocity measurements, capture velocity measurements (if possible))	<p><u>Shale shaker extract system design</u> (upgraded 1999) Fume extraction is from eight separate points (four above the shakers and four along the header box). At each point the extract flow rate is approximately 1 m³/s. It is designed to operate using unassisted fresh air make up from weather louvers on the bulkhead directly in front of the shakers (dispensing with previous supply fans), and providing approximately 2 m³/s extract per shaker, giving a total of 8 m³/s. A curtaining arrangement installed to improve extract capture was not present during sampling (see photos). The exhaust is discharged remotely.</p> <p>Shale shaker extract: Air Flow rate = 1 m³/s Duct velocity = 15 m/s Duct size = 300mm diameter Pressure drop = 9.8 Pa/m</p> <p>There is a baffle plate fitted to prevent any shale carry over. All duct branches to be fitted with a volume control damper to enable good volume control.</p> <p>Volume of shaker house = 222.7 m³ Air change rate = 60 hence minimum airflow rate expected = 3.71 m³/s, Actual air change rate based on an a.f. rate of 8 m³/s = 129, this equates to a full air change in shaker house every 30 s.</p>

	<p>Fans: x2 centrifugal 22 KW, air flow rate = 4 m³/s + 25% margin = 5 m³/s Fan static pressure = 2400 Pa (includes allowance for wind age).</p> <p>See attached LEV system plans and photos of shale shaker walkway & test bench – principal occupied areas.</p>
Drilling mud	<p>Low toxicity oil based mud Oil: highly refined petroleum mineral oil, Boiling point 225-290°C, Flashpoint >100°C</p>
Mud management system	<p>Day 1 (samples 1, 2 & 3): Drilled ahead the 8.5 in section at depth c5000 m at around 18 m/h, except when limestone stringers, when rate drops to as low as 1 m/h. Added lightweight premix with organophilic clay and high water fraction.</p> <p>Day 2 (samples 4 & 5): Still in 8.5 in section at depth of c5100 m with average 2 m/h. LCM pill with coarse material, addition of Safecarb & Sandseal Fine/OM seal.</p>
Rate of penetration	<p>Day 1: 282 m daily with average ROP 12 m/h Day 2: 48 m daily with average ROP 2 m/h</p>
Return mud temperature	<p>Day 1: 150°F (66°C) Day 2: 135°F (57°C) ‘Flow line temp.’ i.e. return mud temperature at the shakers, and so would be slightly lower at the mud pits.</p>
Mud circulation rate	<p>Day 1 520 gpm (gallons per minute) Day 2 440 gpm</p>
Mud composition (% oil and water)	<p>Day 1: o 55%, w 19%, s 26% Day 2: o 56%, w 21%, s 23%</p>
Other comments	<p>Staff wore coveralls and gloves.</p>

Table C2. Visit 2, June 2004 Site Details

<p>Number of workers potentially exposed to drilling mud vapour/aerosol</p>	<p>Two men in the area at any time, normally for the whole 12 h shift. Any rotation is simply in position from shakers to pits.</p> <p>Watch keeping is not permanent and done on a rotation basis with the personnel usually in the mud tank area rather than by the shakers. This manages the exposure risk, probably by accident.</p>
<p>Description of sampling area</p>	 <p>This was a standard rig with single Derek, top drive, etc. Mud pumps, shakers and sack store all on top of each other below the drill floor itself.</p> <p>Shakers and pits are in the same part of the rig (each area 6 m by 20 m). There was strong air movement from the louvers that were open and the wind blew in. The air moved well down the area and ventilated, naturally. To supplement this, the bank of four shakers had hoods fitted above the screens, but unlike most modern shakers in the UK, the sides were not enclosed.</p> <p>There was no forced ventilation. The mud tanks were under deck plates (i.e. under the floor), 90% of which was covered.</p> <p>Spot ToxiRae readings in the mud tank area were between 5 and 12 ppm (as isobutylene) and around the shaker bank were between 15 and 250 ppm (as isobutylene)</p>
<p>Weather conditions</p>	<p>Ambient temperature 6°C. No details on humidity. 25–30 Knot winds from the N.W. blowing straight in the louvers.</p>
<p>Engineering controls</p>	<p>All four shakers had local exhaust, all of which were working. No air-flow measurements were taken, and the Rig did not have any LEV test records. The LEV exhaust discharge was not remote. It went out through the side bulkhead and over the pipe deck.</p> <p>The mud-pit headspace was also extracted.</p> <p>General ventilation was good.</p>

Drilling mud	Low toxicity oil based mud
Mud management system	No additions, circulating at depth.
Rate of penetration	70 feet per hour through a 12.25 inch hole. Depth at sampling was 12,500 feet.
Return mud temperature	106–115°C
Mud circulation rate	850 gallons per hour (14 gpm)
Mud composition (% oil and water by volume)	55% oil, 25.5% solids, 19.5% water.
Other comments	<p>Staff wore standard rig gear, PPE included boots, hard-hat, impervious gloves and safety glasses.</p> <p>The louvers at the aft end (rear of the mud pit area) were open and allowed natural ventilation. This was also the direction of the prevailing wind and as a result there was good air circulation across the pits and down towards the shakers. This air movement disrupted the capture efficiency of the LEV hoods, causing “steam” accumulations at the rear of the shakers and condensation on the bulkhead. However the shaker area had no visible mist or vapour in the working area.</p> <p>The shakers were hosed down with a power washer once only during sampling to free them up. This lasted about 5 minutes and used water.</p> <p>The cuttings are collected into skips from the outflow of the shaker screw feed system. This discharge and skip filling is outside on the pipe deck and is well ventilated.</p>

Table C3. Visit 3, January 2006 Site Details

Number of workers potentially exposed to drilling mud vapour/aerosol	One Derrickman spends significant time in all mud tank / shaker areas. A shaker hand (x2) and mud engineer (x1) is occasionally exposed.
Description of sampling area	Shaker House (approximately 30 m by 10 m) Three new VSM-100 shaker units in an open sided area with tarpaulin roof. Static samples were taken by a work bench in the corner, at head height. Mud Tanks Area (approximately 30 m by 10 m) Open sided area with tarpaulin roof. Static samples taken at Derrickman cabin and test bench above active pits.
Weather conditions	Temperature = 11-12°C (ambient 6-8°C), Humidity = 66-94% Wind speed/direction = 0.2-5 m/s
Engineering controls	No LEV. Open sided for natural ventilation. Mud tanks had open grating, with some mats
Drilling mud	Oil based mud Oil: dearomatised medium boiling hydrocarbon distillate, Boiling point 225-290°C, Flashpoint 92°C
Mud management system	Drilling at 2050 m, 8.5 inch section. Day 1: Mud weight raised to 1.15 sg with 2 MT barite, further barite and Baracarb 5 being mixed to further increase weight. Day 2: 1 MT barite added to maintain weight. 2 barrels/hr pot water added to maintain oil in water ratio.
Rate of penetration	Day 1: 1 m/h Day 2: 25 m/h
Return mud temperature	140-150°F (60-66°C)
Mud circulation rate	570 gpm (gallons per minute)
Mud composition (% oil and water by volume)	Oil 67 %, water 17% (solids 16%)
Other comments	PPE included boots, hard-hat, safety glasses, and Stoko barrier cream (Stockhausen) under disposable PVC gloves. RPE was worn when jet washing the shakers (a combined organic vapour / particulate mask, 3M part 4251 and 3M part 4579). On both days only two of the three shaker units were working, On day one the unit closest to the samplers was on standby (there was minimal cuttings, but mud was circulating). On day two, the two end shakers were running, and the middle shaker was on standby. There was frequent use of the 'Craco' gun on both days. This was a pressure washer using base oil for cleaning the shaker screens. A shaker hand was present in the shaker house most of the time, checking effective operation of the shakers.

Table C4. Visit 1, September 2003 Sample Details

Samples	Details	Duration
visit 1, set 1, (day1)	<p>Personal: Shale Shaker Op Ensures constant mud/cuttings flow over shaker units, takes occasional mud samples and checks shaker screens.</p> <p>Shift: 12 hour (however only 2 hours are spent at the shakers per shift, and at other times he would be in areas unlikely to contain significant fumes)</p>	105 minutes
visit 1, set 2, (day 1)	<p>Static: Shale Shakers Static samples were taken on the main walkway at head height fixed to the bulkhead directly opposite the end shaker unit #1 at a distance of approximately 1 m (adjacent to the faulty LEV).</p> <p>(Spot ToxiRae reading: 10 ppm (as isobutylene))</p>	155 minutes
visit 1, set 3, (day 1)	<p>Static: Mud Tank Module Sampler above active mud pit (circulating hot mud) at a height of approximately 1.5 m above the deck and adjacent to the LEV duct. Air movement was 0.12 m/s.</p> <p>(Spot ToxiRae reading: 20 ppm (as isobutylene))</p>	452 minutes
visit 1, set 4, (day 2)	<p>Static: Shale Shakers Positioned as set 2, but on day 2.</p> <p>(Spot ToxiRae reading: 6 ppm (as isobutylene))</p>	600 minutes
visit 1, set 5, (day 2)	<p>Personal: Shale Shaker Op Duties and shift times as per set 1.</p>	210 minutes

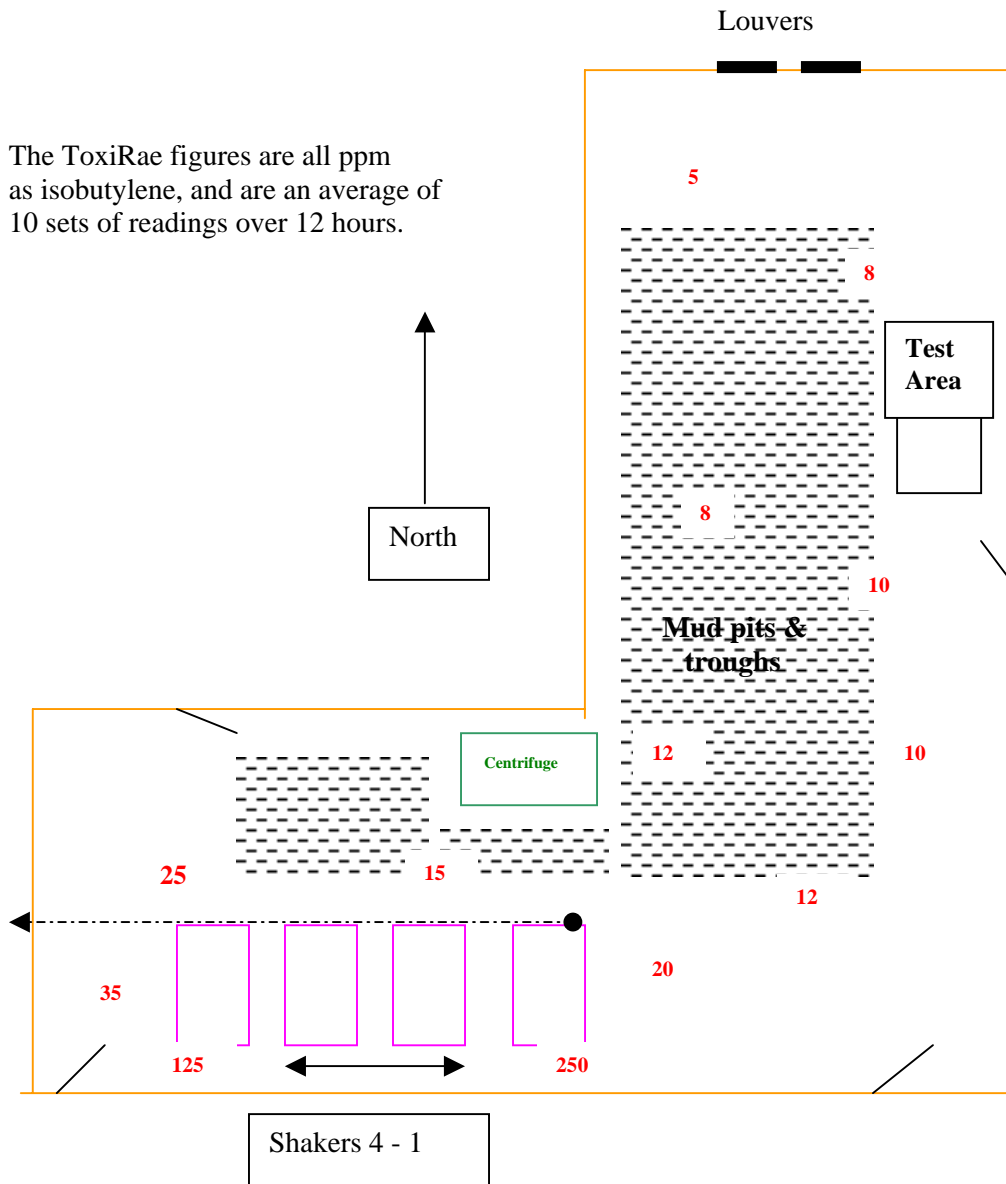
Table C5. Visit 2, June 2004 Sample Details

Samples	Details	Duration
visit 2, set 1	<p>Personal: Derrickman</p> <p>His duties were all in the one area: keeping an eye on the shakers with occasional sampling from the mud trough and pits. The majority of the time was noting tanks levels and rates of return, but done from a distance away from the shakers and in the fresh air stream from the rear louvers. Occasionally he helped with sack handling and addition in the sack store.</p> <p>Shift: 12 hour (midday to midnight)</p>	300 minutes
visit 2, set 2	<p>Personal: Roughneck</p> <p>Duties were the same as above, and in the same area.</p> <p>Shift: 12 hour (midday to midnight)</p>	310 minutes
visit 2, set 3	<p>Static: Behind shaker bank (starboard side).</p> <p>The samples were positioned 1 m above and to the side of the inlet trough. Steam was visibly evolved and dispersed by the natural air movement, there was no impact from the LEV hoods over the shakers themselves. Condensation was running down the rear bulkhead. This area is not usually visited and is considered a “worst case”.</p> <p>No GGP sampler</p> <p>(Spot ToxiRae reading: 125 ppm (as isobutylene))</p>	<p>Pumped 180 minutes</p> <p>Diffusive 600 minutes</p>
visit 2, set4	<p>Static: Behind shaker bank (port side).</p> <p>The samples were positioned 1 m above and to the side of the inlet trough. Steam was visibly evolved but not to the same extent as near set 3. Dispersion was not as effective due to the natural air movement being reduced in this corner. There was still no impact from the LEV hoods over the shakers themselves. Condensation was running down the rear bulkhead but not to the same extent as near set 3. This area is not usually visited but is close to the entrance door and there was a slight “odour”.</p> <p>No GGP sample</p> <p>(Spot ToxiRae reading: 250 ppm (as isobutylene))</p>	<p>Pumped 180 minutes</p> <p>Diffusive 600 minutes</p>
visit 2, set 5	<p>Static: In front of the shaker bank (starboard side).</p> <p>The samples were positioned just above head height using extraction support frame. This is as far as the watch keeper normally goes when he is inspecting the shakers. There was no visible “steam” nor was there a strong odour.</p> <p>Diffusive sample only</p> <p>(Spot ToxiRae reading: 25 ppm (as isobutylene))</p>	Diffusive 570 minutes
visit 2, set7	<p>Static: In front of the shakers (port centre).</p> <p>The samples were positioned using frame of ventilation for support. There was no visible “steam” nor was there a strong odour.</p> <p>No pumped ATD tube sample</p> <p>(Spot ToxiRae reading: 15 ppm (as isobutylene))</p>	<p>GGP 180 minutes</p> <p>Diffusive 570 minutes</p>

Table C6. Visit 3, January 2006 Sample Details

Samples	Details	Duration
visit 3, set 1, (day 1)	<p>Static: Mud tanks test bench The samples were taken adjacent to the active mud pit.</p> <p>The main mist emitted from the tank was between the Op cabin and the test bench. Natural air movement of >0.5 m/s dispersed the mist however the mist could hang over the area. Droplets of water were condensing on the roof.</p> <p>Air temperature: 11°C, RH: 54-93% (average 67%), Air movement: 0.2-2 m/s (at >2 m/s the mist dispersed). Draeger CMS: <20 ppm within plume.</p>	437 minutes
visit 3, set 2, (day 1)	<p>Static: Shale shakers Ops bench The samples were taken in a corner at head height.</p> <p>Shaker samples 'wet' - from mist or jetting.</p> <p>Air temperature: 8 °C, RH: 57-88% (average 62.5%), Air movement: 0.11-4.1 m/s (average 0.62 m/s) Draeger CMS: <20 ppm</p>	428 minutes
visit 3, set 3, (day 1)	<p>Personal: Derrickman Duties included checking / testing mud properties, flowrates, conditioning mud where required, ensuring shakers are operating effectively, sampling tanks, monitoring pump rates and removing cuttings to skips. This sample included two Derrickmen who changed over shift at midday i.e. two people sampled on the same sample train and representative of a typical day shift.</p> <p>Shift: 12 h (06:30-18:30)</p> <p>ToxiRae (6 h 17 min run time): TWA 22 ppm, peak 28-107 ppm (as isobutylene) Draeger CMS: <20 ppm (in plume / over pits).</p>	452 minutes
visit 3, set 4, (day 2)	<p>Personal: Derrickman Duties and shift as per set 3, one person sampled throughout.</p> <p>Draeger CMS: < 20 ppm in both areas.</p>	420 minutes
visit 3, set 5, (day 2)	<p>Static: Mud tanks test bench (as per set 1).</p> <p>Air temperature within mist plume: 8-9°C, outside: 6°C RH: 54-91% (70% average) Air movement: 0.2-3 m/s (1 m/s average) Draeger CMS: c20 ppm Spot ToxiRae reading: peak 34 ppm, average 15 ppm, (as isobutylene) taken above the active tank.</p>	429 minutes
visit 3, set 6, (day2)	<p>Static: Shale shakers Ops bench (as per set 2).</p> <p>Air temperature: 8°C, RH: 70% average, Air movement: 0.2-3 m/s (1 m/s average) Draeger CMS: <20 ppm Spot ToxiRae reading: peaks of ~100 ppm (as isobutylene) taken in the mist cloud.</p>	415 minutes

Figure C1. Visit 2 ToxiRae vapour map of the shaker and mud pit areas



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