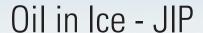
REPORT



Report no.: 23

Measurement of Methane Emissions from Oil Spill Experiments at Svea Test Site, Svalbard, April 2007

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SINTEF Materials and Chemistry

Marine Environmental Technology

Date: 24.05.2010















Preface

SINTEF has in cooperation with SL Ross Environmental Research Ltd and DF Dickins Associates LLC on behalf of the oil companies AGIP KCO, Chevron, ConocoPhillips, Shell, Statoil and Total initiated an extensive R&D program; *Joint industry program on oil spill contingency for Arctic and ice covered waters*. This program was a 3-year program initiated in September 2006 and finalized in December 2009.

The objectives of the program were;

- To improve our ability to protect the Arctic environment against oil spills.
- To provide improved basis for oil spill related decision-making:
- To advance the state-of-the-art in Arctic oil spill response.

The program consisted of the following projects:

- P 1: Fate and Behaviour of Oil Spills in Ice
- P 2: In Situ Burning of Oil Spills in Ice
- P 3: Mechanical Recovery of Oil Spills in Ice
- P 4: Use of Dispersants on Oil Spills in Ice
- P 5: Remote Sensing of Oil Spills in Ice
- P 6: Oil Spill Response Guide
- P 7: Program Administration
- P 8: Field Experiments, Large-Scale Field Experiments in the Barents Sea
- P 9: Oil Distribution and Bioavailability

The program has received additional financial support from the Norwegian Research Council related to technology development (ending December 2010) and financial in kind support from a number of cooperating partners that are presented below. This report presents results from one of the activities under this program.

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Funding Partners













R&D Partners





Cooperating Partners

















Editor's Preface

Further discussions of the expected utility of gas sensors as an Arctic detection tool and a summary of field measurements obtained in this program are contained in the Oil in Ice JIP Report no.:30, Project P5: Remote Sensing Summary.

David Dickins Project P5 Coordinator and Editor Unrestricted EP 2007-5633

Measurements of Methane Emissions from Oil Spill Experiments at Svea Test Site, Svalbard, April 2007 by B. Hirst (EPT-RXF); S. O'Connor (GSUK-GSES)

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SUMMARY

Increased exploration and production interest in cold region operations has fostered industry efforts to improve understanding of the behaviour and responses required in the event of oil spills in ice-infested waters. An elusive goal for several years has been to find methods capable of remotely detecting and tracking oil from such spills. In April 2007, the 3-year Sintef-led Joint Industry Programme, JIP, organised a series of small-scale spills at Svalbard. The spills were primarily aimed at improving understanding of the weathering and ignitability of spilled crude. However, they provided an opportunity for Shell staff – supported under the JIP- to obtain the first ever measurements of methane emissions from such spills. Those emission rates are reported here. Gas dispersion modelling shows that the level of emissions from a significant spill are probably sufficient for its remote detection and mapping from a range of several km using LightTouchTM: Shell's hydrocarbon seepage detection technology.

KEYWORDS

provide keywords

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1. INTRODUCTION

In April 2007 a series of controlled spills of crude oil were made into a re-circulating water flume cut into solid sea ice next to Sintef's arctic research station at Svea on Svalbard. This experimental work was part of a larger Joint Industry Project (JIP) organised to advance understanding of the behaviour of oil spills in ice-infested waters, Sintef (2006) [1]. Shell scientists attended the spills to measure methane emissions and thereby assess the potential for detecting and locating such spills using ultrasensitive gas sensors.

The JIP research programme comprises 5 key goals: one of these is to find ways of detecting, locating and tracking oil spills that might occur in cold regions. A particular problem of such spills is the difficulty of detecting oil that may be under ice, encapsulated within ice, or perhaps covered with subsequently deposited snow/ice concealing it from observation. Oil from such spills can migrate with the ice and only become apparent on melting, perhaps months later, by which time the resulting contamination might be widely dispersed from the original spill site and much more difficult to deal with effectively.

For several decades research has sought ways of remotely detecting and mapping oil spillages concealed under or within ice. Technologies considered in the past include: electromagnetics, ground penetrating radar and acoustics. None have proved adequate and the issue of detecting oil trapped in and/or mixed with rough, dynamic ice remains unsolved. In many instances there is little alternative to undertaking laborious and very hazardous physical sampling by manually drilling through the ice.

2. TECHNOLOGY BACKGROUND

In 2004 work at the US Army's Cold Regions Research Engineering Laboratory, CRREL by Shell Global Solutions, examined the potential for detecting oil under ice by using ultrasensitive gas detection, [3]. An ultrasensitive gas sensor (developed for hydrocarbon exploration by Shell, see [4]) was used in conjunction with a flux chamber to provide the first ever measurements of gas migration fluxes though thick, homogeneous ice sheets of up to 0.4m thick.

When the sensor is used for exploration, atmospheric gas concentration measurements over a large area are combined with simultaneous wind velocity data and advanced gas dispersion modelling to remotely map surface emission fluxes. The system, which is called LightTouchTM, can detect naturally occurring microseepages of hydrocarbon gases from ranges of up to several km. Clearly, if oil spills produced comparable emissions, then the same approach could be used for oil spill detection and mapping. This would be attractive as ultra-sensitive gas sensors could be operated from aircraft, and readily deployed over large distances and rapidly cover large search areas. Key to assessing the feasibility of such an approach is knowing the flux levels (mass release rate per unit area per unit time) of hydrocarbons emitted from oil spills under the conditions of interest. The 2007 Svea spill programme provided a rare opportunity to address that question.

3. THE SVEA 2007 OIL SPILL PROGRAMME

The 2007 spill programme comprised 100 to 200 litre spills of stabilised Grane crude oil into seawater. The spill was contained within a recirculating channel system cut into the sea ice of Van Mijenfjorden adjoining Sintef'sSvea research station on Svalbard at Kapp Amsterdam. The layout of the spill facility is shown in Figure 1. Two submerged propellers provide intensive shear mixing of oil and water and recirculate the mixture around a "race-track" flume. A separate wave machine enhances surface agitation and mixing. In these ways the designers have sought to replicate but accelerate the natural ageing process of spilled oil in the interests of experimental convenience. At the end of each spill the oil emulsion is swept into the pool fire area and ignited; the combustion residues are then cleaned up manually.

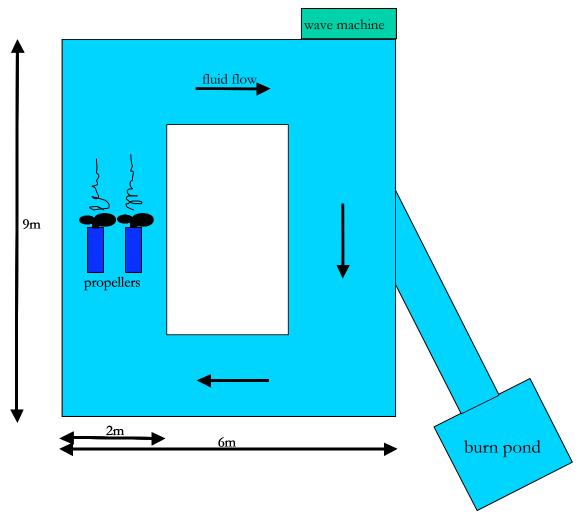


Figure 1: Schematic of the accelerated weathering oil spill facility; showing the recirculated water flume into which oil was spilled, and burn pond where the resulting oil-water emulsions were burnt.

3.1. Gas Sensing for the Svea tests

The primary goal of the gas sensing effort described here was to obtain a useable estimate of the hydrocarbon emission rate resulting from oil spills onto icy water; and use this to estimate the range of detectability of such spills. It was not feasible, within the timing/cost constraints of these tests, to deploy the LightTouchTM system in Svea. However, this was not necessary for our purpose, as we could approach the spills to within a few meters, and hence could use a significantly less sensitive but simpler battery powered gas sensor.

We chose a Boreal Line-Of-Sight LOS methane sensor. This is a path-integrated gas sensor; it is ideally suited to such experiments as -provided the beam encompasses the entire width of the dispersing gas plume- the measurement is not affected by the inevitable changes in plume direction occurring during the spills. The path-integrated measurement is the product of concentration and path-length. This will -on average- be a stable value, provided the mass emission rate and windspeed are stable. Measuring the path-integrated concentration across the plume, along with windspeed and turbulence intensities, allows the source's mass emission rate to be determined.

3.2. Experimental Arrangement

The sensor beam arrangement used for measuring path-integrated concentrations is shown schematically in Figure 2. Two types of measurements are made: the first is across the dispersing gas plume emitted by the crude oil (the downwind measurement); the second is of the background "clean air" or upwind measurement. Path-integrated concentrations are expressed as PPMxMetres, (Parts Per Million times Metres: all concentration measurements discussed here are by volume not mass). For simplicity it is most convenient to express the path-integrated concentration as the equivalent corresponding average concentration that would need to be present along the full path length.

We used the same sensor to make both measurements: alternately pointing the sensor to the upwind or downwind retro-reflector as desired. The strength of the emission source can be inferred from the difference in these two measurements. The calculation is just a simple mass balance. For a steady wind, and steady source, the mass flow rate through any cross-section of the plume (perpendicular to plume transport) is constant anywhere along the plume (by mass conservation). The stability class provides the ratio of the width to height of the plume, and although we do not know the actual plume width, we do know the path-integrated concentration across the plume and hence the corresponding path-integrated concentration of the vertical component. Thus we know the plume cross-sectional area times the average concentration enhancement at the measurement location. The windspeed times the cross-sectional area gives the volume of air per second at this average enhanced concentration; multiplying this by the increase in *mass* concentration provides the mass flux. See equation 1 below for details.

It is important that the downwind beam includes the entire width of the dispersing plume and that the upwind reference beam is completely clear of the dispersing plume. Changes in the measured path-integrated concentration will result from changes in wind speed as well as changes in emission rate. Similarly, changes in background concentration will directly impact both beams; so the differential concentration is unaffected to first order. At Svea there were active coalmines and coal stockpiles, these can be seen in Figure 3. These local sources probably produced some small variations in the background methane concentration but as we will see these were not a significant issue. An attraction of the Svea site is that, located as it is in a steep glacial valley, the wind direction is reliably stabilised

either up -or down- the valley. The wind velocity in spring late afternoons is very stable, as it is primarily driven by cool air draining out of the valley. Figure 3 shows a panoramic photo of the spill facility showing the setting and the arrangement of the beams relative to the water flume and the burn pond. The tarpaulin structure used to prevent overnight freezing of the water can be seen.

The positions of the spill pond, sensors and retro-reflectors were recorded by GPS; critical distances, such as beam lengths, were measured using a tape measure. This simple approach was adequate for the purposes of these tests.

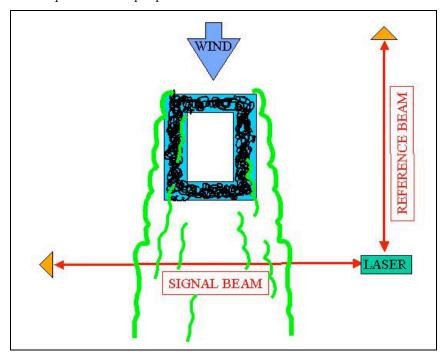


Figure 2: The experimental layout for the gas concentration measurements, showing the Line-Of-Sight path-integrated gas sensor beams in relation to the recirculating flow of oil and water in a channel cut into the surface sea-ice. The beam lengths used were typically ~20m, with the downwind beam passing ≤10m downwind of the spill.

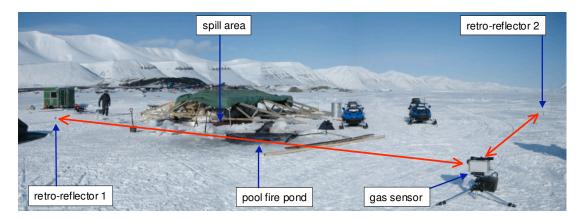


Figure 3: The experimental site at Svea. Red lines indicate the gas sensor beams: the beam to retro-reflector 1 is downwind of the spill. The horizontal field of view in this panoramic photograph is ~120 degrees. Winds were typically coming towards the camera. Some coal stockpiles can be seen in the background; the mine is a couple of km further upwind of the site along the left shore.

3.3. The Spill Procedures

Four spill experiments were completed during the 7 days the gas sensing team were at the Svea Test site. We shall refer to these as Spills 1-4 and include the dates to allow identification within the full test series conducted at Svea in Spring 2007. For each of our 4 spills, a sealed drum of Grane crude oil was opened and spilled through the narrow cap of the drum's lid as a coherent laminar stream into the recirculating water, the drum opening being held approximately 100-200mm above the water's surface. The momentum of the flowing crude carried the oil deep into the channel where it was rapidly sheared into thin sheets and filaments of oil that were carried around the channel by the propeller driven flow. For the early tests the drum was left lying at the spill location with its cap open until later in the spill process when it was removed to the side. After some minutes into the spill the wave machine was switched on. This produced lapping surface waves that splashed against structural supports and walls of the flume channel.

3.4. Experimental Results for Gas Concentration Measurements

The key parameter presented here is the difference between the upwind (background) gas concentrations and those of the downwind beams that traverse the dispersing plumes. The path-integrated concentration is most conveniently displayed as the corresponding effective average concentration along the full beam length. So no distinction is made between a short region of high concentration and a long region of lower concentration: it is the total mass of gas traversed that is being measured. In all the graphs presented here we give the concentration averaged over the full beam length. Thus, given the Earth's current atmospheric background methane concentration is approximately 1.8 PPM, then in the absence of any localised emissions we would expect the average concentration along any beam to be ~1.8 PPM. Any significant enhancement above that background concentration reflects the contribution of local sources.

3.4.1. Spill #1

In Figure 4 we present the path-averaged methane concentration measurements obtained from our first oil spill at Svea. The figure shows concentration from prior to breaking the seal on the drum, to spilling the oil into the water channel; and then through the process of stirring and accelerated ageing that ensues. The graph shows over 4 hours of data.

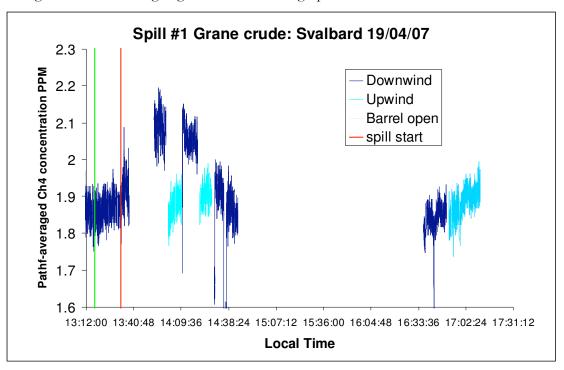


Figure 4: Spill #1 of 200litres of Grane crude, showing enhanced downwind CH4 concentration evolved from the crude oil.

The initial downwind methane concentration is ~1.87 PPM but immediately the spill starts the full beam-averaged downwind concentration increases to just over 2.1 PPM. The dark blue traces show the concentration measured through the dispersing plume from the spill and the lighter blue traces show the background (upwind) measurements at several times during the experiment. The difference is due to methane emitted by the oil.

For spill #1 the average additional concentration seen is \sim 0.19 PPM with this concentration sustained for about 1800 seconds. (However, as will become clearer from later results, these emissions may be largely due to the "empty" drum rather than the oil in the water).

The windspeed was a steady 1.5m/sec and the beam length was 19.4m. Atmospheric stability was class D: which fixes the vertical height as typically ~0.3 of the plume horizontal width for smooth surface conditions, such as over ice. In our case the ground acts as plane of symmetry, "reflecting" the plume: halving the plume's vertical extent but doubling the concentration over this length.

The source mass emission rate is given by:

 $S=A.U.\varrho.\Delta C$ Equation 1

Where:

S= Methane mass emission rate in kg/sec

A= Plume cross-sectional area = $\sim 113 \text{ m}^2 \text{ (=0.3x(cross plume beam length)}^2\text{)}$

U = Windspeed = 1.5 m/sec

 $\varrho = \text{Methane gas density for } \sim -12\text{C} = 0.74 \text{ kg/m}^3$

 ΔC = Additional methane concentration by volume = 0.19 E-06

(The concentration is the beam-length averaged value.)

Thus the source's mass emission rate $S = \sim 24E-06 \text{ kg/sec}$

So total mass emitted during the peak of Figure 4, is S x duration (1800sec)=0.043 kg or $\sim 0.02\%$ by mass of 200 litres of Grane crude.

This compares with a generic analysis value for the CH4 content of stabilised Grane crude of <0.01% by mass which would imply a CH4 content of 200 litres as <0.02kg; Statoil PKS (2004) [2]. However, it is notoriously difficult to measure methane content of crude oil, and the property is usually only of marginal significance to refiners: so we consider the quoted figure as only broadly indicative.

3.4.2. Spill #2

The data from spill #2 are presented in Figure 5. The spill was of 200 litres of Grane crude. For this and all subsequent spills the spill area was covered by a tarpaulin (this was to inhibit freezing of the water overnight). There was a noticeable hiss of gas escaping from the drum cap when the seal was broken, with some bubbles formed around the threaded cap. This gas was immediately picked up by the downwind beam measurement as seen in Figure 5. The windspeed was 1.5 to 2 m/sec at the time of the spill. From about 13:06 it seemed that the wind direction shifted sufficiently for the plume to spill over one end of the beam. Inspection of the data (subsequently corroborated by further spills and tests) suggests that from about that time, movement of an open oil drum compromised the reference beam measurements. This alerted us to the potential for emissions from "empty" drums to be comparable to the emissions from the spilled oil. This will be discussed later.

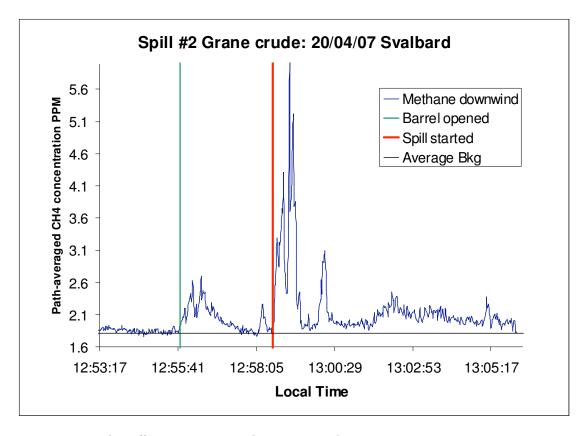


Figure 5: Spill #2 of 200 litres of Grane crude. Gas released as the drum seal was broken is clearly detected, with further significant emissions during pouring of the oil into the recirculated seawater. Some longer term enhanced emissions can be seen but from ~13:06 the plume shifted over the end of the downwind beam.

3.4.3. Spill #3

The data from spill #3 are shown in Figure 6. For this spill there was no noticeable gas release on breaking the cap seal. The windspeed was 3 m/sec at 11:16, 3-4 m/sec at 11:30 and 5 m/sec at 12:00. Again a major gas emission is seen at the time of spilling. We now believe this to be gas emitted from the ullage space created in the drum during pouring, rather than from the oil that is spilled into the water. A second sharp peak is seen a couple of minutes later, this corresponds to disturbance of the drum as it is moved after spilling. The other prominent feature is the "top hat" concentration profile centred on 11:15; we now know this to be related to cleaning activity at a waste drum upwind of the experimental area. Despite these distractions, Figure 7 shows the underlying concentration has risen by ~ 0.15 PPM for a period of at least an hour –and probably significantly longer. It seems likely that this would have decayed back over several hours to the original baseline value, but measurements were not taken for long enough to show this, and no upwind reference signal is available. Based simply on the average long-term concentration increase of 0.15 PPM, for ~3600s, one can estimate the mass release rate and mass emitted. Using a windspeed of 3.5 m/sec, beam length of 17.3m, Pasquil Gifford stability class of D; this yields a mass release rate for the period shown of 34 E-06 kg/sec and a total mass emitted in 1 hour of at least 0.13kg and probably significantly more, given the slow decay back to background concentration levels. This result is ~0.07% by mass of the oil spilled and

seven times that expected from the compositional analysis for stabilised Grane crude; Statoil PKS (2004) [2].

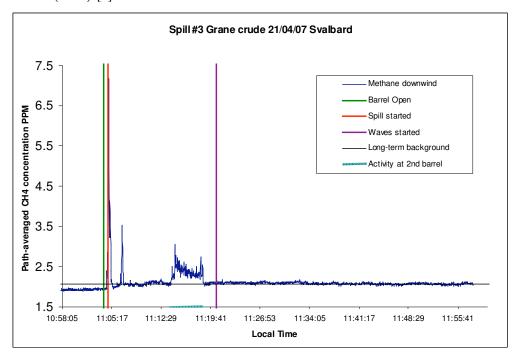


Figure 6: Spill #3 of Grane crude. Significant emissions occur during pouring of the oil into the seawater. The 2nd peak is caused by disturbance of the drum after pouring out the oil. The later "top hat" feature was caused by waste handling at a 2nd drum upwind of the experiment. The underlying long-term concentration behaviour is shown more clearly below.

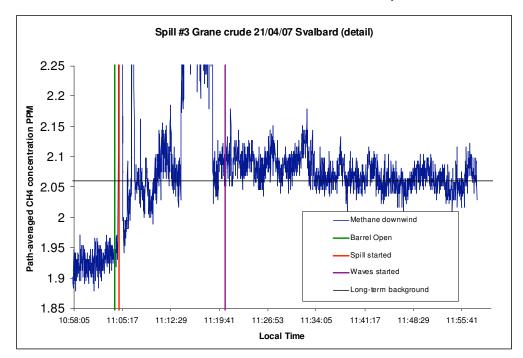


Figure 7: Spill #3 of Grane crude. The long-term concentration is elevated by ~0.15 PPM which gradually decays back. No background reference data are available.

3.4.4. Spill #4

The data from spill #4 are shown in Figure 8. A pressured gas escape was noticeable on breaking the drum seal and immediately registered on the concentration trace. Again significant emissions were measured while by pouring out the crude; with further "top hat" traces appearing due to drum handling and disturbance. However, by this time we recognised the cause of the signal and had the drum sealed and removed from the experimental area. The signal immediately recovered, confirming our diagnosis of this as the cause of the similar signals seen previously.

Subsequent tests on emissions from "empty" drums confirmed that the residual oil within a drum –after pouring- was capable of emitting at these levels for an hour or so; and that further disturbance generated fresh emissions. This clarified our interpretation of earlier spills: particularly Spill #1; where we now believe that the behaviour seen in Figure 4, is predominantly due to emissions from the "empty" drum with longer term emissions from the oil in the water masked by the plume meander off the end of the sensor beam, discussed earlier.

For Spill #4, the windspeed was 4 m/sec at 12:40 and the air temperature was -5.5C; the sustained additional methane concentration over the first hour was ~0.17 PPM. Figure 8 clearly shows a long-term increased concentration compared to the background reference measurements available. Figure 9 shows the result of fitting a simple straight-line regression, the resulting decay time was ~20,000+ seconds.

As before, we can calculate a representative value for the early, but sustained, mass emission rate and infer the total mass of methane emitted from our data:

- The sustained early mass release rate from the spilled oil is 44 E-06 kg/sec.
- The total mass emitted from the oil over 20,000 seconds is thus likely to be \sim 0.4kg which corresponds to \sim 0.2% by mass of 200 litres of oil.

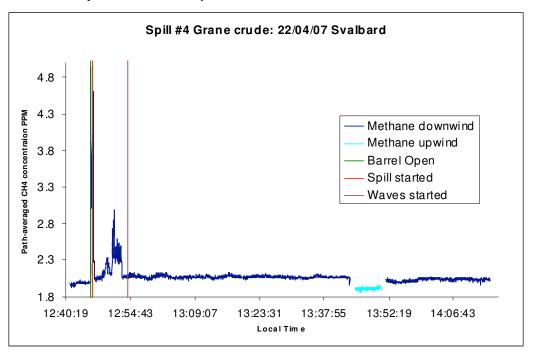


Figure 8: Spill #4 of Grane crude. The long-term baseline is elevated by up to ~0.17 PPM which gradually decays back down towards background levels.

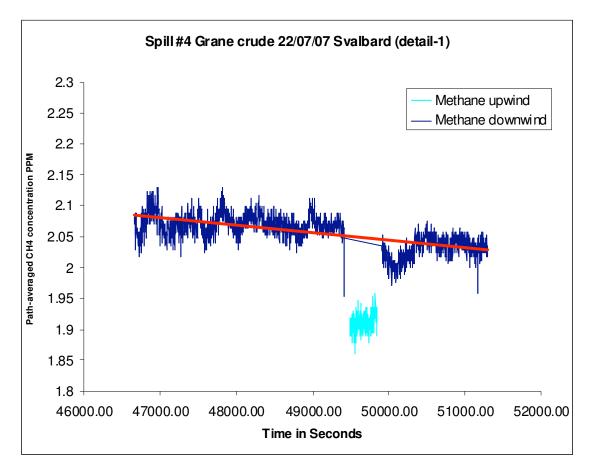


Figure 9: Spill #4 of Grane crude. A simple straight line fit to the concentration decay suggests it is likely to take at least 20,000 seconds to return to zero offset.

4. DISCUSSION OF RESULTS & SUGGESTIONS

The mass emission rates and inferred total methane contents from the spills are given in Table 1. They show a progressive increase in representative methane mass emission rates and still greater increase in the estimates of total methane emissions during the spills. Furthermore, the durations of the emissions seemed also to progressively increase through the test series.

Table 1: The mass emission rates and total methane content of the spills; as inferred from the average concentration enhancement, duration and windspeed.

	Temp	windspeed	Release Rate S	Mass released	% by mass of 200
	С	m/sec	kg/sec	kg	litres of oil
spill 1	-13.0	1.5	0.000024	0.043	0.023
spill 2	-9.5	1.5-20	-	-	-
spill 3	-9.0	3.0-4.0	0.000034	0.130	0.069
spill 4	-5.5	4.0	0.000044	0.400	0.213

Can these results be taken at face value or are other factors affecting the measurements or emissions behaviour? It is clear from the graphs presented that there is a progressive increase in the strength and persistence of methane emissions through the spill series. Interference of background or contamination-related signals cannot be invoked as a confusing mechanism: as the ΔC signals clearly all commence at the spill time, and are referenced to local atmospheric background levels. Thus we believe the observed changes in concentration are real and it is the emissions behaviour of the spills that is changing through the course of the test series.

We list below a few potential mechanisms/processes that might contribute to explaining the observed behaviour. Useful additional input may be available from the oil & water samples taken as part of the separate ageing and ignitability tests. These factors should be considered when designing future spill programmes.

- Is a greater proportion of the oil's methane content absorbed by the water in earlier spills than in later spills? If so, this would correspondingly reduce the methane emissions to atmosphere for the early tests -which is what we have seen.
- If there was a progressive build-up of methane/hydrocarbons dissolved in the water of the spill channel and combustion pond (which were not segregated) this might lead to increasing methane emissions for later spills. In effect, as the degree of hydrocarbon saturation of the closed water system increases, more methane escapes from the oil into the atmosphere. (The water in the water flume and combustion pond was not changed during the spill programme).
- At the end of each spill, the oil was burnt to clear the area. Thermal cracking of larger hydrocarbon molecules –induced by the intense thermal radiation from the optically thick pool fire- may lead to enhanced light hydrocarbon content of the water.
- Breaking down of heavier hydrocarbons (either during the pool fires, by exposure to ultra-violet/sunlight, or perhaps via bio-degradation) might be putting additional methane into the water system.
- The progressive increase in air temperature during the test programme may be a factor: increasing rates of any biodegradation, volatility; but also decreasing methane's

solubility in the water –thereby enhancing the direct transfer of methane from the oil into the atmosphere.

The accelerated weathering of these tests will have dramatically increased the rate of removal of methane from the oil into the water. In particular, the intense shearing (produced by the propellers) increases the oil/water contact area and removal of methane from the oil. For normal oil spills into seawater these processes are absent, and water adjacent to the oil would become saturated with methane: reducing the rate of methane removal. Consequently, normal spills would be expected to have dramatically more enduring methane emissions to the atmosphere than these accelerated weathering spills.

4.1. Suggestions

- Measurements should be made of methane emissions from oil spills under conditions
 more representative of the real spills it is hoped to detect and locate: quiescent oil pools
 on water, melt pools on ice, oil pools amongst water and ice, and spills onto ice
 subsequently covered by snow/ice.
- A more precise analysis should be made of the methane, ethane and other volatile components of stabilised Grane crude. Other species may offer significantly greater detectability than methane.

5. COULD METHANE EMISSIONS FROM REAL OIL SPILLS BE DETECTABLE BY AN AIRBORNE SENSOR?

Consider a hypothetical spill of 1000 tonnes of crude oil into seawater. Using the lowest (most conservative) value for methane content reported here, we would expect that oil to contain ~200kg of methane. Previous measurements of spills into open drift ice (40-60% ice cover) show that after 2-3 hours a reasonable film thickness to expect would be ~1mm, [5]. In such a case the 1000 tonne spill would cover an area of 1 km². If we assume the accelerated weathering process increases the ageing rate by a factor of 20 (a guess) then we would expect real spills to have a lifetime ~20 times that seen in these experiments. Thus, from our observation of Spill #4, we might expect a real spill to emit methane for ~400,000s or 100+ hours, during which its average methane emission rate would be ~2kg/hr.

Using the above release rate, source area, and assuming a 5m/sec wind under Pasquil Gifford stability class D conditions; we use a simple Gaussian plume gas dispersion model to calculate the resulting concentrations, [4]. Under these conditions, an aircraft flying at 80m altitude would see the methane concentration versus range relationship shown in Figure 10. Current generation methane sensors are capable of ~200 PPT precision (1 PPT=1E-12): so such an emission rate would be detectable out to ~5km. Greater methane content, or greater emission rates in the early phases of a spill (both seen in these experiments) would each increase the range out to which the spill could be detected. Furthermore, the rate of atmospheric dilution decreases (compared to the predictions of the simple Gaussian plume model) once gas reaches the top of the atmospheric boundary layer, which for typical arctic conditions might be just a couple of hundred metres. This would typically increase gas concentrations above those shown in Figure 10, for ranges of greater than 1 to 2km.

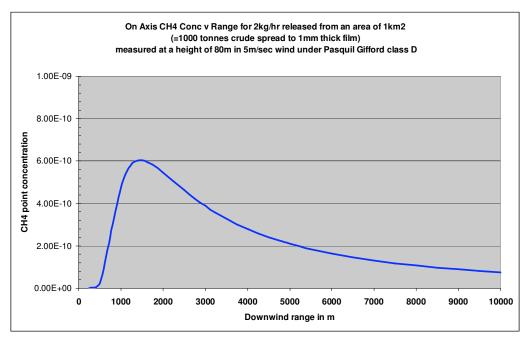


Figure 10: Centreline methane concentration versus range resulting from a 2kg/hr methane release from an area of 1 km², modelled using a simple Gaussian plume dispersion model. Current methane sensors can provide a precision of ~200 PPT, rendering such emissions detectable out to a range of ~5km.

If the gas sensor were mounted on a surface vehicle, such as a boat, rather than on an aircraft, then the measured concentrations will be significantly greater and hence more easily detected. Figure 11 shows the concentrations for the same spill and atmospheric conditions as Figure 10 but with the sensor at a height of 10m. The range of detectability is only slightly greater: 5.5km rather than 5km; but the concentrations are considerably greater at shorter ranges, significantly improving the detectability of the methane plume.

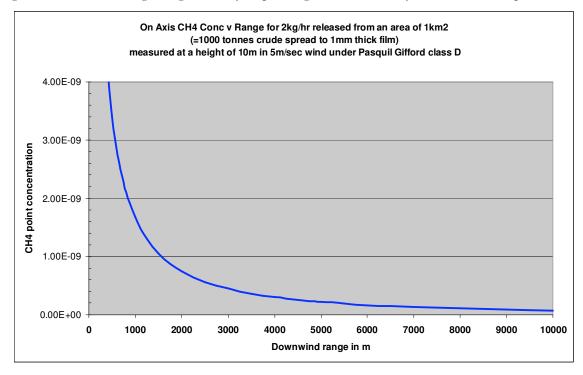


Figure 11: Centreline downwind methane concentration versus range resulting from a 2 kg/hr methane release from an area of 1km² modelled using a simple Gaussian plume dispersion model -but with the sensor at a height of 10m. Current methane sensors can provide a precision of ~200 PPT, rendering such an emission detectable out to a range of ~5.5km but with significantly greater concentrations and detectability at shorter ranges.

6. CONCLUSIONS

- 1. We have been able to quantify methane emission rates from crude oil spills into icy waters; these ranged from 24E-6 to 44E-6 kg/sec for these 200litre spills of stabilised Grane crude oil.
- 2. We observed an apparent progressive increase in the: methane release rate, persistence of emissions and total mass of methane detected through the spill series. We have suggested mechanisms that might account for this.
- 3. The inferred levels of methane content are all greater than would be expected from the compositional analyses provided to us: they ranged from 0.02 to 0.21% by mass; rather than the expected methane content of <0.01%. We believe our figures for total methane content of the crude are distorted by experimental factors related to the accelerated spill procedures used.
- 4. Based on our most conservative estimate of total methane content, representative arctic meteorological conditions, and assumptions on the likely duration of emissions from real spills, we have shown that currently available gas sensor technology would be capable of detecting a 1000 tonne spill of Grane crude from a range of up to 5km or more.

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REFERENCES

- [1] Sintef, 2006; JIP (Joint Industry Programme): Oil Spill Contingency for Arctic and Ice-infested waters; file code: 800358, 19-05-2006.
- [2] Statoil PKS, 2004; Crude Oil Assay, Grane 2003 report issued; 16:02:04
- [3] Dickins, D., Liberty L., Hirst W., Bradford J., Jones V., Zabilansky L., G. Gibson G., and J. Lane. 2005. New and Innovative Equipment and Technologies for the Remote Sensing and Surveillance of Oil in and Under Ice. proceedings 28th Arctic and Marine Oil-spill Program Technical Seminar, Calgary, June 2005.
- [4] Hirst, B., Gibson, G., Gillespie, S., Archibald, I., Podlaha, O., Skeldon, K.D., Courtial, J., Monk, S., and M. Padgett. 2004. Oil and Gas Prospecting by Ultra-sensitive Optical Gas Detection with Inverse Gas Dispersion Modelling. Geophys. Res. Letters, v. 31, pp. 112-115.
- [5] S.L. Ross Environmental Research Ltd and D.F. Dickens Associates Ltd, 1987; Field Research Spills to Investigate the Physical and Chemical Fate of Oil in Pack Ice. Environmental Studies Revolving Funds Report No. 062, Ottawa, 118p.

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