Oil spill into seawater

Evaporation and human exposure to benzene

Ingrid Gjesteland

Thesis for the Degree of Philosophiae Doctor (PhD)
University of Bergen, Norway
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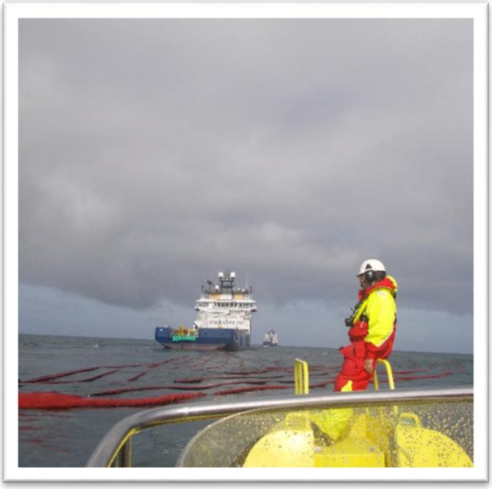

Scientific environment

This research study '*Oil spill into seawater: Evaporation and human exposure to benzene'* was carried out at the Research Group for Occupational and Environmental Medicine, Department of Global Public Health and Primary Care, Faculty of Medicine at the University of Bergen, Norway. The study was part of a PETROMAKS2 competence project for the oil production industry with the title '*Formation and behavior of thin oil films and evaluation of response methods including health, safety and environment*,' with SINTEF Ocean, Department of Environment and New Resources, as the project owner.

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Ingrid Gjesteland
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Abbreviations

1-OH	1-hydroxypyrene
ACGIH	American Conference of Governmental Industrial Hygienists
AM	Arithmetic mean
ANOVA	Analysis of variance
API	American Petroleum Institute
ATD	Automated thermal desorption
ADIOS	Automated Data Inquiry for Oil Spills
BEI®	Biological exposure index
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
DWH	Deepwater Horizon
ECHA	European Chemicals Agency
GC	Gas chromatography
GM	Geometric mean
GSD	Geometric standard deviation
IARC	International Agency for Research on Cancer
ITOPF	International Tanker Owners Pollution Federation
LC	Liquid chromatography
LOD	Limit of detection
mm	Millimeter
mPa.s	Millipascal per second
MS	Mass spectrometry
NCA	Norwegian Coastal Administration
NCS	Norwegian continental shelf

NOFO	The Norwegian Clean Seas Association for Operating Companies
OEL	Occupational exposure limit
OR	Oil recovery
OSCAR	Oil Spill Contingency and Response
OWM	Oil Weathering Model
PAH	Polycyclic aromatic hydrocarbon
PID	Photoionization detector
PPE	Personal protective equipment
ppm	Parts per million (ml/m^3)
RAC	Committee of Risk Assessment
REC	Regional Committees for Medical and Health Research Ethics
RS	Release ship
SPMA	S-phenylmercapturic acid
STEL	Short-term exposure limit
TD	Thermal desorption
TLV®	Threshold limit value
tt-MA	Trans,trans-muconic acid
TVOC	Total volatile organic compound
TWA	Time-weighted average
µmol/mol	Micro mole per mole
VOC	Volatile organic compound
Vol%	Percentage by volume
Wt%	Percentage by weight

Abstract

Background

The Norwegian oil spill preparedness focuses on developing response methods that limits the health risk of personnel performing response operations during oil spills at sea. Two types of crude oil, condensates and light crude oils, are in increasing production and transportation on the Norwegian Continental Shelf (NCS), and it has been assumed that these oils may form oil films that are too thin for effective recovery by traditional response techniques. Condensates and light crude oils may have a high content volatile organic compounds (VOCs), such as benzene, that evaporate when oil is spilled at sea. Some of these compounds are associated with adverse chronic health effects such as cancer and effects on the nervous system. Although several previous studies have attempted to measure or model the exposure levels during actual oil spills at sea, knowledge about personal exposure levels in air and biological uptake of volatile compounds is scarce. Also, the effect of using personal protective equipment (PPE) needs further documentation.

Aims

The main objective of this thesis was to gain more knowledge about personal benzene exposure levels during bulk release of fresh crude oil at sea. The objectives of Paper I was to measure the air concentration of VOCs evaporating from a thin oil film formed on the seawater surface by different condensates and light crude oils, and to study how physicochemical properties of the fresh oil affects the air concentration of benzene with time and temperature. The objective of Paper II was to study the personal exposure to benzene during a two-day field study at sea involving several releases of fresh crude oil. In Paper III the objective was to study the association between airborne exposure and biological uptake and the effectiveness of wearing PPE.

Material and methods

A total of nine condensates and light crude oils were included in an experimental bench-scale study. A glass chamber was filled with seawater before fresh oil was applied to form a thin oil film on the seawater surface. Tests were performed with each

oil at 2°C and 13°C with equal test conditions. Active automated thermal desorption tubes (ATD-tubes) were used to measure the concentration of specific VOCs in air 10 cm above the oil film in 5 min intervals for a total of 30 min. Continuous air measurements of total VOCs (TVOC) were also performed. Air concentration models were developed for benzene for the first 5, first 15 and last 15 min of sampling to identify determinants having a significant effect on the air concentration of benzene.

A total of 22 subjects were recruited during a full-scale field study at sea. Six releases of crude oil were performed over two consecutive days with two different types of fresh crude oil. Personal exposure to benzene was assessed a priori based on the participants work tasks, and three exposure groups (high, low or background) were developed. Continuous air measurements of VOCs were performed in each of the five boats to characterize the overall exposure levels. Full-shift personal exposure measurements were performed with passive ATD-tubes on both days of oil release and urine samples were collected pre- and post-shift to measure biological uptake. All subjects completed a questionnaire before and after their work-shift about their work, smoking habits and use of PPE.

Results

For all oils the highest air concentration of TVOC was measured within 2 min after application of oil, but the concentration rapidly declined to <14 % of the peak concentration within the 30 min of sampling. The TVOC concentration was significantly higher at 13°C than at 2°C during the first 5 and 15 min. The ATD measurements also indicated a rapid decline in the air concentration of benzene, toluene, ethylbenzene and n-hexane, while xylene and naphthalene did not show comparable decline with time. The air concentration models for benzene indicated that content of benzene in fresh oil and oil group (condensate/light crude oil) were significant determinants in the first periods of sampling (first 5 and 15 min). The total variance in the air concentration of benzene explained by these determinants was 63–67 %, while pour point could explain 73 % of the total variance in the last period of sampling (last 15 min). Although temperature was not a significant determinant in the model, the air concentration was higher at 13°C than at 2°C.

In the full-scale field study, the air concentration of TVOC was five times higher during release of light crude oil compared to heavy crude oil. The overall exposure levels were low, characterized by short periods (<1 h) of high exposure associated with release of oil. Subjects in the 'high exposure' group, located in the small boats close and downwind from the oil slick, were exposed to the highest air concentrations of benzene (range: 0.013-1.52 ppm), and four subjects exceeded the 12-hr occupational exposure limit (OEL) for benzene of 0.6 ppm. Five subjects who reported not wearing respirators had detectable concentrations (range: 0.5–3.3 µmol/mol) of S-phenylmercapturic acid (SPMA), a biomarker of benzene exposure, in post-shift urine, but the concentration did not exceed the recommended biological exposure index (BEI). Subjects wearing respirators did not have detectable concentrations of post-shift urinary SPMA, even when exposure levels exceeded the OEL.

Conclusion

Benzene evaporates rapidly from a thin oil film of condensate or light crude oil at both 2°C and 13°C, even when the content of benzene is the fresh oil is relatively high. However, evaporation appears to be slower for oils with a high pour point compared to oils with a low pour point. Personnel located close and downwind from an oil slick during the initial stages of a bulk spill of fresh light crude oil at sea may be exposed to benzene levels exceeding the OEL. Although biological uptake of benzene is possible, use of appropriate respirators prevents uptake at these exposure levels. The risk of exposure is mainly associated with the content of benzene in the fresh oil, but a high content of wax may prolong the time of exposure.

List of publications

PAPER I

Gjesteland I., Hollund BE, Kirkeleit J, Daling PS, Sørheim KR, Bråtveit M:

Determinants of airborne benzene evaporating from fresh crude oils released into seawater

Marine Pollution Bulletin. 2019; 140(March) p.395-402.

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PAPER II

Gjesteland I., Hollund BE, Kirkeleit J, Daling P, Bråtveit M:

Oil Spill Field Trial at Sea: Measurements of Benzene Exposure

Annals of Work Exposures and Health. 2017; 61(6) p.692-699.

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PAPER III

Gjesteland I., Hollund BE, Kirkeleit J, Daling PS, Bråtveit M:

Biomonitoring of Benzene and Effect of Wearing Respirators During an Oil Spill Field Trial at Sea

Annals of Work Exposures and Health. 2018; 62(8) p.1033-1039.

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1. Introduction

1.1 Background

The increased production of condensates and light crude oils in Norway the last years represent a challenge for the Norwegian oil spill preparedness [3]. It has been assumed that if these oils are spilled in calm sea conditions or a subsea blowout, they form thin oil films on the sea surface with less than 0.1–0.2 mm thickness, and today's traditional response methods, such as mechanical recovery, chemical dispersion and in-situ burning, are not effective on thin oil films. Although the lifetime of such thin oil films will depend on the oil's physicochemical properties (e.g. content of volatile compounds and wax) and environmental conditions (e.g. wind speed, sea temperature and wave activity), they are expected to have a short lifetime at sea due to high evaporative loss of volatile organic compounds (VOCs).

VOCs are low molecular weight compounds ($<C_{14}$) associated with adverse health effects including cancer and effects on the nervous system [4-9]. Short-term health effects that have been related to crude oil spill exposure includes respiratory symptoms, headache, nausea and irritation of skin, eyes, nose and throat [10, 11]. Any long-term effects are poorly described [12], and although genotoxic effects after exposure to oil spills have been reported, follow-up studies of cancer have not been performed [13]. The health and safety of cleanup personnel have a high priority in the Norwegian oil spill preparedness, and the Norwegian 'Ship Labor Act' requires that the workplace has the necessary procedures and equipment to prevent or reduce the risk to life and health [14]. Still, information about the airborne levels of VOCs during oil spills is limited, and knowledge about the effectiveness of personal protective equipment (PPE) is also lacking.

1.2 Norwegian oil production and transport

Oil was discovered in the North Sea almost 50 years ago [15]. Since the startup of oil production on the Ekofisk field in 1971, more than 100 fields have produced oil and gas on the Norwegian Continental Shelf (NCS). The NCS extends 200 nautical miles from the coastline from north to south and oil production takes place in the North Sea, Norwegian Sea and Barents Sea. Crude oil is continuously transported to the mainland from the offshore production fields either by tank ships or through a comprehensive network of pipelines. Additionally, blends of crude oil and refined oil products such as diesel oil/marine gas oil and fuel oil are also transported to and from shore. In recent years the transportation of petroleum products along the Norwegian coast has increased, especially transportation of crude oil from Russia [16]. Production and transportation of oil involves a risk of spill. Although only a few major (>300 m^3) oil spills have occurred on the NCS, several smaller acute oil spills occur every year [17]. A spill could be an acute bulk spill of oil from storage tanks, tank ships or general shipping traffic (i.e. fuel), or a continuous spill caused by a subsea blowout from production wells or leakage from pipelines transporting oil.

1.3 Oil spill preparedness

The Norwegian Coastal Administration (NCA) is in charge of coordinating the private, municipal and governmental preparedness [15]. They are responsible for the national preparedness and handle larger acute oil spills, while the municipalities handle minor acute oil spills caused by normal activities within the municipality. The Norwegian Clean Seas Association for Operating Companies (NOFO), who represents the operators on the NCS, are responsible for cleanup of oil spills related to the petroleum industry. About 1,000 trained personnel, located on various ships and at shore throughout the country, are able to participate in the acute phase of an oil spill response operation in Norway [18].

Contingency plans with strategic, tactical and practical assessments and actions have been developed to prevent or limit damage caused by acute oil spills. Today’s main strategies include remote sensing (i.e. aerial surveillance), mechanical recovery, chemical dispersion and in-situ (i.e. on site) burning [19]. Remote sensing from airplanes or satellites with radars and infrared cameras is essential for detecting oil spills, while the response methods depend on oil type and environmental conditions (sea temperature, sea state, wind, ice coverage etc.). Mechanical recovery is currently considered the most common and preferred strategy, as this method involves recovery of surface oil with a combination of booms and skimmers. Oil spill dispersants break up the oil slick into smaller droplets to speed up the natural dispersion of oil by bacteria, while in-situ burning involves burning of oil directly on the sea surface.

The main principle of the preparedness strategy is to combat oil close to the spill source to prevent spreading and drifting of oil to shore (Figure 1), hence the oil may be relatively fresh when response operations are initiated [20]. Because of the risk of explosion, response operations must take place at a safe distance from the source, about 1 km from the discharge point, corresponding to about 2 hours of oil weathering time.

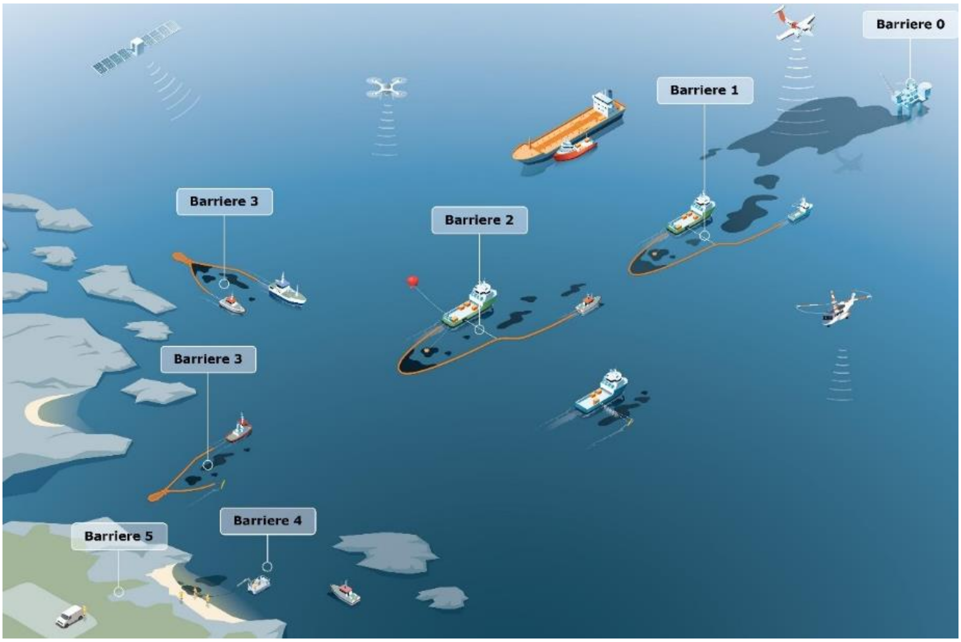


Figure 1. Oil spill response strategies according to barrier; 1, close to the source; 2, between the source and the coast; 3, near the coast; 4, along the coastline; 5, at shore (Courtesy of NOFO).

1.4 Crude oil properties

1.4.1 Chemical properties

Crude oil is a term for liquid petroleum after separation from water and gas [21]. It is a complex mixture of thousands of chemical compounds, mainly hydrogen and carbon, termed hydrocarbons, and small amounts of oxygen, nitrogen, sulphur and trace metals, termed non-hydrocarbons (Figure 2). The hydrocarbons are divided into paraffins, naphthenes and aromatics. The paraffins include straight-chain n-alkanes (e.g n-hexane) and branched-chain iso-alkanes. Waxes ($>C_{20}$) are an important subgroup of paraffins and normally comprise between 2–15 wt% of crude oil. The naphthenes include cycloalkanes with one or more saturated rings (i.e. single bonds only). The aromatics are unsaturated cyclic hydrocarbons (two or three bonds) that are divided into mono-ring (benzene, toluene, ethylbenzene and xylene, BTEX), di-ring (naphthalene) and poly-ring aromatics (polycyclic aromatic hydrocarbons, PAHs). Resins and asphaltenes comprise compounds with high molecular weight. Each crude oil has a unique combination of these compounds, and are often referred to as ‘light’ or ‘heavy’ based on the relative amount of high and low molecular weight compounds.

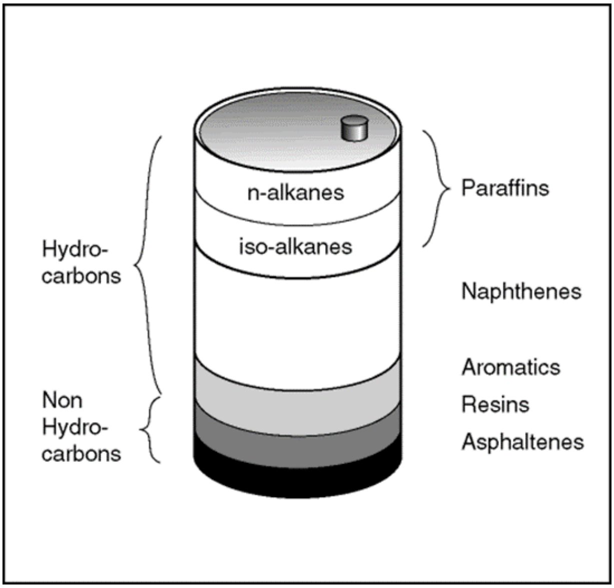


Figure 2. Chemical composition of crude oil (Courtesy of SINTEF Ocean).

1.4.2 Physical properties

The chemical composition of an oil will affect its physical properties. The most important physical properties that affects the behavior of crude oil spilled at sea includes density, volatility, viscosity and pour point [22].

Density

The density of a fresh crude oil depends on the molecular weight of its compounds and usually range from 0.78 to 0.95 mg/l at 15.5°C. The density is often expressed by the American Petroleum gravity (°API), which is an inverse measure of an oil's density relative to the density of water [23]. The API gravity is used to classify crude oils as heavy (<22.3°API), medium (22.3–31.1°API) or light (>31.1°API) crude oil.

Volatility

The volatility represents the oils ability to evaporate (i.e. change from liquid to gaseous form) and is directly related to the substance's vapor pressure. The greater the amount of components with a high vapor pressure, the more volatile the oil is.

Viscosity

The viscosity represents an oils resistance to flow and ranges from < 1 to >2000 mPa.s for fresh crude oils. It increases with decreasing temperature and increasing water uptake (emulsification). The viscosity also increases with evaporation because the heavier, more viscous compounds remain within the oil (Mackay/Zagorski, 1982).

Pour point

The pour point is the temperature below which the oil will not flow and becomes semi-solid and ranges from <-40 to >30°C. Pour point and wax content is highly correlated, thus for oils with a high wax content the pour point will increase dramatically with evaporation.

1.5 Weathering

Oil spilled at sea is affected by natural weathering processes such as evaporation, dissolution, dispersion, emulsification, spreading, drifting, sedimentation, biodegradation and oxidation (Figure 3) [24]. The effect of the different weathering processes differs between oils due to large variations in the physical and chemical properties between oils from different oil fields. The weathering process is also affected by environmental conditions. Weathering affects the oil mass balance and cause changes in the oil properties with time that are of importance for oil spill response. The main weathering processes affecting oils during the early stages of an oil spill is spreading, evaporation, dispersion, emulsification and dissolution [22].

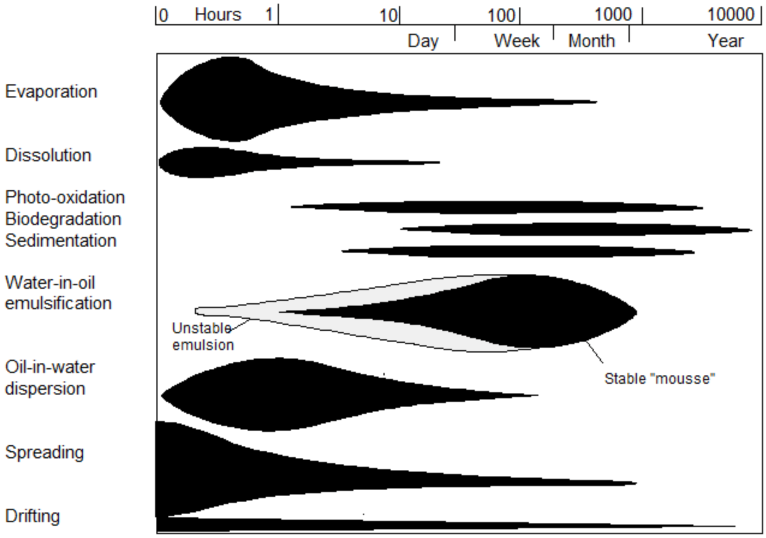


Figure 3. Weathering processes of crude oil and relative importance with time on a logarithmic scale. Adapted from Mackay et al., 1983 [25].

Spreading is an important process that determines the area and thickness of the oil slick [24]. For oils with low viscosities and low densities the spreading may be vast and the final film thickness very thin (<0.5 mm). Evaporation and natural dispersion are important processes that naturally remove oil from the sea surface. Evaporation is the most important weathering process, and oils with a low content of heavier compounds may lose more than 50% of their original volume after a few hours/days on the sea surface due to evaporation, especially if the sea temperature is high. The evaporation is highest at the beginning of a spill and will rapidly decline with time. Dissolution of water-soluble oil components from the oil slick into the water column also occurs during spills in calm weather, however this process is insignificant in relation to evaporation [26, 27]. Natural dispersion involves mixing of oil into the water mass by creating smaller oil droplets, but requires energy in the form of wave activity. Emulsification (water uptake) also requires energy (>5 m/s wind speed), however a slow water uptake may occur in calmer weather. The formation of water-in-oil emulsions contributes to keeping oil on the sea surface and slows down evaporation and natural dispersion.

1.5.1 Weathering models

Oil weathering and oil drift trajectory models have been developed in order to predict the various weathering processes that takes place when oil is spilled at sea. These models are essential in contingency planning and therefore several numerical models exist (e.g. SINTEF OWM, OSCAR, ADIOS and OILMAP) [28, 29]. Laboratory data of fresh and weathered oil samples are entered into the models to predict how the oil's properties change with time at chosen environmental conditions [30]. Some of the models also predict the time window for different operational response methods.

1.5.2 Oil categories

In relation to weathering, the crude oils can be divided into three main categories; (1) crude oils, (2) light crude oils and (3) condensates, based on the content of heavier components, evaporative loss, emulsifying properties (i.e. water uptake) and final oil film thickness, as presented in Table 1 [21]. Crude oils have a higher relative content of heavier components than condensates and light crude oils and therefore a lower evaporative loss (<50 vol%) during spills. Crude oils are able to form stable water-in-oil emulsions due to the content of heavier components, such as resins and asphaltenes, which reduces spreading of the oil on the sea surface and creates an estimated film thickness of 1 mm. In contrast, the evaporative loss of both condensates (>70 vol%) and light crude oils (50–70 vol%) is high due to the high content of light components. The light crude oils may form emulsions with low stability because they may contain a low amount of asphaltenes and heavier waxes, while the condensates do not form emulsions. The final (terminal) film thickness used in the SINTEF oil weathering model (OWM) is 0.05 mm for condensates and 0.5 mm for light crude oils. Furthermore, some condensates and light crude oils contain a large amount of waxes (up to 8 wt%) [31]. The wax may precipitate and contribute to an increased pour point during weathering, which may cause the remaining oil residue to become semi-solid on the sea surface and prevent evaporation [32, 33].

Table 1. Oil categories in relation to weathering and relative content of chemical components.

Oil category	Evaporative loss* (vol%)	Terminal film thickness (mm)	Emulsion	Relative content of		
				Heavier components	Benzene	Wax
Crude oil	<50	1	Stable	High	Low	High
Light crude oil	50–70	<0.5	Unstable	Low	Medium/High	Medium/Low
Condensate	>70	<0.05	None	None	Medium/High	Medium/Low

*Expected evaporative loss of hydrocarbons after one week of weathering.

1.5.3 Thin oil films and response strategies

Because of the increased production and transport of condensates and light crude oils these oils are of particular interest in the development of new preparedness plans [3]. Condensates and light crude oils will presumably break up naturally by wind and waves, with the majority of the oil evaporating within a matter of days. In calm weather conditions or in a subsea blowout however, these oil types are expected to spread rapidly on the sea surface and form thin oil films (<0.5 mm) [28, 34-36], and neither of the existing response strategies, mechanical recovery, chemical dispersants nor in-situ burning, are effective on thin oil films (<0.2 mm) [3].

Condensates and light crude oils forming thin oil films are also of interest because of the high evaporative loss of VOCs, because response personnel establishing and starting cleanup activities the first days at sea during oil spills are at risk of exposure to these compounds. Thus, there is focus on finding solutions that aims to protect personnel from unnecessary risk when developing new preparedness strategies [19].

1.6 Health effects and exposure measurements

Oil spill cleanup may involve direct skin contact with oil during handling of oil-contaminated equipment and recovered oil or inhalation exposure to VOCs evaporating from the oil. The level of exposure will depend on duration of the exposure, the concentration of the chemicals, contact time, physical activity, and route of exposure (i.e. inhalation, ingestion or skin contact) [37]. PPE such as nitrile gloves, disposable chemical protective overalls and half-face air-purifying respirators, could be used to minimize uptake of petroleum-related compounds if used properly.

1.6.1 Health effects

Volatile organic compounds (VOCs)

Volatile organic compounds (VOCs) are low molecular weight compounds that occur naturally in crude oil. VOCs are defined as organic compounds with low boiling points (<250°C, i.e. $<C_{14}$) at standard atmospheric pressure (101.3 kPa) and include several alkanes and aromatics [38]. The high vapor pressure corresponding to the low boiling point means that the compounds easily evaporate from liquid to gaseous form, and therefore inhalation is the main route of uptake in humans. However, dermal uptake is also possible and may contribute significantly to the total dose when the airborne levels of VOCs decrease with time [39].

Some VOCs are generally considered to be more toxic than others in relation to chronic health effects. Ethylbenzene and naphthalene are associated with cancer, and are classified as ‘possibly carcinogenic to humans’ (Group 2B) by the International Agency for Research on Cancer (IARC), while toluene, xylene and n-hexane are mainly associated with effects on the nervous system [40]. The main focus of the present study was benzene, because it occurs naturally in crude oil (up to 2.5 wt%) and is a confirmed human carcinogen (IARC Group 1) associated with hematotoxic and carcinogenic effects, also after exposure to levels below the current occupational exposure limit (OEL) [4-6, 40]. Short-term acute health effects include headache, nausea, eye and throat irritation, and chronic effects include hematotoxicity and cancers. Petroleum workers in the offshore industry have been reported to have an excess risk of acute myelogenous leukemia and multiple myeloma after benzene exposure through contact with crude oil [41, 42]. The metabolism of benzene is an important determinant for its toxicity, but the mechanics of benzene toxicity is complex and not yet fully understood [43].

Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) also occur naturally in crude oil and is a collective term for compounds that consist of two or more aromatic benzene rings [44]. PAHs are often called semi-volatiles and can exist in either vapor phase or adsorbed on particulate matter. The main route of uptake by humans is inhalation, but dermal uptake may contribute significantly to the total exposure. There is little information on human exposure to individual PAHs, but naphthalene, anthracene and benzo[a]pyrene are direct skin irritants. Chronic and long-term health effects are reported to be associated with increased risk of skin, lung, bladder and gastrointestinal cancers. Benzo[a]pyrene is a confirmed human carcinogen (IARC Group 1), while several other PAHs are classified as probably or possibly carcinogenic [45].

1.6.2 Air monitoring

Air monitoring is performed to measure the airborne exposure, i.e. the air concentration of chemical agents [46]. Personal air monitoring is used to measure the exposure in an individual’s breathing zone, and is mainly performed by either active sampling with adsorbent tubes or by passive diffusion onto dosimeters. Active sampling involves pumping a known amount of air (20–200 ml/min) through a tube packed with an adsorbent such as active or synthetic coal, silicagel, molecular sieve and organic polymers (e.g. Tenax, Chromosorb, Anasorb). Passive sampling involves no pump as the components of interest diffuses onto the adsorbent. Tenax TA is a common adsorbent for sampling of VOCs because of the high sensitivity achieved in short-term measurements (<15 min) when analyzed by automated thermal desorption-gas chromatography-mass spectrometry (ATD-GC-MS). For a sampling time of only 15 min this method allows for a low limit of detection (LOD) in both active (0.0013 ppm, with 50 ml/min flowrate) and passive (0.13 ppm) sampling [46].

Direct-reading instruments are also used for air measurements, mainly to measure the variation in exposure levels with time and to identify sources of exposure. The instruments are based on a range of different principles, such as electro chemical sensing, flame ionization detection (FID), photoionization detection (PID), and mass spectrometry (MS), but only some of the instruments are portable and suitable for use in the field. The most common portable detector is the PID, which measures the total VOC (TVOC) concentration in air continuously with high sensitivity (LOD <0.1–0.5 ppm). Cross sensitivity is a major issue with the PID instruments due to the presence of similar compounds in air, thus measurements of specific compounds must be done with care. In the petroleum industry PIDs are used to measure that the air concentration of benzene is below a given level and to assess whether PPE should be used during certain work tasks (e.g tank entering).

1.6.3 Biological monitoring

Biological monitoring (biomonitoring) is the measurement and assessment of chemicals and their metabolites (biomarkers) in exposed individuals and involves analysis of breath, urine, saliva, hair or blood samples collected from a person [47]. Urine collection is often chosen because it detects recent exposure (post work-shift/work-week), is easy to obtain in the field or at the work place and is less invasive compared to other methods. Urine can be collected at the end-of-shift, next morning or end-of-week, depending on the main half-life of the biomarker of interest. Biomonitoring reflects the total uptake of a chemical by an individual by all exposure routes, accounts for increased uptake during increased physical activity and individual variations in uptake and metabolism, and it can also be used to study the effectiveness of PPE [43].

Biomarkers of benzene exposure

Unmetabolized benzene is a sensitive urinary marker suitable to assess benzene exposure below the occupational limit value [48]. However, urine samples are susceptible to contamination and to evaporative loss due to the high volatility of benzene [43], thus metabolites of benzene are often used as urinary markers of benzene exposure [49]. Phenol and its conjugates are the main urinary metabolites, while trans,trans-muconic acid (tt-MA) and S-phenylmercapturic acid (SPMA) are minor urinary metabolites (3 % and 0.1 % of total metabolites, respectively) [43]. Urinary phenol and tt-MA are not suitable biomarkers of low level benzene exposure (i.e. low sensitivity) and are also generated from other sources of benzene (i.e. non-specific) [50], while urinary SPMA is both a specific and sensitive biomarker of benzene exposure (LOD<1 µg/l). Although it is not validated for exposures below 0.3 ppm, it is possible to detect after low level exposure (≈0.1 ppm) [49]. The half-life of SPMA (9–13 h) makes is suitable for measuring recent benzene exposure. An exposure of 1 ppm benzene corresponds to a post-shift urinary SPMA concentration of about 21.3 µmol/mol (45 µg/g) [51].

Biomarkers of PAH exposure

The most commonly used biomarker of PAH exposure is urinary 1-hydroxypyrene (1-OH) [44, 52], the main metabolite of pyrene. Although pyrene itself is not a known carcinogen, 1-OH is considered to be an appropriate marker of occupational PAH exposure because it is always present in PAH mixtures [53]. The suggested half-life for urinary excretion of 1-OH is about 18 h, reported to range from 6 to 35 h [54].

Effect of tobacco smoke

Smoking influences the benzene biomarker concentrations, even at exposure levels above the occupational exposure limits [48]. The concentration of urinary 1-OH is also affected by smoking [55], thus several biomarkers have been proposed to measure the effect of direct and passive exposure to tobacco smoke. The most specific urinary markers are unmetabolized nicotine and cotinine, a major nicotine metabolite [56]. The longer half-life of cotinine (19 h) compared to unmetabolized nicotine (2 h) makes it more suitable for occupational exposure assessments.

1.7 Exposure limits and guidance values

Norwegian occupational exposure limits (OELs) have been established for several airborne chemicals that are common in the workplace [57]. The OELs represent a time-weighted average (TWA), which is the airborne concentration of a compound in the breathing zone averaged over an 8-hr workday. The Norwegian OEL for benzene is 1 ppm, while the American Conference of Governmental Industrial Hygienists (ACGIH) has a threshold limit value (TLV®) of 0.5 ppm [58]. However, the exposure limit for benzene is on decline, and 'the Advisory Committee on Safety and Health at Work in the European Union' has been recommended to lower the OEL to 0.05 ppm benzene [43]. Norwegian OELs also exist for ethylbenzene (10 ppm), naphthalene (20 ppm), n-hexane (30 ppm), and toluene and xylene (37.5 ppm).

For 12-hr work-shifts in the Norwegian petroleum industry the OEL is multiplied by a safety factor of 0.6 (i.e. 0.6 ppm benzene) according to 'The Activities Regulation,' so that the peak body load does not exceed the one that would occur during a normal 8-hr work-shift [59]. A short-term exposure limit (STEL) may also be calculated from the OEL as an acceptable average exposure over a 15-min period (i.e. 3 ppm benzene), as long as the OEL is not exceeded [57].

Biological exposure indices (BEIs®) have been developed for several chemical agents based on the expected concentration of a biomarker after 8-hr exposure to the current TLV® [58]. There is no Norwegian biological limit value for benzene, but the ACGIH recommends a BEI of 11.8 µmol/mol creatinine (25µg/g) in end-of shift urine for SPMA, corresponding to a full-shift exposure of 0.6 ppm benzene. For the proposed OEL of 0.05 ppm benzene the corresponding biological limit value is estimated to be 1 µmol/mol creatinine (2 µg/g) [43]. There is no recommended BEI for 1-OH, but the ACGIH recommends a benchmark guideline of 0.5 µmol 1-OH/mol creatinine (1 µg/l) in end-of-shift urine to be considered as occupational exposure to PAHs [37].

1.8 Previous measurements and model estimates

1.8.1 Evaporation models and experimental studies

Model estimates clearly indicate that the evaporation of benzene from fresh crude oil is rapid [60-64]. The maximum concentrations will occur immediately after a spill before the concentration exponentially declines. The air concentration of benzene at sea level was estimated by Thayer and Tell (1999) for medium crude oils [62]. They varied the oil film thickness and initial benzene content of the crude oil in their model, while wind (0.5 m/s) and water temperature (21°C) were constant. For thin oil films (0.1 mm), the estimated maximum air concentration of benzene was 25 ppm, 180 ppm and 2000 ppm for oils with an initial benzene content of 0.01 wt%, 0.2 wt% and 2.1 wt%, respectively. For thicker oil films the estimated maximum air concentration was lower and the decline in concentration less rapid. For oils with a high content of benzene (2.1 wt), it was estimated that benzene would evaporate within 1 h, 1.5 h and 4 h from oils with a thickness of 0.1 mm, 4 mm and 12 mm. It was also estimated that air concentrations above 1 ppm benzene could be detected up to 1 km from the release point.

Small-, meso- and full-scale methods have been developed in order to test the fate and behavior of oil spilled at sea [33, 65-68]. Small–scale testing (i.e. bench-scale setups) is considered to be a time- and cost-effective way of testing weathering properties of several oils, while meso-scale (i.e. basin setup) and full-scale field testing is valuable for verifying small-scale results under more realistic conditions. The hourly air concentration of benzene was measured in a meso-scale experiment where about 20 L of fresh light crude oil (36°API) was released on seawater in an open fire pan (1.5 m^2) in practically no wind [66]. The initial oil film thickness was 13 mm and the air concentration of benzene at two heights (12.5 cm and 71 cm) above the oil was 26.6 ppm and 8.3 ppm, respectively. In a similar experiment performed by Jones et al., several air measurements of benzene evaporating from fresh light crude oil (36°API) released on water in a steel pan were collected [65]. The initial film thickness was 63 mm and samples were collected at two heights above the oil. The air concertation of benzene declined from 90 to 8 ppm (1.9 cm above oil) and from 18 to 1 ppm (9.5 cm above oil) during the 7 h of sampling. Although the benzene content of the oil was not given in either study, both studies indicated that the sampling distance from the oil film highly affects the air concentration of benzene. In Jones study, the benzene concentration at 9.5 cm above the oil fluctuated during the first 3 h after release of oil before it started to decline, probably affected by varying wind conditions (1.3–4 m/s) and the very thick oil film (62 mm). The air concentration of benzene was also measured during a full-scale ‘oil-on-water’ field trial in the North Sea in the 90’s [69]. About 20m^3 of fresh light crude oil (38°API) with a benzene content of 0.33 wt% was released in 8-12 m/s wind, the average film thickness was 2-3 mm. Air samples were collected 1-2 m above the oil slick after 5 min and 34 min, and the air concentration of benzene was >5 ppm and 0.14 ppm, respectively.

When the API gravity was plotted against the percentage of benzene by volume for 30 crude oils, an upward trend of increasing benzene concentration with increasing API grade was indicated [66]. Other studies have indicated that a high wax content may limit evaporation [32, 33]. Still, there is little information about how specific physicochemical properties such as content of benzene and wax, viscosity and pour point affects benzene evaporation and the concentration levels in air when fresh crude oils are released on water.

1.8.2 Oil spill field studies

Major marine oil spills of fresh crude oil include Deepwater Horizon (DWH), Hebei Spirit, Tasman Spirit, Sea Empress, Braer and Exxon Valdez. All spills involved oil tankers carrying crude oil (29–35°API), except for DWH that involved deep-water release (>1500 m) of 600 000 tons of crude oil (35°API) into the Gulf of Mexico over a period of three months. Major marine oil spills of fuel oil include the Prestige, Erika and Nakhodka oil spills, which all involved oil tankers carrying heavy fuel oil No. 6, a high density, high viscosity oil refinery product [70]. Table 2 presents previous studies that have measured or modelled the air concentration of volatile compounds, such as benzene, or measured urinary markers of benzene and PAH exposure during cleanup of fresh crude oil.

Full-shift personal air sampling of BTEX and naphthalene on workers aboard two vessels working to contain, control and stop the release of oil during the DWH blowout was performed by The National Institute of Occupational Safety and Health (NIOSH), US [71]. The BTEX levels (<0.005 ppm) did not exceed the respective OELs and were below the LOD in the majority of the samples (68 %). British Petroleum also performed personal measurements of BTEX for workers performing tasks offshore during the spill. The levels were well below (<0.12 ppm) the respective OELs, and in most samples (80-99 %) BTEX were not detected [72]. The high number of non-detects was explained by dissolution of BTEX in the water before reaching the sea surface [73]. Model estimates for the first five days of the spill indicated that the BTEX levels did not exceed the OELs under any of the tested exposure conditions (i.e. various wind speed and oil film thicknesses). However, among ship crew participating in the cleanup the concentration of urinary phenol (7.0 mg/l), a marker of benzene exposure, was significantly higher than background levels, thus indicating exposure to benzene [74].

In 2007 a crane barge collided with the supertanker Hebei Spirit outside South Korea. The ship was carrying three different types of crude oil (30–34°API). Model simulations of BTEX estimated that the evaporation of benzene was complete within 10 h, while toluene, ethylbenzene and xylene evaporated almost completely within 48 h [75]. The model predicted that the benzene exposure levels probably exceeded the 8-hr OEL. Urinary markers of benzene (tt-MA) and PAH (1-OH) exposure were significantly higher in post- compared to pre-shift urine among cleanup participants [76], but no difference in metabolite levels between cleanup participants and the reference group or between those wearing and not wearing PPE during cleanup was found [77, 78]. Although the cleanup lasted for several weeks, urine samples were collected two weeks after the spill occurred, and not during the initial stages of the spill when the evaporative loss is highest.

Personal exposure to benzene was measured during the Prestige and Nakhodka oil spills, both involving oil tankers carrying heavy fuel oil. The reported mean air concentration of benzene (0.04 ppm) for exposed subjects participating in the cleanup of the Prestige oil spill, measured with passive ATD- and Radiello®-tubes, was below the OEL [70]. The reported benzene concentrations were even lower (<0.002 ppm) for residents participating in the cleanup of the Nakhodka oil spill, and the concentration of tt-MA in urine samples collected after cleanup was below the LOD [79]. However, tt-MA is a poor marker of low-level benzene exposure, and it was not specified whether these subjects wore respirators or not. The low levels of benzene measured during both oil spills can probably be explained by the low concentration of benzene in heavy fuel oils.

Airborne levels of volatile compounds during the Braer and Exxon Valdez oil spills, both involving oil tankers carrying crude oil (29°API), were estimated by evaporation models. During the Braer oil spill the estimated air concentration of $C_{3\text{-}8}$ hydrocarbons, 1 m above the oil, on day five (0.2–1 ppm) and six (7 ppm) were consistent with field measurements performed on the same two days (0.264 ppm and 6.33 ppm, respectively) [63]. On day six there was a massive release of oil when the vessel broke up and therefore the concentrations were higher on day six than on day five. During the Exxon Valdez oil spill the estimated maximum hourly benzene concentration in air, 10 cm above the center of the oil, was 4.9 ppm [61]. However, the film thickness in both spills was more than 10 mm, which is not representative of a thin oil film.

Table 2: Overview of relevant air and biological measurements performed during crude oil spills.

Oil spill	Reference	Subjects	Method	Results
Deepwater Horizon (US)	D'Andrea & Reddy 2013 [74]	Cleanup participants and unexposed (*n*=247)	Urinary phenol	Urinary phenol (7.0 mg/l) in exposed subjects significantly higher than background levels
	Ahrenholz & Sylvain 2011 [71]	Ship crew close to oil release source (*n*=19)	BTEX (TD-tubes) and naphthalene	Only toluene (0.0026 ppm) and xylene (0.0030 ppm) were detected
	Avens et al. 2011 [72]	Ship crew close to oil release source (*n*=4945)	BTEX (dosimeters)	The mean air conc. (ppm) of BTEX (B<0.013, T<0.051, E<0.037, X<0.12) was well below respective OELs
Hebei Spirit (South Korea)	Kim et al. 2012 [75]		Model estimates of BTEX	BTEX evaporated completely within 48 h (benzene within 10 h). Benzene levels exceeded 8-hr OEL.
	Ha et al. 2012 [78]	Cleanup participants (students) (*n*=105)	Urinary tt-MA, 1-OH, 2-Naphtol	Significantly higher GM levels (µg/g cr.) post-shift (tt-MA: 211.5, 1-OH: 1.58) than pre-shift (tt-MA: 70.2, 1-OH: 0.96)
	Cheong et al. 2011 [77]	Cleanup participants and reference group (*n*=154)	Urinary tt-MA, 1-OH, 2-Naphtol	No sign. difference in GM levels (µg/g cr.) between cleanup participants (tt-MA: 25.1, 1-OH: 0.5, 2-Naphtol: 2.7) and reference group (tt-MA: 25.7, 1-OH: 0.6, 2-Naphtol: 4.0)
	Lee et al. 2009 [76]	Cleanup participants (residents/volunteers) (*n*=288)	Urinary tt-MA, 1-OH, 2-Naphtol	No sign. difference in GM levels (µg/g cr.) between participants wearing (tt-MA: 22.7, 1-OH: 0.7, 2-Naphtol: 4.1) and not wearing PPE (tt-MA: 29.3, 1-OH: 0.7, 2-Naphtol: 4.0)
Prestige (Spain)	Pérez-Cadahía et al. 2007 [70]	Volunteers and hired cleanup workers (*n*=68)	Benzene (passive ATD- or Radiello$^{®}$-tubes)	Mean air conc. of benzene (0.04 ppm) was below OEL
Nakhodka (Japan)	Morita et al. 1999 [79]	Residents (*n*=97)	BTX (active carbon) Urinary tt-MA	Mean air conc. (ppm) of BTX (B<0.002, T<0.009, X<0.002) was below respective OELs. Urinary tt-MA not detected
Braer (UK)	Zhou & Wong 1997 [63]		Model estimates of $C_{3\text{-}8}$ hydrocarbons	Mean air conc. of $C_{3\text{-}8}$ hydrocarbons were 0.2–1 ppm (day 5) and 7 ppm (day 6)
Exxon Valdez (US)	Hanna & Drivas 1993 [61]		Model estimates of benzene	The estimated max hourly air conc. of benzene was 4.9 ppm

DWH, Deepwater Horizon; BTEX, benzene, toluene, ethylbenzene, xylene; TD, thermal desorption; OEL, occupational exposure limit; PAH, polycyclic aromatic hydrocarbons; tt-MA, trans,trans-muconic acid; 1-OH, 1-hydroxypyrene; GM, geometric mean; cr, creatinine; PPE, Personal protective equipment

1.9 Study rationale

Exposure measurements of volatile compounds during previous oil spills are inadequate. This is mainly due to the fact that oil spills are acute, and that air and biological measurements have not been performed during the early stages of the spills when the exposure levels are highest. The continuous release of light crude oil during the DWH blowout presented an opportunity to collect valuable exposure data, however the release conditions led to low exposure levels. The Norwegian oil spill preparedness maintains a high level internationally, and the research activity and technology development is beeing noticed abroad. In the development of contingency plans for thin oil films, major efforts are being made to find response methods that are unmanned, remotely controlled or automated to avoid unnecessary risk for cleanup personnel. Research to characterize the health risk during cleanup of oils forming thin oil films have also been initiated.

The annual oil-on-water field trial in the North Sea organized by NOFO was a unique oppurtunity to study exposure levels during release of fresh crude oil in full-scale. The release conditions were adapted to create a worst-case exposure scenario, i.e. release of fresh light crude oil with a high content of volatile compounds in calm weather conditions at sea. However, it was not possible to study several oils in full-scale, hence a small-scale evaporation study was performed with several condensates and light crude oils expected to form thin oil films at sea. The results may help us understand how the air concentration of volatile compounds change with time and could be used to group oils based on the expected levels of exposure. Bench-scale experiments can also be used to study new oils that come into production, since full-scale studies are normally not an option. Field measurements of exposure levels during spills of condensates and light crude oils are crucial for developing knowledge-based guidelines for oil spill response and to minimize the health risk for cleanup personnel.

2. Study aims

The overall aim of this research project was to investigate how the air concentration of volatile compounds evaporating from thin oil films develops with time after release of condensates and light crude oils on the water surface, and to study the exposure levels of volatile compounds and following biological uptake during release of fresh crude oils at sea.

Specific objectives

To simulate weathering of oils forming thin oil films on the seawater surface in a bench-scale laboratory setup to identify specific physicochemical properties of fresh oil that affects how the air concentration of benzene develops over time at different temperatures (Paper I).

To study full-shift personal exposure levels of volatile compounds, in particular benzene, for subjects participating in a full-scale field trial at sea involving several releases of fresh crude oil (Paper II).

To study the biological uptake of benzene and PAHs among subjects wearing and not-wearing PPE and to investigate the association with airborne exposure levels (Paper III).

3. Materials and methods

This thesis was part of a knowledge-building project for the industry funded through the PETROMAKS2 program by the Research Council of Norway. The project '*Formation and behavior of thin oil films and evaluation of response methods including health, safety and environment'* had several objectives, including the present study named '*Oil spill into seawater: Evaporation and human exposure to benzene*.' SINTEF Ocean was the project owner and provided bench–scale laboratory facilities for performing an experimental study of the evaporation of volatile compounds from oils forming thin oil films. A full–scale field trial in the North Sea, organized by NOFO, was carried out for two consecutive days in June 2016 to assess human exposure to volatile compounds during release of fresh crude oil at sea.

3.1.1 Selected oils

Nine condensates and light crude oils were included in the laboratory study (Figure 4). The oils were selected from the internal SINTEF oil database of previous weathering studies and represented the variation of condensates and light crude oils on the NCS regarding physicochemical properties. The oils were still in production, available in stock and were assumed to form thin oil films (<0.3 mm) on the sea surface when spilled. In addition, the oil companies involved in the project were represented with at least one oil.

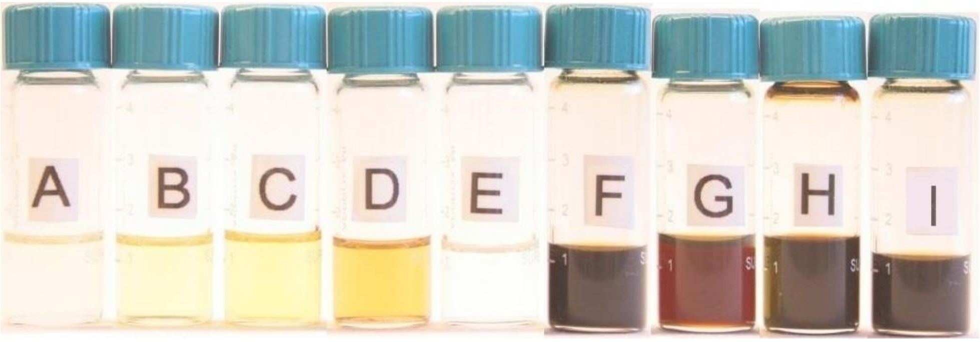


Figure 4. Overview of the five condensates (A-E) and the four light crude oils (F-I) included in the small-scale laboratory study.

Two oils were included in the field study, a light crude oil (Åsgard Blend) also tested in the laboratory study (oil F), and a heavy crude oil (Grane Blend) that was not included in the laboratory study described below. The light crude oil was selected because of its availability in large quantities and ability to form a thin oil film (<0.3 mm), and was used to test mechanical dispersion of a thin oil film with high-capacity water flushing [80]. The heavy crude oil was selected because of its availability and ability to form a thick oil film (>1.0 mm), and was used to test the effectiveness of in-situ burning of oils with and without the use of herders, a liquid agent used to concentrate oil to a thickness suitable for burning.

The physical and chemical properties of the oils included in the laboratory study (A-I) and the field study (F and J) are presented in Table 3. The data for each oil was retrieved from previous quantitative analysis of stabilized, fresh crude oil, and from previous laboratory weathering studies performed by SINTEF Ocean. The analytical methods are described by Daling et al. (1990) [67]. The oils tested in the small-scale laboratory study were grouped as either condensates or light crude oils based on weathering properties. The density, often expressed by the American Petroleum Institute gravity (°API), ranged from 0.73–0.84 g/ml. Benzene content ranged from 0.38–1.98 wt%, while the sum of selected VOCs ($C_{6\text{-}10}$) ranged from 17–51 wt%. All oils had a low content of asphaltenes (0.00–0.16 wt%), the wax content varied between low (<2 wt%) and medium (2–5 wt%), and the viscosity varied between non-viscous (1 mPa s) and viscous (5–37 mPa.s). The pour point, the temperature where the oil loses its ability to flow, also varied (-36–6°C), with a few oils having a potential of solidifying within 30–60 min of weathering due to a relatively high pour point (> -10°C). The mean density, asphaltene content and wax content of the light crude oils were slightly higher than for the condensates, while the mean content of benzene and VOC was slightly higher for the condensates than for the light crude oils. The heavy crude oil (Grane Blend) used in the field study had very different properties than the other oils because it was not a part of the original selection of oils. Compared to the mean of the condensates and light crude oils, the VOC and benzene content of the heavy crude oil was only 10 % and 4 %, respectively, the viscosity and content of asphaltenes was more than 10 times higher and the wax content was twice as high.

Table 3. Fresh oil properties of the oils included in the laboratory (A-I) and the field study (F and J), sorted by oil group and benzene content.

Oil group	Oil ID	Density (g/ml)	API (API°)	Benzene (wt%)	VOC (wt%)	Asphaltenes (wt%)	Wax (wt%)	Viscosity* (mPa.s)	Pour point (°C)
Condensate	A	0.75	58	1.98	46	0.02	0.5	1	-36
	B	0.83	39	1.21	34	0.01	2.2	6	6
	C	0.80	46	0.96	32	0.03	5.0	9	0
	D	0.76	55	0.42	50	0.00	0.0	1	-36
	E	0.73	62	0.42	51	0.04	1.2	1	-33
	Mean	**0.77**	**52**	**1.00**	**43**	**0.02**	**1.8**	**4**	**-20**
Light crude oil	F (Åsgard Blend)**	0.78	50	1.02	32	0.00	3.9	1	-36
	G	0.82	42	0.91	22	0.03	3.3	37	-9
	H	0.83	38	0.43	17	0.16	4.1	12	-9
	I	0.84	38	0.38	19	0.03	1.5	5	-36
	Mean	**0.82**	**42**	**0.69**	**23**	**0.06**	**3.2**	**14**	**-23**
Heavy crude	J (Grane Blend)**	0.89	27.7	0.03	3.7	0.97	8.1	64	-3

Notes: API, American Petroleum Institute grade; VOC, Volatile Organic Compounds; wt%, percentage by weight
*Measured at 13°C with a shear rate of 10s^{-1}
**Oils included in the field study

3.2 Laboratory study of evaporation: Paper I

3.2.1 Study design

SINTEF has been using a bench–scale test apparatus since the 80's, developed by Mackay, Nadeau and Steelman (MNS), to study the effectiveness of oil dispersants on weathered oils [67, 81]. A modified version of this test apparatus was used in this project to perform several weathering experiments with identical conditions for each of the selected oils to study the evaporation of volatile compounds (Figure 5). The glass chamber (20 l) was filled with filtered seawater (6.14 l) and a known amount of oil (16.5 ml) to create a thin oil film (0.25 mm) on the water surface. The glass camber was then closed with a lid, with air blowing through the chamber via a ventilator. Both temperature and air flow were adjustable, but the air flow (2.1 l/s) was kept constant to simulate calm weather conditions (1 m/s wind) and no breaking waves. Each oil was tested first at 13°C and then at 2°C to reflect summer and winter/arctic temperatures, respectively, on the NCS.

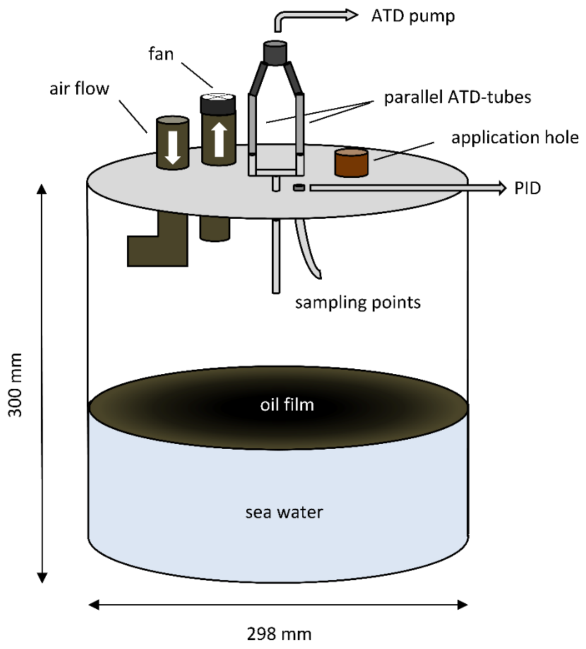


Figure 5. Schematic drawing of the test apparatus and sampling points.

3.2.2 Air measurements and analysis

Stainless steel automated thermal desorption tubes (ATD-tubes, Markes Int./PerkinElmer, Boston, US-MA), were used for active air sampling for later quantification of BTEX, naphthalene and n-hexane (Appendix VII). ATD tubes were placed in parallel in an airtight, customized hole at the center of the glass chamber lid, 10 cm above the oil film. The tubes were attached to an AirChek 52 Personal Sample Pump (SKC Inc, Eighty Four, US-PA) with a low flow rate (50 ml/min) that was started simultaneously with oil application. Active air sampling was done in intervals of 5 min from application of oil and for the following 30 min to get a total of 6 consecutive air samples in each experiment. Air samples were stored at 4°C before quantitative/semi-quantitative analysis (ISO 16017–1 and ISO 16017–2) by thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) at SINTEF Molab AS.

MiniRAE 3000 (RAE systems Inc, San Jose, US-CA) photoionization detectors (PIDs) equipped with a 10.6 eV lamp were calibrated with isobutylene (100 ppm) to estimate the air concentration of TVOCs ranging from C_6–C_{14}. Silicon tubes attached the PIDs to the glass chamber lid, and the sampling point was 10 cm above the oil film.

3.2.3 Statistics

The air concentration of BTEX, naphthalene and n-hexane was given as the arithmetic mean (AM) and standard deviation (SD) of all oils at each temperature for three chosen time periods; first 5, first 15 and last 15 min of sampling. Only the air concentration of benzene was presented for each oil in 5 min time periods from release of oil and the following 30 min. Paired samples t-tests were performed to test the difference in the air concentration of benzene between the two water temperatures, 2°C and 13°C.

Mixed-effects air concentration models for benzene were developed to adjust for repeated measurements for the respective oils. In preparatory analysis the correlation between the continuous variables; benzene content in fresh oil (potential determinant) and log transformed air concentration of benzene, was tested by Pearson correlation test. Independent t-tests were used to analyze differences in the air concentration of benzene for potential determinants; water temperature (2°C/13°C), oil group (light crude oil/condensate), density (<0.80 g/ml/0.80–0.85 g/ml), pour point (<-33°C/-9–6°C), viscosity (1 mPa.s/5–37 mPa.s) and wax content (<2 wt%/2–5 wt%). Content of asphaltene was not tested, because of low content in all oils. Collinearity between potential determinants was tested by a nonparametric Spearman correlation test, and only one determinant was tested in the model if the correlation was significant ($p \leq 0.05$).

Three separate linear mixed-effects models were developed for the log-transformed air concentration of benzene for the first 5, first 15 and last 15 min of sampling. The oil ID was used as a random effect to account for repeated measurements. Potential determinants associated ($p \leq 0.2$) with at least one of the outcome variables in preparatory analysis were entered as fixed factors in the mixed effects models and were retained in the final models when significant ($p \leq 0.05$). The total variance explained by the fixed effects for each time period was calculated as the percentage change in total variance between the random- and the mixed-effects model. SPSS 22 for Windows (IBM Inc., Chicago, IL, USA) was used to analyze data.

3.3 Field study: Paper II and III

3.3.1 Study design

An annual ‘oil-on-water’ field trial has been performed by NOFO for several years, to test various response methods on different crude oils. The exercise takes place at the Frigg field in the North Sea in June, about 150 km northwest of Stavanger, Norway. A timeline for the 2016-exercise is presented in Figure 6, when 73 people participated. A total of six oil releases (4–10 m^3 each) were performed with two different crude oils on two consecutive days. There was sun, no breaking waves and a gentle breeze (2–5 m/s) on the first day of oil release, and overcast, breaking waves and a moderate breeze (7 m/s) on the second day. The water temperature was 12.5°C. The light crude oil (Åsgard Blend, oil F) was released with the wind in three separate bulk releases taking 6-7 min each, to create a thin oil film with 0.3 mm average thickness. The heavy crude oil (Grane Blend, oil J) was released as a point release in three separate releases taking 3-4 min each, to create an initial oil film with about 3.0 mm average thickness.

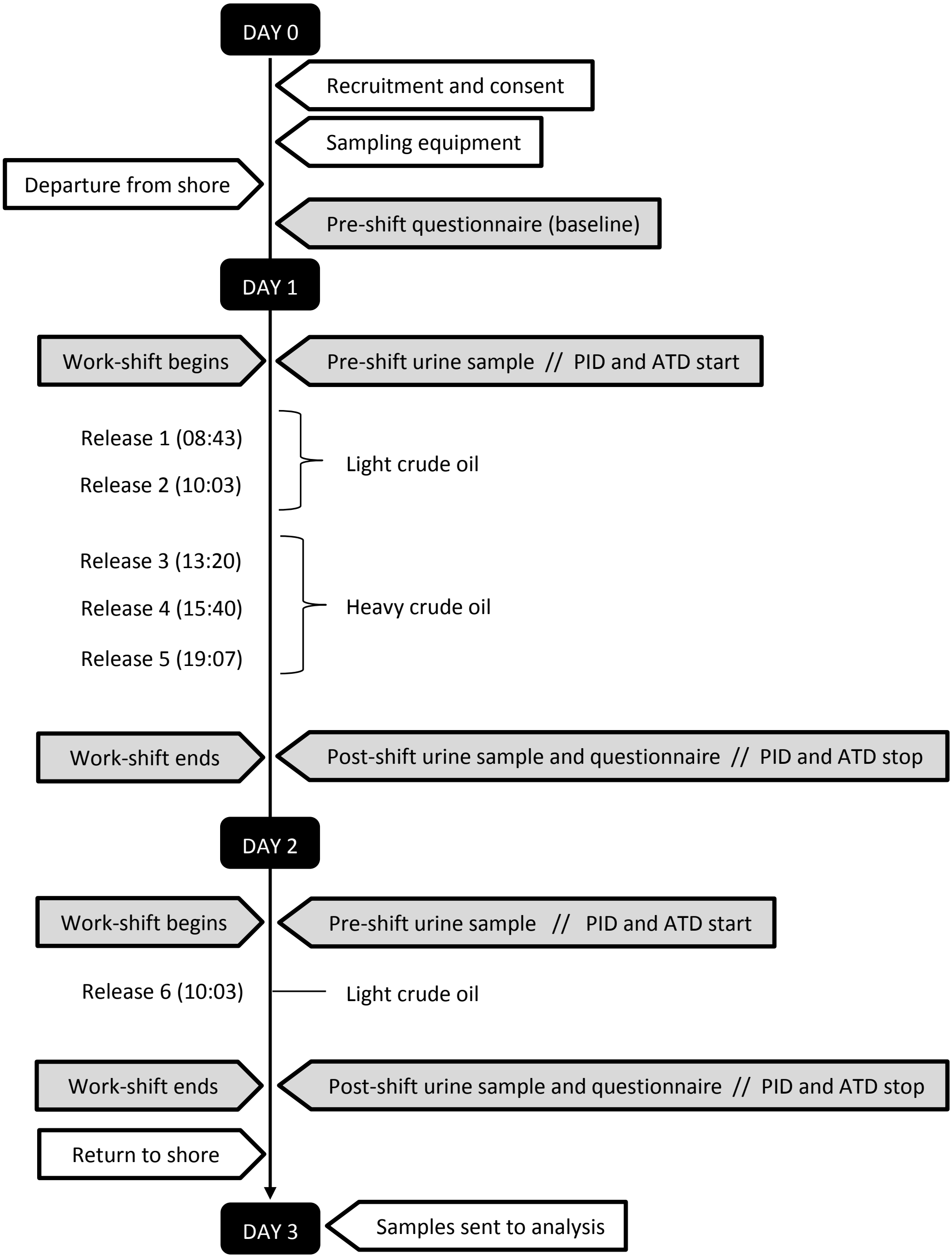
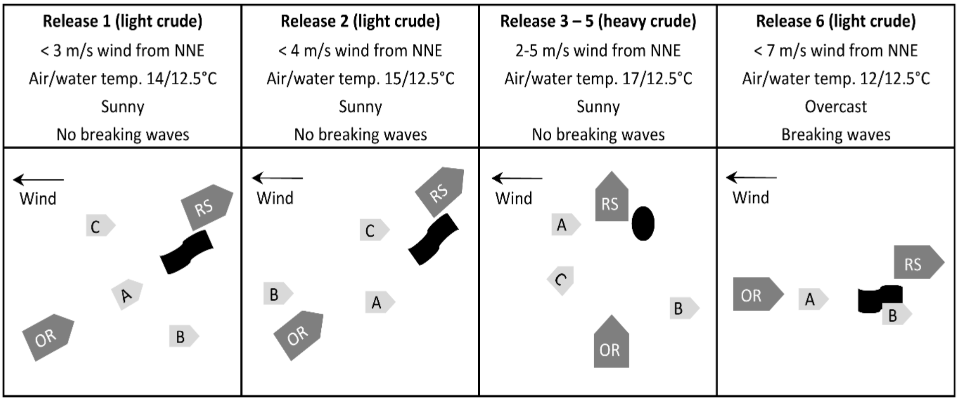


Figure 6. Timeline for the field trial. Overview of the recruitment, sampling strategy, oil releases and work-shifts. PID: photoionization detector (stationary), ATD: Automated thermal desorption (personal)

3.3.2 Organization of the field study

Field trial participants were accommodated on two ships (75–95 m), and two researchers were responsible for air and urine sampling, one on each ship (Appendix II and V–VII). The participants were a mix of ship crew, contingency advisors, researchers and observers, all with different work tasks and goals during the trial. Work tasks included navigation, exercise management, oil release and recovery, oil sampling, drone and aerostat operation, air and urine sample collection, oil herding and ignition, ship maintenance, kitchen service and observations. The ship crew followed their regular work-shifts (12 h), while everyone else worked from morning to evening, except during meals.

The two ships were in charge of either releasing the oil (release ship, RS) or oil recovery (oil recovery ship, OR), respectively. In addition, three small, open boats (5–8 m) were used for oil sampling, air sampling and oil herding/ignition. The starting position of the five boats in each release is illustrated in Figure 7. One of the small boats (boat A) was dedicated to air sampling, while the other two small boats (boat B and C) performed oil sampling and herding/ignition. Oil was released against the wind (in best efforts) by the RS. During and after the release the small boats were located downwind and close to the oil slick (<50 m) while the OR was located further away (100–200 m). Various response techniques were initiated by the OR ship after 30 min or more, while the other boats moved around according to work tasks.



Release 1 (light crude)	Release 2 (light crude)	Release 3 – 5 (heavy crude)	Release 6 (light crude)
< 3 m/s wind from NNE Air/water temp. 14/12.5°C Sunny No breaking waves	< 4 m/s wind from NNE Air/water temp. 15/12.5°C Sunny No breaking waves	2-5 m/s wind from NNE Air/water temp. 17/12.5°C Sunny No breaking waves	< 7 m/s wind from NNE Air/water temp. 12/12.5°C Overcast Breaking waves

Figure 7. Starting position of the participating boats; release ship (RS), oil recovery vessel (OR), and sampling boats A, B and C relative to wind, oil slick and each other during each release of oil. Weather conditions are included.

3.3.3 Study population

Based on studies of the relationship between benzene exposure in air and SPMA in urine, a power analysis was performed a priori to determine the sample size required to detect a significant change between pre- and post-shift urinary SPMA concentrations [82, 83]. According to the analysis, a minimum of 15 exposed subjects had to be included in a paired t-test to detect a change from 0.5 to 1.9 µmol SPMA/mol creatinine (SD=0.5 and 2.4 µmol/mol, respectively) and to achieve a statistical power of 80% at a p-level of <0.05. A concentration of 1.9 µmol /mol creatinine should correspond to a benzene exposure of 0.2 ppm [82].

Three exposure groups were defined a priori according to the assumed benzene exposure levels (high exposure, low exposure and background) based on the location of the five boats and ships. All personnel performing tasks in open air were invited to participate in the study. One person refused to participate, resulting in 17 subjects in the ‘exposed group’. People with observational tasks located on the command bridge on either ship during the releases were assumed to be unexposed, hence 5 persons were recruited as ‘background’. A risk assessment made prior to the field trial indicated that the air concentration of benzene at sea level could exceed the Norwegian STEL (3 ppm) immediately after release of oil. Hence, half-face air purifying respirators with a combination of particle filter (P3) and organic vapor cartridge (A2) were recommended to use during release of oil. Disposable chemical protective overalls and nitrile gloves were also available to all exposed subjects. Smoking was prohibited in open air, but each of the two ships had a designated smoking room.

3.3.4 Sampling strategy and analytical analysis

All subjects completed a pre-shift questionnaire after departure from shore (baseline) and a post-shift questionnaire on both days of oil release (Appendix III and IV). The pre-shift questionnaire requested personal information, employment status, tobacco use, allergies and acute symptoms, while the post-shift questionnaire requested information about work tasks, location, length of work-shift, smoking habits, direct contact with oil, use of PPE and acute symptoms.

Air measurements

Full-shift (5–15 h) personal exposure to six compounds, BTEX, naphthalene and n-hexane, was sampled with ATD-tubes (n=42). Tubes were attached to the participants' helmet outside the protective mask (exposed group) or chest pocket (background group). The work-shift for the exposed group started when the participants arrived on deck or in the sampling boats to prepare for the first release of the day and ended when arriving in the locker rooms after the last release of the day. The work-shift for the background group corresponded to the exposed group. See chapter 3.2.2 for details of the analysis. The limit of detection (LOD) for BTEX, naphthalene and n-hexane ranged from 0.002 to 0.005 ppm for the shortest sampling time (324 min) and from 0.001 to 0.002 ppm for the longest sampling time (876 min). Direct reading measurements were performed with PIDs (see chapter 3.2.2) on the main deck of the two ships and in all the sampling boats.

Biological measurements

Urine samples were collected pre- and post-shift (n=83) both days, in sampling tubes (5 mL) containing concentrated hydrochloric acid (HCL, 5 µl) as a preservative. All samples were stored at 4°C and shipped to the Health and Safety Laboratory (HSL), UK, on ice for analysis. The samples were analyzed for SPMA by liquid chromatography-tandem mass spectrometry (LC-MS-MS) [84], 1-OH by LC-fluorescence detection (LC-MS) [85], and cotinine by LC-MS [48], which are urinary markers of benzene, PAHs and nicotine, respectively. The limit of detection was 0.8 µmol/mol creatinine for SPMA, 0.1 µmol/mol creatinine for 1-OH and 0.06 µmol/L urine for cotinine.

3.3.5 Statistics

The exposure levels for the two days were merged and presented as arithmetic mean (AM), geometric mean (GM), geometric standard deviation (GSD) and range (minimum and maximum) over the respective sampling time. SPMA measurements below the LOD were included in the analysis as the LOD/2 [86]. Differences between the three exposure groups were analyzed using one-way, independent measures, ANOVA. The correlation between airborne benzene exposure and post-shift urinary SPMA was analyzed by Pearson correlation after log transformation of the data and the personal measurements were stratified by the use of respirator (yes/no). The level of significance was set to 0.05. SPSS Statistics 25 for Windows were used for analyzing the data.

3.4 Ethics

The study was approved by the Regional Committee for Medical Research Ethics of Western Norway (REC West, case no. 2015/63) and the Data Protection Official for Research. Informed written consent was obtained from all subjects (Appendix I) after receiving both oral and written information about the study. Participants did not receive any payment and were able to withdraw at any point. All information was treated with confidentiality and was only available to the project group, as defined in the REC application.

The study was part of a competence and knowledge building project funded (52 %) by the Research Council of Norway through the PETROMAKS2 program (233981/30). Additional funding (48 %) was provided by the oil companies participating in the project; AkerBP, Spirit Energy, Eni Norge, Neptune Energy, Shell Technology Norge, Equinor and Total E&P Norge. The industrial partners also contributed with professional input and fresh crude oils, but had no role in the design of the study, sample collection, analysis, interpretation of data, writing of the manuscripts or in the decision to publish the results.

4. Summary of results

4.1 Laboratory study of evaporation

Peak air concentrations of TVOC were measured within 2 min after application of oil in all tests, and were significantly higher at 13°C than at 2°C during the first 5 and 15 min. The concentration rapidly declined at both temperatures, and within 30 min the concentration had been reduced to 80-100 % of the peak concentration. The air concentration of benzene, toluene, ethylbenzene and n-hexane also rapidly declined, while xylene and naphthalene did not show comparable decline with time. The air concentration models for benzene predicted that 63–73 % of the total variance in the air concentration of benzene could be explained by three determinants; content of benzene in fresh oil, oil group (condensate/light crude oil) and pour point. The former two were significant determinants in the first periods of sampling (first 5 and 15 min), while pour point was a significant determinant in the last period of sampling (last 15 min). The air concentration of benzene (3.4 to 18.3 ppm) varied between oils during the first 5 min of sampling, and was positively correlated with the content of benzene in fresh oil, also during the first 15 min of sampling. The air concentration of benzene was higher for the light crude oils than for the condensates when adjusting for the content of benzene in fresh oil. During the last 15 min of sampling the model predicted that the air concentration of benzene (AM=0.9 ppm) for oils with a high pour point was 13 times higher compared to oils with a low pour point (AM=0.07 ppm). Furthermore, the air concentration of benzene was higher at 13°C than at 2°C during the first 5 and 15 min, although not significantly.

4.2 Full-scale field study

The air concentration of TVOC was five times higher during release of light crude oil (Åsgard Blend) compared to heavy crude oil (Grane Blend), but the concentrations rapidly declined for both oil types. Subjects in the small boats, located close and downwind from the oil slick during and after release of oil, were exposed to the highest concentrations of benzene (0.013–1.52 ppm). The mean exposure level (0.43 ppm) averaged over the work-shift (5–15 h) did not exceed the OEL for benzene, but four individual subjects exceeded the 12-hr OEL of 0.6 ppm. Subjects not wearing respirators, all located in the small boats, had detectable concentrations of SPMA in post-shift urine (0.5–3.3 µmol/mol), and the highest concentration was detected in the urine of a non-smoker. However, the SPMA concentrations did not exceed the BEI recommended by the ACGIH of 11.8 µmol/mol. Subjects wearing respirators did not have detectable concentrations of urinary SPMA, even when exposure levels exceeded the OEL.

5. Discussion

5.1 Main findings

5.1.1 Laboratory study of evaporation

According to the air concentration models for benzene, the total variance in the air concentration of benzene was explained by the content of benzene in the fresh oil and oil group (condensate/light crude oil) during the first 5 and 15 min of sampling, and pour point during the last 15 min of sampling. The air concentration if both TVOC and benzene was higher at 13°C than at 2°C, although temperature was not a significant determinant in the model. The air measurements indicated that benzene, toluene, ethylbenzene and n-hexane rapidly evaporated from the oil, thus yielding higher air concentrations than xylene and naphthalene, which evaporated more slowly.

5.1.2 Full-scale field study

The exposure was characterized by short-term (<1 h) peak exposure associated with release of oil. Subjects in the small boats, located close and downwind from the oil slick, were exposed to the highest levels of benzene and exceeded or approached the OEL. Five of these subjects did not wear respirators and had detectable concentrations of SPMA in post-shift urine. However, the concentrations did not exceed the recommended BEI. Subjects that did wear respirators did not have detectable concentrations of SPMA in post-shift urine, thus indicating that the respirators prevented biological uptake of benzene and that the dermal exposure was negligible.

5.2 Comparison with previous studies

5.2.1 Laboratory study of evaporation

Our study indicates that most of the benzene evaporates within 1 h. This is similar to model simulations by Thayer and Tell, who estimated that benzene evaporates within 1 h (from 2000 to 0 ppm at the sea surface) from a thin oil film with an initial content of 2.1 wt% benzene [62]. Previous air measurements of benzene during a full-scale field trial in the North Sea reported that the air concentration of benzene was >5 ppm 5 min after release of oil. Within 34 min after release of oil the concentration was <0.1 ppm, thus indicating a rapid evaporation of benzene from the oil [69]. The sampling instrument was not able to detect benzene concentrations above 5 ppm, hence the exact peak concentration is not known. The average film thickness was 2-3 mm and the content of benzene in the fresh oil was 0.33 wt%. Several experimental studies and model estimates have indicated a less rapid evaporation of benzene, however these studies have involved considerably thicker oil films (10–62 mm) [65, 66].

In our study the air concentration of benzene, toluene, ethylbenzene and n-hexane rapidly declined while xylene and naphthalene did not show comparable decline with time. Previous model simulation studies have estimated a rapid decline (exponential) in the air concentration of benzene, toluene and n-hexane and a less rapid (linear) decline in the air concentration of ethylbenzene and xylene [61, 63]. This is in line with our results, except for ethylbenzene, which declined more rapidly than xylene. The air concentration and evaporation rate of volatile compounds is a function of the vapor pressure and the content of the compound in the fresh oil. Crude oil is a complex mixture of several hydrocarbons, and the evaporation rate of the individual compounds is affected by the relative composition of the fresh crude oil and changes in the relative composition that occur during the weathering process.

We measured significantly higher air concentrations of TVOC at 13°C than at 2°C during the first 5 and 15 min of sampling, but at both temperatures the air concentration rapidly declined. The same trend was found for benzene, although temperature was not a significant determinant in the model, probably due to few measurements and low statistical power. The temperature affects the viscosity, which in turn affects the evaporation rate, thus the water temperature is likely to have a significant effect on the evaporation rate during oil spills at sea, as reported in previous studies [33, 61, 87].

According to our air concentration models for benzene for the first 5 and 15 min of sampling, the content of benzene in fresh oil and oil group (condensate/light crude oil) explained 63–67 % of the total variance in the air concentration of benzene. Our model predicted that the air concentration of benzene doubles with each wt% increase of benzene in the fresh oil during the first minutes after release of oil. A previous study used a simplified air dispersion model to estimate the air concentration of benzene evaporating from a thin oil film (0.1 mm) with a low (0.01 wt%), medium (0.2 wt %) and high (2.1 wt%) benzene content [62]. The wind speed was 0.5 m/s and the water temperature 21°C. The model estimated an almost linear relationship between the content of benzene in the fresh oil and the air concentration of benzene, which is in accordance with our model estimates. Furthermore, our model predicted a significantly higher air concentration of benzene (40-70 % higher) during the first 5 and 15 min of sampling for the light crude oils than the condensates when adjusting for the content of benzene in fresh oil. This may be due to the higher content of VOCs in the condensates, which may delay the evaporation of benzene. However, the evaporation of benzene will be dependent on film thickness, and condensates are expected to form thinner oil films than light crude oils during spills at sea, and thus expected to yield a higher evaporative loss of benzene [60, 62, 87].

Our air concentration models predicted that pour point, the temperature below which the oil will not flow and becomes semi-solid, could explain 73 % of the total variance in the air concentration of benzene during the last 15 min of sampling, with significantly higher air concentrations for oils with a high compared to a low pour point. During the last 5 min of sampling, at both 2°C and 13°C, our benzene measurements ranged from 0.01 ppm to 0.09 ppm for oils with a low pour point (< -33°C), indicating near complete evaporation of benzene within 30 min. For oils with a higher pour point (-10 to 6°C) the air concentration of benzene ranged from 0.3 ppm to 1.5 ppm, thus indicating a less rapid evaporation from these oils. Our results indicate that the pour point affects the evaporation of benzene, and that oils with initially high pour points will yield a slower evaporation of benzene. Previous studies have suggested that a high wax content may limit evaporation [32, 33]. Wax and pour point was positively correlated in our study, and a high pour point is often a result of a high content of wax components (i.e. paraffins > C_{20}), thus our results are in line with previous findings.

5.2.2 Full-scale field study

We measured the highest air concentration of TVOC (510 ppm) within 10 min after the first release of light crude oil (Åsgard Blend), which was nearly five times higher than the highest concentration (114 ppm) measured during release of heavy crude oil (Grane Blend). The air concentration rapidly declined in all the releases of oil, and the concentration of VOCs was below the LOD within 20 min and 60 min after release of heavy crude oil and light crude oil, respectively. The air concentration of VOCs was lower during the release of heavy crude oil, probably because of the low content of VOCs in this oil, which have also been suggested in previous studies [70, 79].

Our calculated mean air concentration of benzene (0.43 ppm) averaged over the work-shift (5–15 h) for subjects in the ‘high exposure’ group did not exceed the 12-OEL for benzene of 0.6 ppm. We found considerable variations in the exposure levels (0.003–1.52 ppm) between subjects in this group, and four individual subjects exceeded the 12-hr OEL. The Committee for Risk Assessment (RAC) has proposed to lower the OEL for benzene to 0.05 ppm (in the breathing zone) in order to avoid risk for chromosomal damage in workers and because no significant residual cancer risk or other adverse effects are associated with this level of benzene [43]. All but five subjects in our ‘high exposure’ group and a few subjects in the ‘low exposure’ group would exceed the proposed OEL of 0.05 ppm.

We measured short periods of exposure during bulk release of fresh crude oil at sea. This rapid decline in the air concentration of the volatile compounds is in agreement with our experimental studies in the laboratory. Model simulations of the Hebei Spirit oil spill (30–34°API) estimated that airborne benzene levels on the ocean floor would exceed the OEL of 1 ppm on the first day of the spill [75]. In contrast, the reported air concentrations during the DWH blowout were much lower [71, 72]. Not because the potential risk of exposure was low, but because oil was released more than 1500 m below the sea-level, which allowed the volatile, water soluble compounds to dissolve in the water column before reaching the sea surface [73]. In contrast to the first day of oil release, when the air concentration of VOCs rapidly declined, we measured a fluctuating air concentration of TVOCs (300-500 ppm) after release of light crude oil on the second day. Wind has been reported to result in fluctuating air concentrations of volatile compounds in previous studies [65, 88], and on the second day of release there was more wind (8 m/s) compared to the first day (2-5 m/s). There was also breaking wave conditions on the second day, which may have affected the evaporation. About 30 min after the release the concentration of TVOC was below the LOD.

Because of the high exposure levels associated with the bulk releases of oil in our study, it is possible that all of our study subjects located in the small boats exceeded the Norwegian 15-min STEL for benzene of 3 ppm. This was also indicated by measurements and model estimates for the Braer and Exxon Valdez oil spills reporting a maximum benzene concentration of 7 ppm and a maximum hourly concentration of 4.9 ppm, respectively [61, 63]. However, RAC has not recommended a STEL for benzene because acute effects on the central nervous systems is only associated with very high levels of benzene (300-3000 ppm) [43]

Subjects in the ‘high exposure’ group, located in the small boats close and downwind from the oil slick, were exposed to considerably higher levels of airborne benzene compared to subjects located on the ships further downwind or upwind from the oil slick. This was not surprising considering that the concentrations are highest at sea level near the oil slick and decrease with increasing distance from the oil slick. Considerable differences were also found for the various exposure groups in the job-exposure matrix (JEM) of airborne total hydrocarbons (THC), developed for the workers responding to the DWH oil spill [89]. Personnel onboard vessels in the hot-zone (<2 km from the source) who operated remotely operated vehicles (ROVs) were identified as the highest exposed group. Model simulations of the Braer oil spill also indicated that the exposure levels may be high directly above the oil slick, but rapidly drops with increasing distance from the oil [63].

Five of the subjects located in the small boats, identified as highly exposed a priori, did not wear respirators on the first day of oil release. They all had detectable concentrations of SPMA in post-shift urine (0.5–3.3 µmol/mol creatinine), thus indicating uptake of benzene. Ha et al. (2012) also found significantly higher levels of tt-MA, a biomarker of benzene exposure, in post-shift urine compared to pre-shift urine in volunteers participating in the cleanup of the Hebei oil spill [78]. However, tt-MA is not a specific marker of benzene. Based on the mean half-life (9–13 h) of urinary SPMA, an exposure to 0.2 ppm benzene (during a work-shift) should correspond to an average SPMA concentration of 3.9 µmol/mol [51]. Our subjects had lower concentrations of SPMA after being exposed to this level of benzene. A possible explanation to this discrepancy is that urine was collected at the end of the work-shift, which was more than 7 h after the last release of light crude oil (see Figure 6), when the exposure was highest according to the TVOC measurements. The post-shift SPMA concentration measured in our study did not exceed the BEI recommended by the ACGIH of 11.8 µmol/mol. However, the recently proposed OEL of 0.05 ppm corresponds to a BEI of 1 µmol SPMA/mol creatinine, and our subjects either exceeded or approached this concentration [43].

None of our study subjects who reported wearing respirators had detectable concentrations of SPMA in post-shift urine on either day, even when exposure levels exceeded the OEL. This indicates that dermal uptake of benzene was negligible. We did not find a correlation between the air concentration of benzene and post-shift urinary SPMA concentration as indicated by previous studies [90, 91], probably because most subjects used respirators and only a small number of subjects did not.

Our study suggests that the respirators (half-face air purifying respirators with a combination of a particle filter and an organic vapor cartridge, A2) used by our study subjects prevented biological uptake of benzene at levels approaching or exceeding the OEL. In contrast, Lee et al. did not find any difference in the metabolite concentration of tt-MA, a biomarker of benzene exposure, between subjects wearing and not wearing masks during cleanup of the Hebei Spirit oil spill [76]. However, benzene and its metabolites have short half-lives (≤16 h), and samples were collected two weeks after the spill occurred [49].

We can assume that the time of exposure would be less than 1 h for the four oils with a low pour point, due to the rapid evaporation of benzene measured in our bench-scale study, similar to Åsgard Blend. Two oils (A and B) had a higher benzene content than Åsgard Blend and yielded a higher air concentration of benzene, thus the exposure levels could have been higher if one of these oils had been tested in our field study. The exposure levels could also have been different if we had tested one of the oils with a high pour point, because benzene evaporated less rapid, thereby prolonging the time of exposure.

5.3 Methodological discussion

5.3.1 Laboratory study of evaporation

Study design

Although a few experimental evaporation studies of fresh crude oil released on water have been performed, the majority of the previous studies are model simulation studies using a variety of environmental conditions, oil types and slick thicknesses. To our knowledge, no previous studies have investigated the association between physicochemical properties of crude oils and the air concentration of benzene. Neither have previous studies involved more than one oil or performed repeated tests with the same test conditions, although one of the advantages with an experimental study design is repeatability. Hence, an experimental bench-scale study (Paper I) with repeated tests of several fresh crude oils with a variety of physicochemical properties and content of benzene was performed to investigate how the relative air concentration of VOCs, benzene in particular, is affected by temperature, time and oil type.

Air measurements

Air measurements of benzene evaporating from thin oil films have not been reported before, only for thicker oil slicks. Model estimates have indicated a very rapid evaporation of benzene from thin oil films, regardless of the content of benzene in the fresh oil. This was confirmed by pilot tests we performed in an early stage of the project with a few of the selected oils. Based on these tests we chose a total sampling time of only 30 min, with short sampling intervals of 5-min to characterize how the air concentration of benzene developed with time. Active ATD-tubes packed with Tenax TA were the only available option sensitive enough for these short-term measurements. The tubes fitted our experimental setup well and were easy to manage. The experimental settings for temperature, air flow and film thickness in the bench-scale experiments were pre-defined in accordance with the main objectives of the overall project. The pour point increase and the benzene content decrease during the weathering process due to evaporative loss of VOCs. However, our main focus in the air concentration models for benzene was fresh oil, because this information is often available for crude oils, which makes it possible to use the model predictions on other oils.

We assumed complete evaporation of benzene within the 30 min of sampling, and found a discrepancy in the mass balance between the reported content of benzene in fresh oil and the measured amount of benzene that evaporated. Possible explanations are incomplete mixing of benzene in the chamber because of short-cut of the airflow from the air inlet to the air outlet, evaporative loss during preparation of the oil, saturation of the ATD-tube sorbent or dissolution of benzene in the water during our period of sampling. Dissolution of benzene was considered unlikely because we collected water samples that indicated that less than 0.6 % of the initial content of benzene dissolved in the water. Saturation of the sorbent was assumed to be negligible because our sampling duration and concentration levels were within the safe sampling volume of the sorbent [92]. Because all the tests followed the same protocol and were performed by the same person, we assumed that the factors affecting the mass balance were equal in each test. Temperature was not a significant determinant in our air concentration models for benzene, probably due to low statistical power, although we performed several tests, and the very rapid evaporation of benzene. Nevertheless, the discrepancy in the mass balance calculations is probably a combination of the factors explained above.

Human and technical errors are a disadvantage of experimental studies and cannot be excluded. We tried to limit the errors by using the same procedure and setup in each experiment, and the tests were performed over a short period of time by the same person. Smoke tubes used in the pilot study to visualize air mixing indicated homogenous mixing of air, and real-time measurements performed outside the test chamber indicated no leakage of VOCs. The test chamber was washed and dried before each test and then filled with filtered seawater tempered in the test room. The air temperature was logged continuously, and the water temperature was measured before application of oil. A weight was used to measure the amount of oil to be applied with a syringe in each test and the empty syringe was control-weighed afterwards. All equipment was calibrated before each test. The ATD-tube flow was measured before and after each test and the tubes were stored in a cold room (4°C) before shipment to an accredited (ISO 17025) analyzing laboratory.

Selection of oils

In order to study the air concentration of benzene we could have selected several oils with a high content of benzene. However, because this study was part of a larger research project, several criteria had to be fulfilled. Each of the oil companies participating in the project had to be represented by at least one oil, which had to be in production and have an available previous laboratory weathering study (performed by SINTEF). The selected oils were categorized as condensates and light crude oils based on previous weathering studies performed by SINTEF and included light condensates, condensates with the ability to form residues on the sea surface due to high pour point/wax and light crude oils with the ability to form unstable emulsions. Thus, the selected oils represented a variety of physicochemical properties of oils produced and transported on the NCS. In addition, one oil (oil H) was included as a reference of typical paraffinic crude oils on the NCS.

We grouped oils in the mixed model analysis according to the International Tankers Owner Pollution Federations (ITOPF) classification of oils [22]. ITOPF have defined four oil groups based on the oil's API gravity, because it is likely that these oils will behave in a similar way if spilled at sea. Group 1 includes oils with density below 0.80 g/ml and viscosity less than 3 mPa.s. Group 2 includes oils with density between 0.80 and 0.85 g/ml and viscosity above 4 mPa.s. ITOPF also distinguish between oils with high (above 5°C) and low (below 6°C) pour point, because oils with high pour points will become semi-solid on the sea surface at low temperatures. Hence, oils with the ability to become semi-solid at low temperatures (i.e. 2°C) were grouped as high pour point oils in our model, although the pour point for some of these oils were less than 6°C. Grouping based on wax content was done according to how SINTEF have reviewed the wax content of each oil included in this study in their weathering reports, because ITOPF have not included wax content in their groups. In these reports, the oils were referred to as either low wax (less than 2 wt%) or moderate wax (2–5 wt%) oils. The weathering reports were also used to define oil group (light crude oil or condensate), which is a categorization of oils related to weathering that is used in the SINTEF OWM [93].

External validity

Our evaporation experiments are relevant for similar oil types. Although some oils may differ from the oils included in our study, the selected oils cover a range of physicochemical properties of oils produced and transported on both the NCS and worldwide. The water temperature (2°C and 13°C) was chosen to reflect temperatures on the NCS, but are low compared to temperatures elsewhere, such as the Mexico Gulf, Persian Gulf and Pacific Ocean. Thus, at higher temperatures the concentrations may be higher and the evaporation more rapid than in our study, when the same conditions apply. Although the sampling point (10 cm above the oil film) does not represent the breathing zone and the ventilation conditions in the test chamber are not representative of actual atmospheric conditions, the study is still considered relevant for understanding how the relative air concentration of benzene varies with temperature, time and oil type under the chosen test conditions.

5.3.2 Full-scale field study

Study design

Previous full-scale oil spill exposure studies have either been cross-sectional or model simulation studies of real oil spills. This study was a cross-sectional study with a repeated measures design, with the aim of investigating human exposure to VOCs during release of fresh crude oil in a full-scale field study at sea. Exposed and unexposed subjects were recruited to study personal exposure to airborne benzene (Paper II) and to study the concentration of urinary markers indicating biological uptake (Paper III). The study design was chosen to study exposure levels between pre-defined exposure groups, and by including biomonitoring we could measure the exposure by all routes and account for individual variations in uptake and metabolism. Although the number of exposed subjects in our study was low due to use of respirators, our pre- and post-shift sampling of urine made it possible to account for the baseline concentration of benzene (pre-shift) within each subject and assess the uptake of benzene during the work-shift.

Airborne exposure assessment

Previous measurements of VOCs and benzene exposure levels have been performed during real oil spills and therefore the measurements have not been initiated during the first stages of the spill, when oil is released and the exposure is assumed to be highest. We were able to measure personal benzene exposure levels for subjects participating in a full-scale ‘oil-on-water’ field trial at sea and characterize the overall exposure levels by continuous monitoring of TVOC. We had detailed information about the participant’s work tasks and the composition of the oils, and were able to identify exposed and unexposed subjects a priori. In order to detect benzene exposure levels of 0.2 ppm, our study required air samplers with high sensitivity. Both active and passive ATD-tubes were available options for full-shift personal sampling, but we chose passive sampling because they are less obstructing to work with and do not require pumps. Selection bias may occur in cross-sectional studies, but we recruited everyone assumed to be exposed. We also recruited everyone who had observational tasks on the command bridge of either ship during release of oil as background referents. A total of 23 field trial participants fitted our inclusion criteria. Only two of these participants were females, of whom one declined to participate in the study. Two subjects were only exposed to crude oil on the first day of oil release, hence they were not included on the second day of oil release.

Biological exposure assessment

We managed to recruit the required number of subjects (>15) to achieve a statistical power of 80 % in a paired test with a p-level of <0.05. However, use of respirators affected our measurements. We chose urinary SPMA as a marker of benzene exposure because of its specificity and high sensitivity. However, the relatively long work-shifts (up to 15 h) of subjects not wearing respirators possibly affected the concentration of urinary SPMA, because urine was collected between 7–11 h after release of light crude oil, when the exposure was highest. SPMA is a suitable marker for low level benzene exposure, although it has not been validated for exposure levels below 0.3 ppm and smoking may be a confounding factor at very low benzene exposure levels. To account for direct and passive exposure to tobacco smoke we measured cotinine, a specific urinary marker of nicotine. All subjects completed a questionnaire about smoking habits before and after work-shift, thus we had detailed information about the subjects. VOCs were not detected in air before or in between releases, thus indicating a negligible contribution from exhaust and that crude oil was the only source of benzene. We could disregard exposure to benzene prior to our study because the study was performed one day after leaving shore and the half-life of SPMA is less than 12 h.

The majority of our urine samples had SPMA concentrations below the LOD, but several methods are available to address this issue [86, 94]. The simplest method is to include values below the LOD as LOD/2, which is suitable for data that are highly skewed or when the number of samples with concentrations below the LOD is high [86]. The resulting AM and GM of our predefined exposure groups were low and not significantly different from each other. We found a positive correlation (r=0.54) between the personal benzene exposure level and the concentration of post-shift urinary SPMA among the five subjects not wearing respirators. The association was not significant due to low statistical power, and we also had too few samples with SPMA above LOD to model this association and adjust for smoking. Furthermore, non-smokers also had detectable concentrations of SPMA in post-shift urine. Cotinine, a marker of nicotine, was not detected, thus possible contribution from passive exposure to cigarette smoke was negligible, which indicates that the source of SPMA was oil exposure.

Selection of oils

The crude oils included in the field study were selected to evaluate different response methods, which required two very different oil types. The light crude oil (Åsgard Blend) was selected to test high-capacity water flushing of thin oil films because of its ability to form a thin oil film on the sea surface and because it was the only relevant oil available in the necessary quantities. The heavy crude oil (Grane Blend) was selected to test in-situ burning, which required a minimum film thickness of 1 mm. Although the heavy crude oil was not a part of the originally selected crude oils and the human exposure was assumed to be low, we were able to study the difference in the exposure levels between light and heavy crude oil. Preferably, our field study should have included two or more oils tested in the bench-scale study or relevant oils with a relatively high content of benzene to simulate a worst-case exposure scenario.

Logistical constraints

We had the unique opportunity to use the ‘oil-on-water’ field trial for our full-scale field study. However, we did not have the opportunity to influence either the weather, release strategy, number of participants, work tasks or working hours. We managed to recruit all participants assumed to be exposed, but one. Ideally, the exposed subjects should have been located at the same place on both days, but for several subjects the work tasks on the two days varied. It would have been valuable to characterize the exposure levels and biological uptake for the light and heavy crude oil separately, which could have eliminated the issues regarding the short half-life of SPMA. However, the release order and number of releases were modified from the original plan after departure from shore due to changes in the weather conditions. Since our sampling equipment had already been distributed, we chose to maintain our original sampling strategy with full-shift air sampling and pre-/post-shift urine sampling on each day of oil release.

External validity

Although the study has some limitations, the exposure levels measured during our full-scale field study are relevant for bulk spills of condensates and light crude oils with a relatively high content of benzene. The personal exposure levels may be even higher if the benzene content of the fresh oil is higher than the oils tested in our study. The water temperature (12.5°C) in our study may be lower compared to other regions where oil is produced and transported, thus evaporation may be faster than indicated by our study in areas where the temperature is higher. Current response strategies normally do not involve man overboard (MOB) boats operating close to the oil slick, but MOB boats are often used to operate mechanical equipment or for other purposes. The 'low exposure' group is probably more representative of the exposure levels that may occur during a real oil spill response operation. However, it is unlikely that response personnel are present at the spill site during the initial stages of an acute spill at sea because it takes time to mobilize. Hence, the risk of exposure may be more relevant for continuous spills (such as the DWH spill) of fresh crude oils or condensates with a relatively high content of benzene than for bulk spills. Furthermore, thin oil films are expected to break up naturally by wind and waves, with the majority of the oil evaporating within a matter of days, and for spills that occur in rough weather conditions it may be sufficient with aerial surveillance (i.e. remote sensing), which do not involve any risk of exposure.

6. Conclusions and recommendations

Our study showed that the benzene exposure levels for cleanup personnel may approach or exceed the Norwegian OEL during bulk release of condensates and light crude oils forming thin oil films on the sea surface. Exposure is possible in both calm weather and in breaking wave conditions with higher wind speeds. However, the OELs are based on repeated exposure to hazardous chemicals at the work-place, which is not the case during bulk spills of oil at sea. If response measures must be carried out on fresh crude oil (e.g. in a continuous spill), cleanup personnel should wear appropriate PPE, such as respirators, to avoid exposure when operating downwind. Because the risk of exposure in drops rapidly with time, the response operations should be performed on oil slicks that have been subjected to at least one hour of weathering. Although bulk spills of condensates and light crude oils are associated with short periods of high exposure immediately after spill, the benzene levels are not expected to be high enough or of sufficient duration to cause adverse short-term health effects. Furthermore, the risk of exposure is highly dependent on the content of benzene in the fresh oil, however the effect of pour point should be investigated, considering that the evaporation of benzene is less rapid for oils with initially high pour points.

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Determinants of airborne benzene evaporating from fresh crude oils released into seawater

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ABSTRACT

Benzene, toluene, ethylbenzene, xylenes, naphthalene and n-hexane evaporating from a thin oil film was measured for 30 min in a small-scale test system at 2 and 13 °C and the impact of physicochemical properties on airborne benzene with time after bulk oil release was studied. Linear mixed-effects models for airborne benzene in three time periods; first 5, first 15 and last 15 min of sampling, indicated that benzene content in fresh oil, oil group (condensate/light crude oil) and pour point were significant determinants explaining 63–73% of the total variance in the outcome variables. Oils with a high pour point evaporated considerably slower than oils with a low pour point. The mean air concentration of total volatile organic compounds was significatly higher at 13 °C (735 ppm) compared to 2 °C (386 ppm) immediately after release of oil, but at both temperatures the concentration rapidly declined.

1. Introduction

Crude oil production and offshore transport of crude oil is associated with a risk of spills from wells, ships and pipelines. A National oil spill preparedness has therefore been established to limit oil pollution at sea on the Norwegian Continental Shelf (NCS). Formation of thin oil films from blowouts or acute releases of condensates and light crude oils are of particular interest for the Norwegian Environment Agency. Blowouts of crude oil may produce wide-spread, initially thin oil films (< 0.3 mm) on the sea surface depending on the release conditions (Johansen et al., 2003; Johansen, 2003; Rye et al., 1997; Daling et al., 2017). Condensates and light crude oils could also form thin oil films in surface spills and may have a longer lifetime on the sea surface in non-breaking waves conditions. Condensates and light crude oils are low density oils (< 0.85 g/mL) associated with a high content (up to 50%) of volatile organic compounds (VOCs; C_6-C_{10}), and these compounds would rapidly evaporate from a thin oil film on the sea surface (Jordan and Payne, 1980; Thayer and Tell, 1999).

Several petroleum-related VOCs are toxic to humans and are mainly taken up by inhalation. 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 (IARC), 2012; Chemical Assessment Summary: Benzene, 2016). Benzene is the main focus because of the associated hematological effects that are reported, also after chronic exposure to a low concentration of benzene (Glass et al., 2003; Health Council of the Netherlands, 2014; Kirkeleit et al., 2008; Vlaanderen et al., 2010).

People located close to a spill, in particular oil spill cleanup personnel, have the highest risk of exposure to benzene. The potential exposure in bulk spills of oil may be high immediately after a spill, while continuous spills may yield high exposure over time. The exposure will depend on the type of oil spilled, because both the physicochemical composition of fresh crude oil and weathering behavior at sea varies between oil types. Distance from the release point and weathering time of the oil will presumably also affect the exposure, as well as environmental conditions such as wind speed and sea temperature.

The reported benzene and VOC concentrations in air during cleanup of the Deepwater Horizon oil spill were low because benzene, toluene, ethylbenzene and xylene (collectively called BTEX) dissolved in the water before reaching the sea surface (Ahrenholz and Sylvain, 2011). Also in the Nakhodka and the Prestige oil spills the reported benzene and VOC concentrations in air were low, but these spills involved heavy bunker fuel oils with a low content of benzene and VOCs, and are less

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relevant for spills of condensates and light crude oils (Morita et al., 1999; Pérez-Cadahía et al., 2007). A recent Norwegian field study indicated that most TVOCs evaporates within 1 h from an initially thin oil film formed by a bulk oil release of light crude oil in calm weather conditions at sea (Gjesteland et al., 2017). Both previous field studies of benzene evaporation and full-scale exposure models indicate an elevated concentration of benzene in air after oil spills (Eley et al., 1989; IKU Petroleum Research, 1995; Jones et al., 1992; Hanna and Drivas, 1993; Kim et al., 2012; Lehr, 1996). As reported, the air concentration of benzene will depend on the amount of benzene in the oil and the release conditions, but no studies have assessed how other oil properties may affect the air concentration of benzene with time.

In the present study a small scale, oil-on-water test system was used to carry out several laboratory experiments to compare the air concentration of benzene and other selected VOCs evaporating from thin oil films (< 0.25 mm) of different oil types under equal test conditions. The main objective was to study the impact of possible determinants; water temperature, oil group, density, pour point, viscosity and content of benzene and wax in the fresh oil, on the air concentration of benzene with increasing time after bulk oil release.

2. Methods

2.1. Selection and grouping of oils

A research project was initiated to study human exposure to benzene during release of fresh crude oil in a full-scale field study in the North Sea. The present study was performed as a supplement to this project, to measure the air concentration of benzene and other volatile compounds evaporating from several different crude oils in small-scale. The internal SINTEF Ocean register of previous oil weathering studies was used to select nine oils that are still in production and representative of the NCS (Fig. 1) (Daling et al., 1990). The oils included in this study were selected based on their availability, the assumed ability of the oils to form thin oil films (< 0.3 mm) in a spill, and their physicochemical and weathering properties analyzed with standardized analytical methods in weathering studies performed by SINTEF between 2009 and 2014 (Daling et al., 1990; SINTEF Ocean, 2014).

Fig. 1. Visual presentation of the oils included in the study. The condensates (A–E) were clear or yellow and the light crude oils (F–I) were dark red or brown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Oils with similar physicochemical properties are likely to behave in a similar way if spilled at sea. The project oils consisted of two types of oils according to SINTEF, condensates and light crude oils, categorized as oil group (Table 1). Light crude oils contain heavier compounds than condensates and are also able to emulsify significant amounts of water (SINTEF Ocean, 2014). SINTEF also group oils as either low wax (< 2 wt%) or medium wax (2–5 wt%) oils. Furthermore, the oils were grouped according to the Internation Tanker Owner Pollution Federation (ITOPF) grouping, which is based on the American Petroleum Institute gravity (API grade), viscosity and content of light and heavy components (ITOPF, 2011). The oils either belonged to ITOPF Group 1 (low density < 0.80 g/ml, low viscosity < 3 mPa.s and high VOC content: > 50%) or Group 2 (medium density: 0.8–0.85 g/ml, medium viscosity > 4 mPa.s and medium VOC content: 20-50%). The pour point, the temperature where the oil loses its ability to flow, may result in limited evaporation. Previous weathering studies of the oils included in this study showed that within 30–60 min the pour point of oil B, C, G and H rapidly increased to > 5 °C, which is classified as a high pour point by ITOPF. The other five oils all had low pour points (< −33 °C), meaning they would not solidify with time.

Six compounds; benzene, toluene, ethylbenzene, xylene (BTEX), naphthalene and n-hexane, with high volatility had previously been measured by SINTEF in the fresh, stabilized crude oil collected at 1 bar in clean cans after the separation process at the platforms or from storage stocks (Fig. 2). The compounds were quantified by use of a purge-and-trap gas-chromatograph mass-spectrometer (PT-GC–MS) operating in full-scan mode, using a modified EPA 8260 analysis method. The arithmetic mean (AM) content of benzene (0.9; range = 0.4–2.0 wt%), ethylbenzene (0.4; 0.2–0.7 wt%) and naphthalene (0.1; 0.01–0.2 wt%) was lower than the mean content of toluene (2.4; 1.2–4.6 wt%), xylene (2.4; 1.2–3.8 wt%) and n-hexane (1.8; 0.7–3.5 wt%). In total the condensates contained a higher content of the six selected compounds (8.4–12.3 wt%) than the light crude oils (3.8–7.7 wt%).

2.2. Study design

A modified version of the Mackay weathering chamber (MNS) was used to study the air concentration of the selected compounds above a thin oil film (0.25 mm) of stabilized condensate or light crude oil (Mackay and Szeto, 1981). The glass chamber (Pyrex glass, 20 l) was partly filled with filtered seawater (6.14 l) and closed with a plexiglas lid (Fig. 3). Water circulation (3 rpm) was generated by an axial DC-fan (D300K) attached to the air inlet of the lid, and with the outlet connected to a vent. This fan is smaller compared to the high capacity fan used in the original MNS setup and does not generate heat. The airflow (2.1 l/s) provided a nominal air change (0.15/s) corresponding to light wind speed (1 m/s) over the film and no waves. Air flow test tubes (Dräger) were ised to visually test air mixing in the chamber. Fresh crude oil (≈16.5 ml) was applied (in 5–10 s) through a hole in the lid that was immediately capped after application. To create a homogenous film most oils were applied below the water surface through a hydraulic steel tube (Swagelok, 0.5 mm) attached to a syringe (BD Plastipak, 20 ml), but two oils were applied with a larger syringe (60 ml) as oil droplets in filtered seawater to avoid solidification of oil during application. All oils except oil F were tested once at two different water temperatures, chosen to reflect winter/arctic (2 °C) and summer (13 °C) temperatures (± 1 °C) on the NCS. In each test a sample of the oil film was collected 1 h after application of oil and the content of VOCs were analyzed according to the PT-GC-MS method mentioned earlier. Oil F was not tested at 2 °C, but was tested three times at 13 °C instead to assess the reproducibility of the setup. The experiments were carried out at SINTEF SeaLab, Trondheim, Norway.

Table 1
Oil characteristics of the fresh crude oils.

Oil group	Oil ID	Density[a] (g/ml)	API (API°)	Benzene (wt%)	TVOC (wt%)	Asphaltenes (wt%)	Wax[b] (wt%)	Viscosity[c] (mPa s)	Pour point[d] (°C)
Condensate	A	0.75	58	1.98	46	0.02	0.5	1	−36
	B	0.83	39	1.21	34	0.01	2.2	6	6
	C	0.80	46	0.96	32	0.03	5.0	5	0
	D	0.76	55	0.42	50	0.00	0.0	1	−36
	E	0.73	62	0.42	51	0.04	1.2	1	−33
	Mean	0.77	52	1.00	43	0.02	1.8	2	−20
Light crude oil	F	0.78	50	1.02	32	0.00	3.9	1	−36
	G	0.82	42	0.91	22	0.03	3.3	37	−9
	H	0.83	38	0.43	17	0.16	4.1	12	−9
	I	0.84	38	0.38	19	0.03	1.5	5	−36
	Mean	0.82	42	0.69	23	0.06	3.2	14	−23

Notes: API, American Petroleum Institute gravity; TVOC, Total Volatile Organic Compounds.

[a] Density, low: < 0.8 g/ml, medium: 0.8–0.85 g/ml.

[b] Wax, low: < 2 wt%, medium: 2–5 wt%.

[c] Viscosity, low: < 3 mPa·s, medium: > 4 mPa·s (measured at 13 °C with a shear rate of 10 s^{-1}).

[d] Pour point, low: < −33 °C, high: > −9 °C.

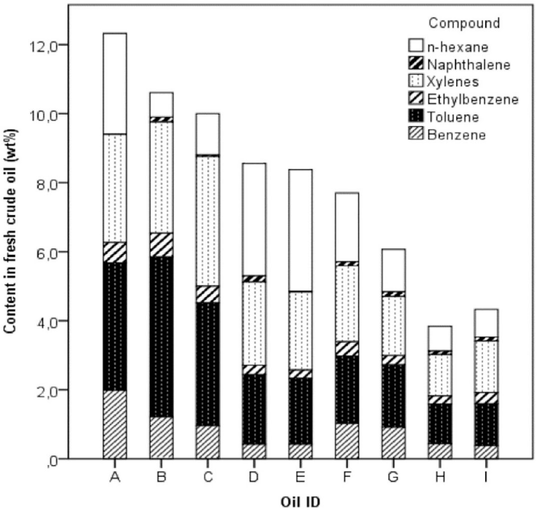

Fig. 2. Content (weight %) of selected compounds in the fresh, stabilized crude oils included in the study, analyzed by GC–MS.

2.3. Air monitoring

Stainless steel, automated thermal desorption tubes (ATD, Markes int/PerkinElmer, Boston, US-MA), were used for active air sampling and quantification of BTEX, naphthalene and n-hexane. The ATD tubes were packed with a Tenax TA sorbent (porous polymer, 220 mg) with a mesh size of 35/60 and a low surface area (35 m^2/g), suitable for sampling and analyzing the selected compounds for a wide concentration range (Markes International, 2013/2014). ATD tubes were placed in parallel to an airtight, customized hole at the center of the lid 10 cm above the oil film, and attached to an AirChek 52 Personal Sample Pump (SKC Inc., Eighty Four, US-PA) with a low flow rate (50 ml/min). The pump was started simultaneously with oil application, and flow rate changed < 1% during sampling. Active air sampling was done in intervals of 5 min from application of oil and the following 30 min to get a total of 6 consecutive air samples per oil. Air samples were stored at 4 °C upon shipment with public mail transport to SINTEF Molab AS, Oslo, for analysis.

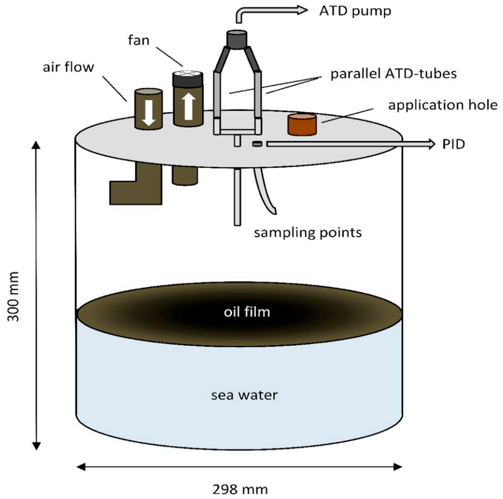

Fig. 3. Schematic drawing of the experimental setup; a modified version of the Mackay weathering chamber.

Real-time monitoring of total VOC (TVOC) was carried out with two MiniRAE 3000 (RAE systems Inc., San Jose, US-CA) photoionization detectors (PIDs) equipped with a 10.6 eV lamp. The PIDs were calibrated with isobutylene (100 ppm) to estimate the air concentration of TVOCs ranging from C_6–C_{14}. The PIDs were connected to a silicon tube, and attached to an airtight hole close to the center of the lid. In pilot tests of a few oils PID measurements were carried out for > 12 h and revealed that most VOCs (> 90%) had evaporated within 30–60 min. TVOC was therefore logged every 10 s from application of oil and the following 60 min. Mean TVOC in air of all oils was calculated for each temperature (2 °C and 13 °C), but oil B was excluded due to rapid solidification.

2.4. Analytical analysis and quantification

Quantitative/semi-quantitative analysis (ISO 16017-1 and ISO 16017-2) of BTEX, naphthalene and n-hexane collected on the ATD-tubes was done by thermal desorption-GC–MS at SINTEF Molab AS. All samples were within the safe sampling volume (SSV) of the Tenax sorbent tube (Health and Safety Executive, 1993). The level of detection was 0.002 µg (≈0.0025 ppm benzene) with a relative uncertainty of ± 25%. The results are presented as the AM air concentration and standard deviation (SD) of all oils for the selected compounds at 13 °C and 2 °C.

2.5. Data analysis

The air concentrations of benzene are presented by the AM and SD of all oils at 2 °C ($n = 7$) and 13 °C ($n = 9$). Oil B solidified immediately after application at 2 °C and was excluded from the calculations at this temperature. Normal distribution was achieved by log transforming the air concentration of benzene before the statistical analysis to adjust for the skewed frequency distribution.

In preparatory analysis for the concentration models the correlation between the continuous variables; benzene content in the fresh oil (potential determinant) and log transformed air concentration of benzene, was tested with Pearson correlation test. Differences in the air concentration of benzene for the potential determinants; water temperature (2 °C/13 °C), oil group (light crude oil/condensate), density (low/medium), pour point (low/high), viscosity (low/medium) and wax content (low/medium) were analyzed by independent *t*-test. Content of asphaltene was not considered a potential determinant due to the low content in all oils. The potential determinants were also tested with a nonparametric Spearman correlation test for collinearity between variables, and only one determinant was tested in the model if the correlation was significant ($p \leq 0.05$). The difference in the air concentration of benzene between the two water temperatures, 2 °C and 13 °C, was analyzed by paired samples *t*-test.

Three separate linear mixed-effects models were developed by using the log-transformed air concentration of benzene for three outcome variables; first 5, first 15 and last 15 min after release of oil as dependent variables, and potential determinants as fixed effects. Each oil was tested with identical conditions first at 2 °C and then at 13 °C. This was treated as repeated measurements and accounted for by using oil ID as a random effect. Potential determinants associated ($p \leq 0.2$) with at least one of the outcome variables in preparatory analysis were entered as fixed factors in the mixed effects models, and were retained in the final models when significant ($p \leq 0.05$). The total variance explained by the fixed effects for each time period was calculated as the percentage change in total variance between the random- and the mixed-effects model. SPSS 22 for Windows (IBM Inc., Chicago, IL, USA) was used to analyze data.

3. Results

3.1. Air concentration

3.1.1. PID measurements of TVOC

The mean air concentration of TVOC, in isobutylene equivalent ppm values, was significantly higher at 13 °C than at 2 °C during the first 5 ($p < 0.03$) and first 15 min ($p < 0.04$) after application of oil. Fig. 4 shows that the highest concentration was measured almost immediately after release of oil at both 13 °C (735 ppm) and 2 °C (386 ppm), and rapidly decreased to about 50% of these values within 5 min and to 6% within 60 min at both temperatures.

3.1.2. ATD measurements of specific hydrocarbons

The first 5 min after release of oil the mean air concentration (at 13 °C) of n-hexane (6.0 ± 1 ppm), benzene (10.0 ± 4.5 ppm), toluene (11.2 ± 2.9 ppm) and ethylbenzene (9.9 ± 3.7 ppm) was considerably higher than the last 15 min of sampling (Fig. 5). At 2 °C the concentrations were lower and the decline in concentration less rapid. The mean air concentration of xylene (1.4–1.9 ppm) and naphthalene (0.06–0.10 ppm) remained more or less constant throughout the sampling period. Also at 2 °C the concentrations remained almost constant (xylene: 0.8–1.1 ppm, naphthalene: 0.01–0.03 ppm).

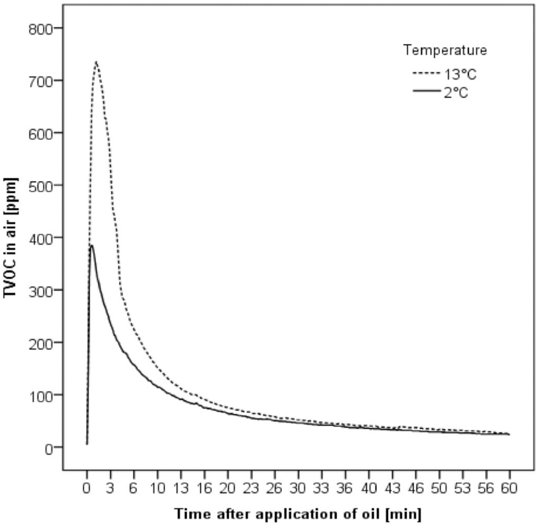

Fig. 4. Arithmetic mean concentration of total volatile organic compounds (TVOC) in air with time for all oils at 13 °C ($n = 9$, black line) and 2 °C ($n = 7$, dotted line), measured with PID.

The air concentration of benzene in 5 min time periods from release of oil and the following 30 min is presented for each oil at 13 °C (Fig. 6). Oil F is presented by the mean and SD of the three tests to show the reproducibility. The oils with the highest content of benzene (A, B, C, F and G) also yielded the highest air concentration of benzene and a rapid decrease in the air concentration with time was found for all oils. After 30 min the measured air concentration of benzene was higher for four of the oils (B, C, G and H: 0.3–0.6 ppm) compared to the other five oils (A, D, E, F and I < 0.1 ppm), with oil G yielding the highest concentration at both 13 °C (0.6 ppm) and 2 °C (1.5 ppm). The oils behaved fairly similar at the two temperatures, but at 2 °C the initial air concentration of benzene was lower than at 13 °C and the decrease in concentration was less rapid resulting in a higher concentration of benzene in air after 30 min at 2 °C than at 13 °C.

3.2. Linear mixed-effects models for benzene

3.2.1. Preparatory analysis

Although not significant, the air concentration of benzene at 13 °C was higher the first 5 ($p = 0.20$) and first 15 min ($p = 0.31$) and lower the last 15 min ($p = 0.19$) than at 2 °C. Content of benzene in applied oil and measured concentration of benzene in air was associated the first 5 ($r = 0.74$, $p < 0.001$) and first 15 min ($r = 0.61$, $p = 0.07$), but not for the last 15 min ($r = 0.17$, $p = 0.51$). The air concentration of benzene was higher for light crude oils compared to condensates both the first 15 ($p = 0.06$) and the last 15 min ($p = 0.06$), and for oils with a high compared to a low pour point the last 15 min ($p < 0.001$). There was a significant intercorrelation between the pour point and the wax content ($r = 0.73$, $p < 0.001$), and between the pour point and the viscosity ($r = 0.81$, $p < 0.001$), and therefore only pour point was tested in the mixed effects models (Table 2).

3.2.2. First 5 min

The model predicted a 2.0 times increase ($e^{0.71}$) in the air concentration of benzene the first 5 min with each wt% increase of benzene in fresh oil ($p < 0.001$) and a 1.4 times higher air concentration of

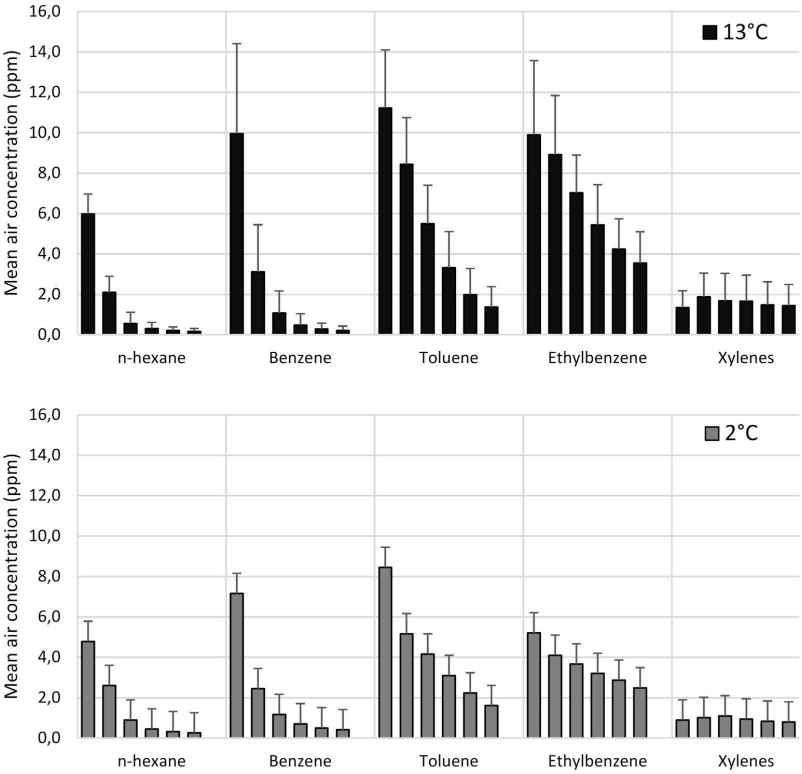

Fig. 5. Arithmetic mean air concentration (ppm) and standard deviation of all oils for the selected compounds at 13 °C (top) and 2 °C (bottom). Each bar represents a 5 min TWA air concentration of the respective compound collected with ATD-tubes from release of oil and the following 30 min.

benzene for light crude oils compared to condensates when adjusting for the content of benzene in fresh oil ($p = 0.02$). In total 63% of the total variance could be explained by these two determinants. Temperature was not a significant determinant ($p = 0.11$), but when forced into the model (not shown) the predicted air concentration of benzene was 1.3 times higher at 13 °C compared to 2 °C.

3.2.3. First 15 min

The model predicted a 2.3 times increase in the air concentration of benzene the first 15 min with each wt% increase of benzene in fresh oil ($p = 0.009$) and a 1.7 times higher air concentration of benzene for light crude oils compared to condensates when adjusting for the content of benzene in fresh oil ($p = 0.047$). In total 67% of the total variance could be explained by these two determinants. Temperature was not a significant determinant ($p = 0.21$), but when forced into the model (not shown) the predicted air concentration of benzene was 1.2 times higher at 13 °C compared to 2 °C.

3.2.4. Last 15 min

The model predicted a 13 times higher air concentration of benzene in air the last 15 min for oils with a high pour point compared to oils with a low pour point ($p = 0.002$). In total 73% of the total variance could be explained by this determinant. Temperature was not a significant determinant ($p = 0.32$), but when forced into the model (not shown) the predicted air concentration of benzene was 1.3 times higher at 2 °C compared to 13 °C.

3.2.5. Evaporation trends

In order to compare the evaporation trends of the oils the total amount of evaporated benzene during the 30 min test was defined as 100%. The percentage evaporation of the total was then calculated for each of the 5-min time periods. At both temperatures 98% of benzene evaporated during the first 15 min for the five oils with low pour points (Fig. 7, white boxes). For the four oils with high pour points (Fig. 7, grey boxes) 78% of the total amount of evaporated benzene evaporated the first 15 min while 22% evaporated the last 15 min at 2 °C. Although the difference between the two groups was less at 13 °C, the trend was the same.

4. Discussion

The mean TVOC concentration in air was highest immediately after release of oil, and almost twice as high at 13 °C compared to 2 °C. The concentration decreased rapidly to about a half within 5 min and a tenth within 30 min at both temperatures. Toluene, followed by benzene, ethylbenzene and n-hexane, yielded the highest air concentration immediately after release of oil, decreasing rapidly with time, while xylene and naphthalene yielded a lower air concentration and did not show analogous decrease during the 30 min of sampling. The most important determinants for the air concentration of benzene during the first 5 and first 15 min of sampling were content of benzene in fresh oil and oil group, while pour point was the most important determinant the last 15 min of sampling. These determinants explained 63–73% of the total variance in the air concentration of benzene for the three chosen time periods. According to the models the air concentration of benzene

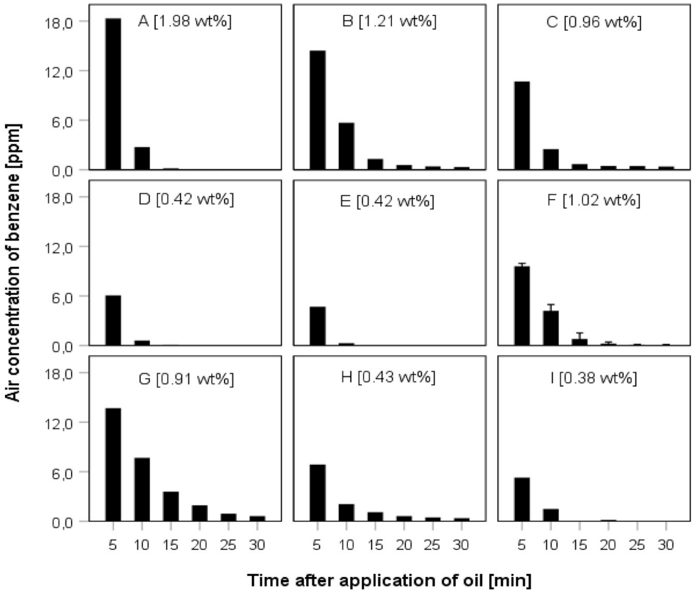

Fig. 6. Measured air concentration (ppm) of benzene in 5 min periods for each oil (A–I) at 13 °C (n = 9). Weight % of benzene in the fresh oil is included in brackets. Standard deviation is included for oil F, which was tested three times.

was higher the first 5 and 15 min and lower the last 15 min at 13 °C than at 2 °C, although not significantly.

As expected the content of benzene in fresh oil was a statistically significant determinant of the air concentration of benzene the first 5 and 15 min after application of oil. The models predicted a 2.0 (first 5 min) and 2.3 (first 15 min) times increase in the air concentration of benzene with each wt% increase of benzene in the fresh oil. Previous studies have also reported that the air concentration of benzene is very sensitive to the amount of benzene in the crude oil (Thayer and Tell, 1999). In the model for the last 15 min benzene content in the fresh oil was not a significant determinant because benzene was almost depleted from the oil film during the first minutes after oil was applied.

Oil group was also identified as a statistically significant determinant of the air concentration of benzene the first 5 and 15 min after application of oil. The models predicted a 1.4 (first 5 min) and 1.7 (first 15 min) times higher air concentration of benzene for the light crude oils compared to the condensates when adjusting for the benzene content in fresh oil. Light crude oils normally contain a lower amount of VOCs than condensates, thus it is possible tat benzene will evaporate faster from light crude oils than condensates if the initial film thickness and benzene content of the oil is the same. However, the evaporation of benzene is highly dependent on the oil film thickness during spills at sea, and condensates are expected to form thinner oil films than light crude oils that will result in a faster evaporation of benzene (Thayer and Tell, 1999).

Pour point was a statistically significant determinant affecting the air concentration of benzene the last 15 min. The mixed-effects model predicted that the decrease in air concentration of benzene was considerably slower for the oils with the highest pour points compared to oils with low pour points (< −33 °C). The pour point, the temperature where the oil loses its ability to flow, depends on the wax content of the oil and the amount of light hydrocarbons that are able to keep the waxes dissolved in the oil (SINTEF Ocean, 2014). At low temperatures oils with a high pour point tends to solidify at the sea surface. The

Table 2
Linear mixed-effects models. Random model represents the oil ID.

Log benzene	First 5 min		First 15 min		Last 15 min	
	ppm		ppm		ppm	
Effects model	Random	Mixed-1	Random	Mixed-1	Random	Mixed-2
	β (SE)	β (SE)	β (SE)	β (SE)	β (SE)	β (SE)
Intercept	2.09 (0.15)*	1.30 (0.17)*	1.32 (0.18)*	0.35 (0.20)	−1.80 (0.50)*	−3.33 (0.52)*
wt% benzene, fresh oil		0.71 (0.14)*		0.83 (0.17)*		–
Condensate (0) vs light oil (1)		0.33 (0.14)*		0.52 (0.18)*		–
Low (0) vs high (1) pour point		–		–		2.56 (0.49)*
Within-oil variance (S^2)	0.09	0.09	0.08	0.09	0.26	0.25
Between-oil variance (S^2)	0.14	0	0.25	0.02	2.14	0.40
% tot. variance explained by the fixed effects		63		67		73

Notes: Regression coefficient (β), Standard error (SE) of the regression coefficient, significant at $p < 0.05$*.

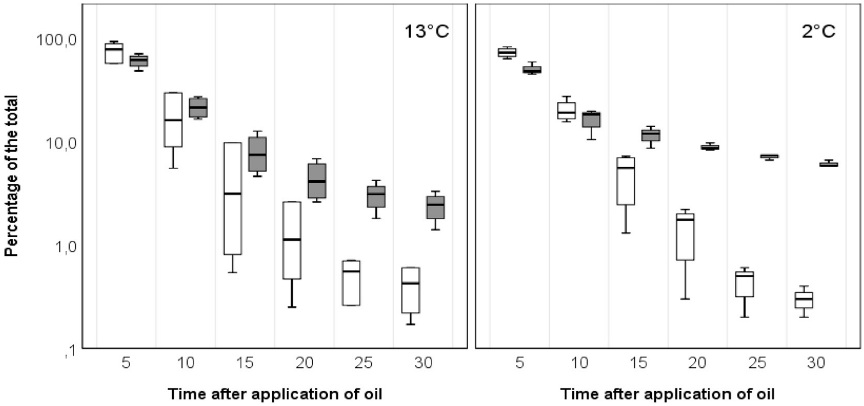

Fig. 7. Box-plot of evaporated benzene (%) in 5 min TWA intervals on a log scale, calculated from the total amount of evaporated benzene in 30 min at 13 °C (left) and 2 °C (right). White boxes represent low pour point oils and grey boxes represent high pour point oils.

results in this study suggest that this might slow down the evaporation of benzene, prolonging the period of time when benzene is present in air. Mackay and McAuliffe suggested that a rigid film is formed at the evaporating surface of waxy oils that limits evaporation from the oil (Mackay and McAuliffe, 1989), thus supporting that pour point is an important determinant of the air concentration of benzene.

The mean air concentration of TVOC, measure with PIDs, immediately after release of oil was significantly higher at 13 °C (735 ppm) compared to 2 °C (386 ppm) during the first 5 and 15 min after application of oil. This temperature difference was not significant in the exposure models, most likely due to few measurements and low statistical power. This was expected because low water temperatures make the oil more viscous and decreases the vapor pressure, resulting in slower evaporation. Temperatures on the NCS are relatively low compared to other areas where oil is produced, and oils forming thin oil films on the sea surface in areas with higher temperatures would most likely result in faster evaporation than on the NCS.

The rapid evaporation of TVOC from the thin oil films measured with the PIDs corresponds well with a recent field study by Gjesteland et al. (2017) where two releases of light crude oil (oil F) were performed in calm weather conditions (< 4 m/s wind and no breaking waves) at sea. The oil formed an initially thin oil film (0.2–0.5 mm) on the sea surface and an air concentration of about 500 ppm TVOC was measured immediately after release of oil on a small, open boat close (< 50 m) and downwind of the oil film. The VOCs evaporated quickly, and neither benzene or other light-end hydrocarbons were detected in the air 1 h after the release. The results also corresponds to a previous North Sea field study of a light crude oil spill (38°API) where the measured benzene concentration declined from > 5 ppm to 0.14 ppm within 34 min (IKU Petroleum Research, 1995). Their conclusion was that rapid dissipation of benzene in the air was expected due to relatively high wind speeds (> 8 m/s) and significant air dilution. The indication of rapid removal of benzene and TVOC from air above fresh crude oil within an hour differs from a field study performed by Jones et al. (1992) where it took 6–8 h for the benzene concentration to decrease from 90 ppm to 8 ppm. Although both the temperature and the wind speed in the Jones study was higher than in the present study their oil film was considerably thicker (62 mm) which presumably yielded a prolonged evaporation time compared to a thin oil film. Previous field studies report that benzene exposure is highly dependent on the benzene content of the oil, weather conditions such as temperature, wind speed and turbulence, distance from the release point and weathering time of the oil, but thin oil films have not been studied (Eley et al., 1989; IKU Petroleum Research, 1995; Jones et al., 1992). Full-scale exposure models are able to take all of these factors into account (Thayer and Tell, 1999; Hanna and Drivas, 1993; Kim et al., 2012; Lehr, 1996), and could be further developed to include the effect of physicochemical properties, such as pour point, to predict potential exposure with time more precisely, also for thin oil films.

4.1. Strength and limitations

In order to find possible determinants of the air concentration of benzene we tested several oils at two temperatures to increase the variability, instead of testing a few oils repeatedly. We assumed low variability between repeated tests with the same oil because of standardized settings for seawater amount, film thickness, water temperature, airflow and air sampling. Two different temperatures were tested while the airflow was kept constant.

The amount of benzene that evaporated in each test, when assuming complete evaporation of benzene in 30 min, was estimated from the total concentration of benzene measured with the ATD-tubes and the air volume blowing through the glass chamber in 30 min. Compared with the amount of benzene in fresh oil the estimated amount of benzene that had evaporated was 35%. There could be several reasons for this discrepancy between the expected and the estimated amounts based on the measured air concentration of benzene. Potential loss of benzene during sample weigh-in prior to application of oil into the water cannot be excluded due to the high volatility of benzene. The air inlet was constructed to provide proper mixing of air in the glass chamber and to avoid short-cut of the airflow from air inlet to air outlet. Although smoke tubes indicated homogenous mixing of air, the evaporated benzene might not have been completely mixed. Because the evaporation of benzene is affected by wind speed and turbulence a lower air exchange rate could have yielded a slower evaporation and thus limited possible turbulence and bypassing of benzene and the other hydrocarbons by the air sampling device (Jones et al., 1992). Potential loss of hydrocarbons during preparation of the oil samples cannot be excluded either.

Potential loss of benzene by dissolution into the water column was tested by collecting water samples in a time series of 5, 10, 15 and 30 min after release of oil for two of the oils at 13 °C. The amount of benzene dissolved in water did not exceed 0.6% of the initial content of benzene in the oil in any of the water samples, meaning dissolution of benzene in the water contributed to only a small part of the discrepancy in the mass balance. Furthermore, visual observations indicated that no significant amounts of oil adsorbed to the edge of the chamber, most likely due to the rapid water circulation (3 rpm). Loss of benzene by breakthrough in the Tenax sorbent tube was assumed to be negligible because the concentration levels were within the safe sampling volume of the sorbent.

The 30 min of sampling was too short to detect a decrease with time for xylene and naphthalene, but the main focus of this study was benzene, and therefore frequent sampling for a short period of time was chosen. The measured air concentrations cannot emulate open sea conditions because the ventilation conditions are not representative of actual atmospheric conditions. However, the measurements can be used to compare evaporation trends for different oil types tested with equal test conditions.

5. Conclusions

This study has demonstrated that benzene evaporates rapidly from a thin oil film on the seawater surface in a bulk release of oil, even for oils with an initially high content of benzene. Apart from the content of benzene in fresh crude oil, oil group and pour point were found to be important determinants of the air concentration of benzene when condensates and light crude oils forming thin oil films are released in seawater and should be included in future exposure models to predict the air concentration of benzene with time. The results also indicate that benzene evaporates more slowly from oils with a high pour point that may become semi-solid within short time of weathering compared to oils with lower pour points. This study tested a limited selection of oils and physical factors. For future experiments other temperatures and airflows could be tested and a wider range of oil types should be included.

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IV

INFORMATION LETTER WITH CONSENT FORM

This is an inquiry to participate in the project **«Air monitoring of volatile organic compounds with respect to risk of human exposure during oil spill response operations offshore».**

Our aim in this project is to study the workers that might be exposed to benzene and polyaromatic hydrocarbons (PAHs). Benzene and PAHs are carcinogenic compounds that are present in crude oil, hence oil spills at sea might be a risk of exposure to these compounds. We wish to study the air concentration of benzene in addition to biological uptake of benzene and PAHs to map potential health risk associated with oil spill combat. You will (1) carry a **personal sample tube** throughout you work shift, (2) answer a **questionnaire** before and after your work shift and (3) take **urine samples in** the morning before your work shift and immediately after your work shift for two work shifts during the field trial.

Information about you will only be used for the purposes described above. All information will be treated with confidentiality, and will be anonymized in a database. A code will link your results and your information through a name list. We emphasize that your employer do not have access to your data, and that only project participants from the University of Bergen, with confidentiality, will have access to your data. It will not be possible to identify you in the reported results.

The project is carried out cooperation with your employer. A report from the study will be sent to your employer and the results will be published in scientific journals. The results will **only** contain information about exposure, and only unidentifiable data so that it is not possible to identify you. The results will be used to make a guideline to improve your work place regarding exposure to chemicals. The project has been approved by the Regional Comittee for Medical and Health Research Ethics (REK west) and the Data Protection Official (NSD). The project will finish in 2017.

If you need further information, please contact:
Ingrid Gjesteland, 488 99 011, ingrid.gjesteland@uib.no
Magne Bråtveit 555 86 073, magne.bratveit@uib.no

Regards,

Ingrid Gjesteland
Phd, University of Bergen

Magne Bråtveit
Professor, University of Bergen

CONSENT FORM

I have read the information letter for the project, «*Air monitoring of volatile organic compounds with respect to risk of human exposure during oil spill response operations offshore*», and have been given a verbal explanation. I agree to participate in the project with the following terms:

The urine samples will only be analyzed for:

- a metabolic product of benzene: S-phenylmercapturic acid (SPMA)
- a disintegrate of PAH: 1-Hydroxypyrene
- cotinine and 2-naphtol

The test-results will be sent to PhD Ingrid Gjesteland at the Research group for occupational and environmental medicine, University of Bergen.

I wish to be provided with my personal results and an explanation of these:

☐ Yes ☐ No

We emphasize that participation in the survey is voluntary, and you have the right to withdraw from the project at any time and withdraw the consent. My sample(s) will then be destroyed in agreement with the Biobank act § 14. I can also claim that health- and personal information, collected with the sample(s), or emerged through analysis or examination of the material, will be deleted or extradited. The opportunity for withdrawal of such a consent or demanding destruction, deleting or extradition is limited by the Biobank act § 14.

I am willing to participate in this study:

Signature____ Date _______________

CUSTOMER REQUEST FOR BIOMEDICAL INVESTIGATION

Sample Reception, Room L/2/51, Health & Safety Laboratory, Harpur Hill, Buxton, Derbyshire, SK17 9JN Tel: 01298 218099
Please complete all parts of this form, including the **How To Pay** Section overleaf.

HEALTH & SAFETY LABORATORY

Factory (Name & Address)	Tests requested	Request authorised by (person to whom results will be sent): Name : Address Tel:
Exposure Hazard:	**Signature:**	Date of collection:
Nature of specimen: Blood ☐ Urine ☐ Other (specify)	**Email address (for receipt of results – see below*)**	Date of receipt:

Serial No.:	Surname	Forenames	Date of birth	Sex	Smoker	Laboratory No.	Remarks	I consent to provide a sample for the test(s) specified. I do (✓) / do not (x) agree for my results to be made available to the company management.	✓/X
								Signed:	
								Signed:	
								Signed:	
								Signed:	
								Signed:	
								Signed:	
								Signed:	
								Signed:	

Please be aware that your details will be held on a database and may be made available to HSE staff. ***Receipt of results:** Please give your email address if you would like to receive a pdf version of your results by email instead of receiving hard copy by post. Please note these results are Official – Sensitive [Personal] and we will send a test email to verify its authenticity.

Completion of this form is subject to HSL's standard terms and conditions of business, a copy of which is available on request

I:\hsl\ebms\group\forms\Biomon\Customer request form issue 12.doc

WHO Collaborating Centre

Questionnaire (pre-shift)

Name	Date of birth	Sex (M/F)

Employer	Work place (city/base/vessel)
Employment title	Work tasks

I have had training in oil spill combat	☐ Yes	☐ No

I smoke ☐ **I snus** ☐

I smoke/snus daily	☐ Yes	☐ No
How many years have you smoked/snused?		
Number of cigarettes/snus per day?		
Did you use to smoke?	☐ Yes	☐ No
When did you quit smoking? (year)		
Number of cigarettes/snus per day before you quit?		

Do you use pain killers, anti-inflammatory drugs or medications to prevent blood clots? (Aspirin, Novid, Voltaren, etc)

Mark your answer with an X	**No, never**	**Yes, now**	**Yes, earlier**	**If earlier, what age?**
Are you often cold?				
Have you had asthma?				
Have you had hay fever/nasal allergy?				

Symptoms before exposure

Have you had any of the following symptoms the last 3 days?
Mark the degree with an X.

	Never	**Trivial**	**Moderate**	**Severe**	**Very severe**
EYES					
Itching					
Runny					
NOSE					
Itching					
Blockage					
Sneezing					
Runny					
SINUSES/THROAT					
Headache/pain in face					
Blowing out thick mucus					
Postnasal drip in back of throat					
Throat clearing/hoarseness					
BREATHING					
Cough					
Wheeze					
Shortness of breath					
Shortness of breath while walking					
Nausea					
Nausea					

Comments:

Questionnaire (post-shift)

Date	Name	Date of birth

I smoke ☐	I snus ☐	How many cigarettes/snus today?

Work information

Work vessel
Work areas (MOB, on deck, at bridge, etc)
Work tasks (oil application, boat driver, etc)

Which of the following personal safety equipment did you use? (mark with an X)

	Yes	No	Brand/type
Protective suit			
Gloves			
Respiratory protection			
Filter type (particle/coal)	Particle ☐		Coal ☐

Were you in contact with oil/chemicals during the work day?

Direct contact with skin?	☐ Yes	☐ No
Where?		
What oils/chemicals?		
How long?		

Symptoms after exposure

Have you had any of the following symptoms the last 3 days?
Mark the degree with an X.

	Never	**Trivial**	**Moderate**	**Severe**	**Very severe**
EYES					
Itching					
Runny					
NOSE					
Itching					
Blockage					
Sneezing					
Runny					
SINUSES/THROAT					
Headache/pain in face					
Blowing out thick mucus					
Postnasal drip in back of throat					
Throat clearing/hoarseness					
BREATHING					
Cough					
Wheeze					
Shortness of breath					
Shortness of breath while walking					
Nausea					
Nausea					

Have you experienced any other symptoms today?:

Sampling of urine and air

DATE:		**Time of day (hh:mm)**			
Name	D.O.B	Urine Pre-shift	Urine Post-shift	ATD Start	ATD Stop

SINTEF MOLAB

PRØVETAKINGSSKJEMA – passiv prøvetaking av løsemidler/VOC i arbeidsmiljø/inneklima

Bedrift:
Avdeling:
Utført av:
Telefon:
Rapport sendes til:
e-post:

Faktura sendes:
Adresse:

Kontaktperson:
Org.nr:

Fylles ut av Molab:
Oppdragsnr:
Antall ATD-rør utlevert:
Antall diffusjonshetter:
Adsorbent:
Utlevert/sendt:
Mottatt lab:

Nr.	ATD-rør Prøve A (nr.)	ATD-rør Prøve B (nr.)	Anvendt diff.hette? (sett kryss)	Arbeidsoperasjon/ prøvetakingssted	Start		Stopp		Antall min.	Kommentar (verneutstyr, driftsforhold m.m.)
					Dato	Kl.	Dato	Kl.		

Formål med undersøkelsen	Analyseparametre		
		Arbeidsmiljø	Inneklima

Sett kryss

Kontaktpersoner: Lilian Karlsen, lilian.karlsen@sintefmolab.no, tlf. 98 42 11 92 (analyse)
Oscar Espeland, oscar.espeland@sintefmolab.no, tlf. 918 17 793 (yrkeshygiene)
Tove Ravnåmo, tove.ravnaamo@sintefmolab.no, tlf. 990 36 032 (yrkeshygiene)
Tone Gardsjord, tone.gardsjord@sintefmolab.no, tlf. 922 98 513 (yrkeshygiene)

Returadresse: SINTEF Molab as, Kjelsåsveien 174, 0884 OSLO

SINTEF MOLAB **SINTEF**

PRØVETAKINGSSKJEMA – aktiv prøvetaking av løsemidler/VOC i arbeidsmiljø/inneklima

Bedrift:
Avdeling:
Utført av:
Telefon:
Rapport sendes til:
e-post:

Faktura sendes:
Adresse:
Kontaktperson:
Org.nr:

Fylles ut av Molab:
Oppdragsnr:
Antall ATD-rør utlevert:
Antall diffusjonshetter:
Adsorbent:
Utlevert/sendt:
Mottatt lab:

Nr.	ATD-rør Prøve A (nr.)	ATD-rør Prøve B (nr.)	Pumpe nr.	Dato	Arbeidsoperasjon/ prøvetakingssted	Flow start (ml/min)		Start (kl.)	Flow stopp (ml/min)		Stopp (kl.)	Antall min.	**Kommentar** (verneutstyr, driftsforhold m.m.) Skriv evt. på baksiden av arket.
						A	B		A	B			

Formål med undersøkelsen	Analyseparametre	Innstilt flow*	Holder A (ml/min)	Holder B (ml/min)
		Pumpe nr:		
		Pumpe nr:		

Kontaktpersoner: Oscar Espeland, oscar.espeland@sintefmolab.no, tlf. 918 17 793 (yrkeshygiene og analyse)
Lilian Karlsen, lilian.karlsen@sintefmolab.no, tlf. 984 21 192 (analyse)
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Tone Gardsjord, tone.gardsjord@sintefmolab.no, tlf. 922 98 513 (yrkeshygiene)

* Etter avtale med Molab as

Returadresse: SINTEF Molab as, Kjelsåsveien 174, 0884 OSLO

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