

Oil Spill Field Trial at Sea: Measurements of Benzene

Exposure

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Abstract

Objectives: Characterize personal exposure to airborne hydrocarbons, particularly carcinogenic benzene, during spill of two different fresh crude oils at sea.

Methods: The study included 22 participants taking part in an «oil on water» field trial in the North Sea. Two types of fresh crude oils (light and heavy) were released six times over two consecutive days followed by different oil spill response methods. The participants were distributed on five boats; three open sampling boats (A, B and C), one release ship (RS) and one Oil Recovery (OR) vessel. Assumed personal exposure was assessed *a priori*, assuming high exposure downwind and close to the oil slick (sampling boats), low exposure further downwind (100-200 m) and upwind from the oil slick (main deck of RS and OR vessel), and background exposure indoors (bridge of RS/OR vessel). Continuous measurements of total volatile organic compounds (TVOC) in isobutylene equivalents were performed with photoionization detectors (PIDs) placed in all five boats. Full-shift personal exposure to benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene and n-hexane was measured with passive thermal desorption tubes (ATD).

Results: Personal measurements of benzene, averaged over the respective sample duration, on day 1 showed that participants in the sampling boats (A, B and C) located downwind and close to the oil slick were highest exposed (0.14-0.59 ppm), followed by participants on the

RS main deck (0.02-0.10 ppm) and on the bridge (0.004-0.03 ppm). On day 2 participants in sampling boat A had high benzene exposure (0.87-1.52 ppm) compared to participants in sampling boat B (0.01-0.02 ppm), on the ships (0.06-0.10 ppm), and on the bridge (0.004-0.01 ppm). Overall the participants in the sampling boats had the highest exposure to all of the compounds measured. The light crude oil yielded a five times higher concentration of TVOC in air in the sampling boats (max 510 ppm) than the heavy crude oil (max 100 ppm), but rapidly declined to <20 ppm within 24 min after release of oil, indicating short periods of exposure.

Conclusions: The personal exposure to benzene downwind and close to the oil slick during spills of light crude oil was relatively high, with concentration levels approaching the OEL for several participants. For bulk spill scenarios like in this study, cleanup should not be initiated the first 30-60 min to allow for evaporation, while appropriate personal protective equipment (PPE) should be used in continuous spills when working downwind and close to the oil slick.

Keywords: benzene exposure; fresh crude oil; cleanup personnel; marine oil spill; TVOC

Introduction

The Norwegian Clean Seas Association for Operating Companies (NOFO) and the Norwegian Coastal Administration (NCA) have conducted «oil on water» field trials in the North Sea for one week in June almost yearly since the early 80's. The purpose is to create realistic, full-scale conditions for research experiments and oil spill response in order to verify, maintain and develop the Norwegian response methods. Cleanup of oil close to source and as soon as possible is part of the oil spill preparedness strategy and as a result the current oil spill preparedness consists of 27 continuously manned Oil Recovery (OR) vessels operating on the Norwegian Continental Shelf (NCS).

Production and transport of petroleum offshore can lead to oil spills caused by blow-outs or leakage from pipelines and oil tankers. Cleanup personnel are at risk of exposure to volatile organic compounds (VOCs) such as benzene during oil spill response that are mainly taken up by inhalation, but can also be absorbed through the skin (International Agency for Research on Cancer, 2012). Benzene is a confirmed human carcinogen associated with

hematotoxic effects, also after exposure to low concentrations of benzene (Health council of the Netherlands, 2014; Kirkeleit *et al.*, 2008; Vlaanderen *et al.*, 2010). Exposure could particularly be high in blow-outs when fresh oil is continuously formed on the sea surface and the evaporation of VOCs is high, but there is also a risk of exposure in bulk spills if cleanup personnel or offshore workers are nearby when the spill occurs.

The main oil properties affecting the fate of spilled oil at sea are volatility, viscosity and pour point (International Tanker Owners Pollution Federation, 2011). Oils are also classified in four groups based on the oils specific gravity, often expressed as American Petroleum Institute gravity (API°). Most oils on the NCS are high API grade (>35°) oils from group 1 and 2, called light crude oils and condensates, and may form thin oil films that are difficult to cleanup with traditional methods (Johansen *et al.*, 2003). Because high API grades usually are associated with a high content of VOCs the potential response strategies for these oils needs to include documentation of the risk for human exposure.

Although a few studies have tried to measure the personal exposure to hydrocarbons during oil spill cleanup there is still a lack of knowledge about the concentrations in the working atmosphere. No exposure to benzene was measured in personal samples collected during the Deepwater Horizon (DWH) spill of light crude oil because many of the VOCs dissolved in the water before reaching the sea surface (Ahrenholz and Sylvain, 2011). In the Prestige and Nakhodka spills of heavy fuel oil the measured benzene exposure was low because the content of VOCs was low (Morita *et al.*, 1999; Pérez-Cadahía *et al.*, 2007).

Several models have been developed for prediction of human exposure during spills, but the models lack input of actual personal exposure data. The objective of this study was therefore to characterize the potential personal exposure to airborne benzene and other harmful VOCs during spill of different fresh crude oils at sea.

Methods

Study design and crude oil composition

The 2016 «oil on water» field trial took place at the Frigg field in the North Sea about 150 km northwest of Stavanger, Norway. The trial, approved by the Norwegian Environmental Agency, was carried out to test different response methods and was used as a platform to study the risk of human exposure during release of fresh crude oils in open sea. Two types of

fresh crude oils from the NCS were released six times over two consecutive days (Table 1). Paraffinic light crude oil (53°API) was used to test water treatment of thin oil films with and without the use of dispersant (Dasic Slickgone NS). The viscosity of the oil was low (1 mPa s, at 13°C), and the content of benzene (1.02 wt%) and sum of selected C₅-C₁₀ VOCs (28.6 wt%) was high. Heavy crude oil (26°API) was used to test burning of crude oil with and without the use of oil herders (ThickSlick 6535), a liquid agent used to concentrate the oil to a thickness suitable for burning. The heavy crude oil had high viscosity (64 mPa s, at 13°C) and a low content of benzene (0.03 wt%) and sum of selected C₅-C₁₀ VOCs (3.7 wt%).

On day 1 the wind increased from 3 to 5 m/s throughout the day and there were no breaking waves. On day 2, oil was released in breaking waves and 7 m/s wind. The oils were released through a floating weir release system on starboard side of the release ship. Light crude oil was released (1.5-2 m³/min) in 6-7 minutes almost parallel with the wind and produced an initial oil film about 30 m wide, 400 m long and 0.3 mm average thickness. Heavy crude oil was released (2 m³/min) in 3-4 minutes as a point release and produced an initial oil film about 35 m wide, 50-80 m long and 3.0 mm thick. The different response methods for the two types of oil required different amounts of oil.

Participating boats and positioning

Two large (75-95 m) command ships; one release ship (RS) and one Oil Recovery (OR) vessel, and three small (5-8 m) open sampling boats; A, B and C, participated in the field trial. All five boats were moving during the exercise according to work task, but Figure 1 describes the starting position of the boats in the six releases of oil. Oil was released against the wind (in best efforts) from the RS in all six experiments, and the ship kept its position upwind from the oil slick. The OR vessel was positioned about 100-200 m downwind from the oil slick during release and started oil spill response, both upwind and downwind from oil slick, after 30-180 minutes. Sampling boat A performed air monitoring about 50 m downwind from the oil slick. Sampling boat B and C were used for taking oil samples, herding and ignition. Sampling boat B was mainly positioned downwind, but also did work upwind and inside the oil slick, while sampling boat C stayed mainly downwind, but at varying distances from the oil slick.

Sampling strategy

A total of 73 people, distributed on the two ships, were involved in the field trial. The work tasks included navigation, exercise management, oil application, cleanup and sampling, drones and aerostat operation, air sampling, ship maintenance, kitchen service and observations. Everyone involved were grouped *a priori* based on assumed exposure to hydrocarbons (Table 2). Of 18 people assumed to be exposed all but one person consented to participate in the study (n=17). Participants in the exposed group were located in all five boats and consisted of researchers, naval staff and cleanup personnel. A few people located on the bridge of either ship assumed not to be exposed (n=5) were invited to participate to measure background exposure. This group consisted of researchers and contingency advisors. In total 22 participants were recruited, 21 male and 1 female. Based on Norwegian occupational exposure limits and exposure modelling no participants were allowed to be in areas exceeding 1800 ppm TVOC. The study was approved by the regional committee for medical and health research ethics, western Norway.

Selected compounds and occupational exposure limits (OEL)

Benzene, ethylbenzene and naphthalene, have been classified as certain or possible carcinogens, while toluene, xylenes and n-hexane can affect the nervous system (International Agency for Research on Cancer, 2012; United States Environmental Protection Agency, 2014). The Norwegian 8-hr occupational exposure limit (OELs) for benzene (1 ppm), ethylbenzene (10 ppm), naphthalene (20 ppm), n-hexane (30 ppm), and toluene and xylene (37.5 ppm) is set on the basis of technical, economic and medical assessments (Norwegian Labor Inspection Authority, 2014). For longer work shifts (12 hours) the recommended OEL for benzene is 0.6 ppm (Petroleum Safety Authority Norway, 2006) while the 15-min short-term exposure limit (STEL) is 3 ppm benzene. No OEL for VOCs in general exists.

Air sampling and analytical analysis

Photoionization detectors (PIDs) were set up on the main deck of both ships and placed in all the sampling boats to compare the air concentration of total volatile organic compounds (TVOC) in the different boats. Several types of PIDs were used; MiniRAE 3000 (RAE Systems

Inc., San Jose, US-CA), VX500 (Industrial Scientific Corp., Oakdale, US-PA) and Firstcheck+ (Ion Science Ltd., Fowlmere, UK). All were equipped with a 10.6 eV lamp and calibrated with isobutylene (100 ppm) to continuously measure TVOC (C₅-C₁₄) in air in isobutylene equivalents every 1-10 sec, with a measurement range of 0.1-15000 ppm.

Full-shift personal exposure to the selected compounds (C₆-C₁₀) was measured with passive thermal desorption tubes (TD-tubes, Markes int/PerkinElmer, Boston, US-MA) packed with Tenax TA (porous polymer, 220 mg) with a mesh size of 35/60. Tubes were attached to participants' helmet outside the protective mask (exposed) or chest pocket (background). The work shift started when the participants arrived on deck or in the sampling boats to prepare for the first release, and ended when arriving in the locker rooms after the last release. Sample duration, corresponding to the work shift, varied from 5.4-14.6 h on day 1 and from 5.2-14.0 h on day 2. Outdoor smoking was not allowed, and sampling equipment was left in the locker rooms (no smoking area) during breaks. After sampling the tubes (n=42) were stored cold before shipping to SINTEF Molab Oslo for quantitative/semi-quantitative analysis (ISO 16017-1 and ISO 16017-2) with thermal desorption - gas chromatography - mass spectrometry (TD-GC-MS). The limit of detection (LOD) for the compounds measured was 0.001 ppm and 0.005 ppm for the longest and shortest sampling time respectively. The personal exposure is presented as the measured concentration of benzene over the respective sampling time.

Results

TVOC measurements

On day 1 the light crude oil yielded about five times higher TVOC concentrations in air in the sampling boats than the heavy crude oil (Fig. 2). The concentration rapidly declined to <20 ppm within 48 min and 24 min in the releases of light and heavy crude oil respectively. The highest concentrations (max 510 ppm) of TVOC were measured in sampling boat A during release 1 and in sampling boat C (max 502 ppm) in release 2. The TVOC concentration was much lower during both release 3 (max 70 ppm) and release 4 (max 100 ppm), measured in sampling boat A. Two very short periods of elevated TVOC concentrations in air were measured during release 4 in sampling boat C when the boat moved inside the oil slick to prepare for ignition of the oil. Because of technical failure PID logs were not retained for

sampling boat B in any releases and sampling boat C during release 1 and 3. Elevated concentrations of TVOC in air was only detected on the OR vessel for a few minutes (6 min, max 104 ppm) during release 2, and on the RS for less than a minute during release 3 and 4 (max 114 and 151 ppm respectively). In release 5 (of heavy crude oil) TVOC was detected (max 20 ppm) in sampling boat A. Application of dispersant and herder did not produce elevated TVOC concentrations.

On day 2 elevated TVOC concentrations (up to 500 ppm) in air were measured in sampling boat A and the concentration remained high (300-500 ppm) during the 30 min of downwind sampling in contrast to day 1. Sampling boat B moved inside the oil slick 10 min after release of oil and measured elevated concentrations of TVOC (0-180 ppm) for a 25 min period with a short period of high TVOC (max 335 ppm) about 20 min after release. Less than 10 ppm was measured on the RS, and no PID logs were retained on day 2 for the OR vessel due to technical failure.

Personal exposure

A total of 22 personal air measurements of benzene were collected on day 1 (Fig. 3). The exposure was highest for participants in the sampling boats (0.14-0.59 ppm), followed by participants on the RS (0.02-0.10 ppm) and on the bridge (0.004-0.03). No participants worked on the main deck of the OR vessel. The average work shift was 12 h, but the work shifts varied from 5.4-14.6 h. The high variability in exposure between participants in sampling boat B and in C on day 1 was due to one participant in each boat who worked only during release of one of the oil types.

A total of 20 personal air measurements of benzene were collected on day 2 (Fig. 3). The exposure was high among participants in sampling boat A (0.87-1.52 ppm) relative to participants in sampling boat B (<0.02 ppm), on the main deck of the RS (0.06-0.10 ppm) and the OR vessel (0.002-0.005ppm), and on the bridge (0.004-0.01 ppm). No participants worked in sampling boat C. The average work shift was 8.3 h, but work shifts varied from 5.2-14.0 h.

When merging the personal measurements for the two sampling days (Table 3) the exposure differed between the three main groups (sampling boats, ships and bridge), and overall the participants in the sampling boats had the highest exposure to all of the

compounds measured, followed by participants on the ships and on the bridge. All compounds except for benzene were low compared to respective OELs.

Discussion

The measured personal exposure to benzene indicates that cleanup personnel working close to an oil slick are potentially exposed to benzene concentrations close to the relevant occupational exposure limits (OEL). In this study the participants in the sampling boats located downwind and closest to the oil slick had considerably higher exposure than participants on the ships located further downwind (100-200 m) or upwind. The total volatile organic compound (TVOC) measurements indicate that the periods of exposure were short because of the fast evaporation, and as expected the light crude oil yielded about five times higher concentrations of TVOCs than the heavy crude oil because the heavy crude oil had a much lower content of VOCs and a thicker oil slick that limits the evaporation.

The highest mean benzene exposure (0.43 ppm) was found for participants in the sampling boats located downwind and close to the oil slick, but the variability within the group and between the two days was high. Some of the variability between participants within the groups was due to variation in length of the work-shifts and also due to two participants on day 1 who only participated in spill of one of the respective oil types. Furthermore, the PID measurements indicated that the air concentration of TVOCs was highly dependent on the type of oil, time after release, position relative to oil slick and weather conditions. Thus, most of the personal exposure measured was during the releases of light crude oil, indicating a short exposure time on both days. The breaking wave conditions on day 2, and possibly better positioning of the sampling boat, might also partly explain the variability between days as these conditions might have caused more VOCs to evaporate. The low mean benzene exposure (0.05 ppm) found for participants on the ships indicate that exposure is low when working upwind or further downwind (>100 m). This is in agreement with TVOC measurements for the release ship (RS), located upwind, that only measured two peaks of TVOC probably caused by handling of equipment used to release oil, and the Oil Recovery (OR) vessel, located further downwind, that only measured TVOC during release 2 of light crude oil when moving close downwind of the oil slick to initiate

cleanup. As expected the lowest mean benzene exposure (0.02 ppm) was found for participants on the bridge.

No participants had benzene levels exceeding the Norwegian 12-hr OEL (0.6 ppm) on day 1, but two participants (1.34 and 1.52 ppm) exceeded both the 8-hr OEL (1 ppm) and the 12-hr OEL on day 2. The TVOC measurements showed that the exposure were characterized by repeated peak exposures, hence it is likely that some participants exceeded the short-term exposure limit (STEL) for benzene (3 ppm) several times during their work shift. Because of the hematotoxic health effects most likely also associated with low concentrations (<1 ppm) of benzene (Rappaport *et al.*, 2012; Vlaanderen *et al.*, 2010) an 8-hr OEL of 0.2 ppm benzene has been suggested (Health council of the Netherlands, 2014). All participants in the sampling boats would approach or exceed this level on day 1. Exposure to toluene, ethylbenzene, xylenes, naphthalene and n-hexane did not exceed respective OELs.

During the Deepwater Horizon (DWH) oil spill the measured concentration of VOCs on the two vessels operating closest to the ongoing release were low (<0.01 mg/m³) and benzene was not detected in any of the 19 full-shift (12 h) personal samples (Ahrenholz and Sylvain, 2011). This was explained by dissolution of many of the VOCs, including benzene, before reaching the sea surface (>1000 m above). In the Prestige spill of heavy fuel oil the highest concentration of TVOC (<0.5 mg/m³) and mean benzene exposure (<2.4 ppb) averaged over 4 hours in the most exposed group was low (Pérez-Cadahía *et al.*, 2007). Also in the Nakhodka spill of similar heavy fuel oil the highest concentration of VOCs (<1.51 ppm) and mean benzene exposure (<1.1 ppb) averaged over 2 hours was low (Morita *et al.*, 1999). The low exposure can be explained by the low content of VOCs in heavy fuel oils and cleanup carried out on the shoreline when the most volatile VOCs would have already evaporated. Because of the limited data published on hydrocarbon and benzene exposure during oil spill cleanup, several models for estimating the exposure have been made. However, some models underestimate the exposure (Lehr, 1996) and some models overestimate the exposure (Lehr *et al.*, 2002), while other models lack input of real exposure data (Hanna and Drivas, 1993; Thayer and Tell, 1999).

In order to characterize the personal exposure in more detail the measurements should have been made for light and heavy crude oil separately. This would also have made the results more available as input in exposure models, but logistical constraints did not allow for this. Because both personal and real-time measurements were carried out in this study,

the analysis of the PID measurements made it possible to descriptively explain much of the variability in the personal exposure. The photoionization detectors (PIDs) were useful for locating the plume of VOCs and for comparing oil types and weather conditions. They were also used to make sure the TVOC levels were within the safety level (1800 ppm) assessed beforehand, and confirmed that there was no contribution of TVOC in air from fuel, exhaust, herder or dispersant, as expected.

Normally cleanup personnel will not be as close to the surface during oil spill cleanup as the participants in the sampling boats. Hence, the exposure measurements represent a worst case scenario for acute spills of relatively small sizes such as bulk spills from offshore installations or tankers. When spills occur the cleanup personnel need time to mobilize, and in bulk spills the personnel will probably not be at the spill site when benzene evaporates. In continuous spills however, there is a potential of exposure to benzene because fresh oil will continuously form on the sea surface leading to evaporation of benzene. Unless the spill occurs at great water depth (>500 m), appropriate personal protective equipment (PPE) should be used in continuous spills.

Conclusions

We found benzene exposure approaching and exceeding the OEL during spills of light crude oil. In our scenario exposure could have been avoided by waiting with cleanup for 30-60 min, in real oil spills however the exposure time will depend on oil type and the release conditions (subsea/surface, bulk/continuous). Appropriate PPE should be used the first hours in bulk spills of light crude oils high in VOCs if immediate cleanup of oil is necessary, and always in continuous spills when operating downwind. The oil operators on the Norwegian Continental Shelf (NCS) are in the process of implementing guidelines for human health during oil spill cleanup based on the findings of this study.

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