

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

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Highlights

- The evaporation of VOCs from thin oil films was very rapid and significantly higher at 13 °C compared to 2 °C.
- Determinants of airborne benzene evaporated from thin oil films were identified with linear mixed-effects models
- The air concentration and content of benzene in the fresh oil was significantly correlated the first min after release of oil
- Benzene content in the fresh oil, oil group and pour point explained between 63-73% of the tot. variance in the air conc. of benzene.
- Benzene evaporated more slowly from oils with a high pour point compared to oils with a low pour point.

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 significantly 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 involves a risk of oil spill from production wells, ships and pipelines. A national oil spill preparedness has therefore been established to limit oil pollution into the 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 (Daling et al., 2017; Johansen, 2003; Johansen et al., 2003; Rye et al., 1997). 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 (IARC, 2012a, b), while toluene, xylenes and n-hexane can affect the nervous system (ACGIH, 2001a, b, 2007). 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 exposure levels 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 oils 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 the length of exposure, physical activity, route of exposure and environmental conditions such as sea state, 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 were low, but these spills involved heavy bunker fuel oils with a low content of benzene and VOCs, and are less 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 release of light crude oil in calm weather 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; Hanna and Drivas, 1993; IKU Petroleum Research, 1995; Jones et al., 1992; 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 (Gjesteland et al., 2017, 2018). 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 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 to form thin oil films (< 0.3 mm) in a spill, and their physicochemical properties analyzed with standardized analytical methods in weathering studies performed by SINTEF between 2009 and 2014 (Daling et al., 1990; SINTEF Ocean, 2014).

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 International 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 ITOPI. 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%), xylenes (2.4; 1.2-3.8 wt%) and n-hexane (1.8; 0.7-3.5 wt%). In total the condensates contained a higher amount 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 it 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 used 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). The two oils with the highest pour points (oils B and C) were applied with a larger syringe (60 ml) and were shaken with filtered seawater to avoid solidification of oil during application. The oils were first tested with a water temperature of $2\text{ }^{\circ}\text{C}$ ($\pm 1\text{ }^{\circ}\text{C}$) and then $13\text{ }^{\circ}\text{C}$ ($\pm 1\text{ }^{\circ}\text{C}$) to reflect winter/arctic and summer temperatures 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 earlier. Oil F was not tested at $2\text{ }^{\circ}\text{C}$, but was tested three times at $13\text{ }^{\circ}\text{C}$ instead to assess the reproducibility of the setup. The experiments were carried out at SINTEF SeaLab, Trondheim, Norway.

2.3. Air monitoring

Stainless steel, automated thermal desorption tubes (ATD-tubes, 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 ($35\text{ m}^2/\text{g}$), 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 ($50\text{ ml}/\text{min}$). The pump was started simultaneously with oil application, and the 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.

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 C₆–C₁₄. The PIDs were connected to a silicon tube, and attached to an airtight hole close to the center of the lid, 10 cm above the oil film. In pilot tests of a few oils the PID measurements were carried out for more than 12 h and revealed that most VOCs (> 90%) had evaporated within 30-60 min. TVOC was therefore logged every 10 seconds from application of oil and the following 60 min. The mean air concentration of TVOC of all oils was calculated for each temperature (2 °C and 13 °C).

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 for each oil 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 the 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 concentrations (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 5 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).

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, 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 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 for 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% 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% 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 one 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 the xylenes 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 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 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 the fresh oil. Light crude oils normally contain a lower amount of VOCs than condensates, thus it is possible that 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 benzene (Thayer and Tell, 1999).

Pour point was a statistically significant determinant affecting the air concentration of benzene the last 15 min of sampling. The mixed-effects model predicted that the decrease in the air concentration of benzene was considerably slower for the oils with the highest pour points compared to oils with low pour points ($< -33^{\circ}\text{C}$). 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 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; Yang and Wang, 1977), thus supporting that pour point is an important determinant of the air concentration of benzene.

The mean air concentration of TVOC, measured 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. The 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 decreased 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 at 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 (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 (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 (Hanna and Drivas, 1993; Kim et al., 2012; Lehr, 1996; Thayer and Tell, 1999) 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 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 the xylenes 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 types of crude oil 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. Apart from the content of benzene in fresh crude oil, oil group and pour point were found to be significant 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 high pour points that may become semi-solid within short time of weathering compared to oils with low 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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Figure 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.

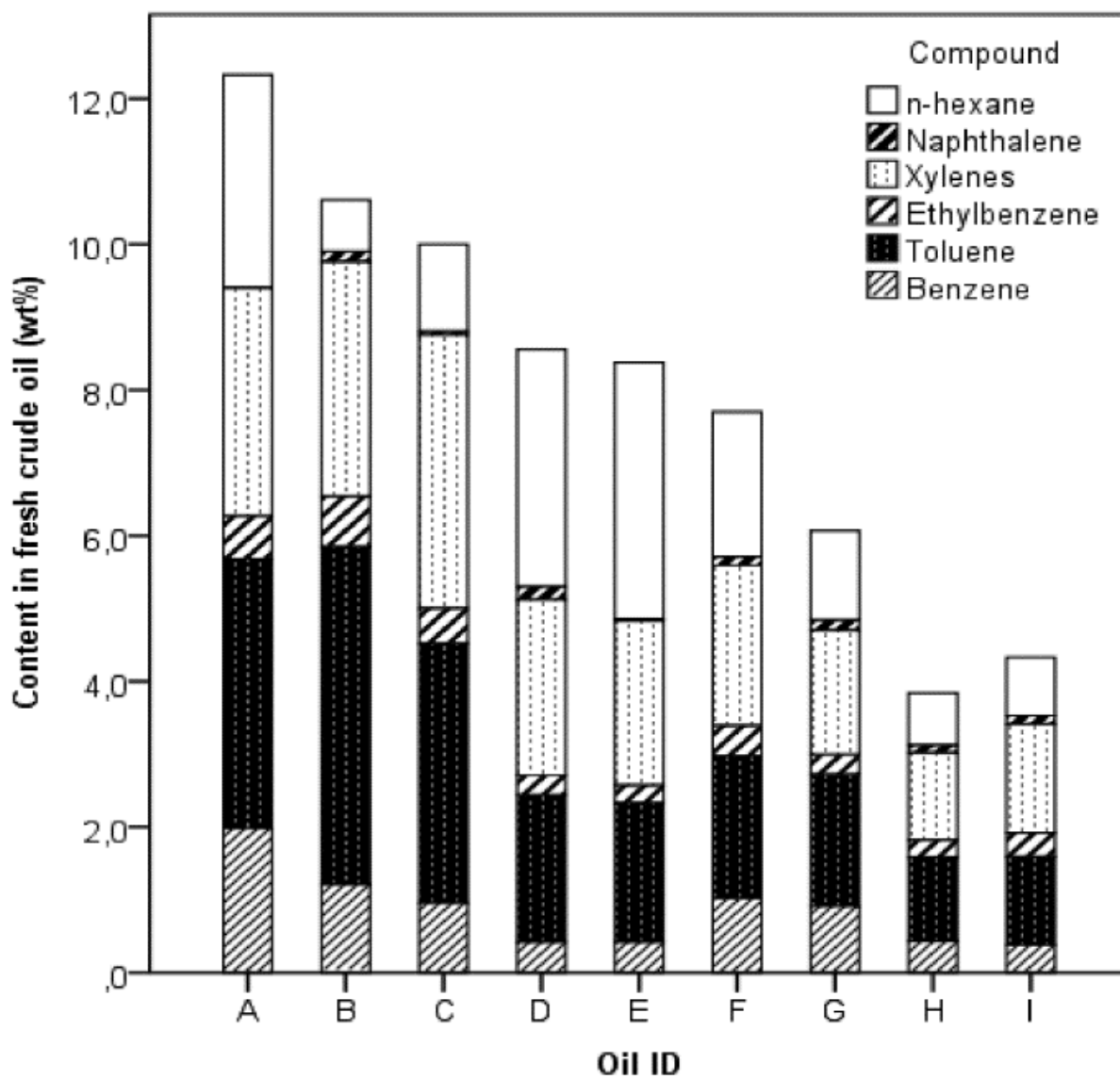


Figure 2. Content (weight %) of selected compounds in the fresh, stabilized crude oils included in the study, analyzed by GC-MS.

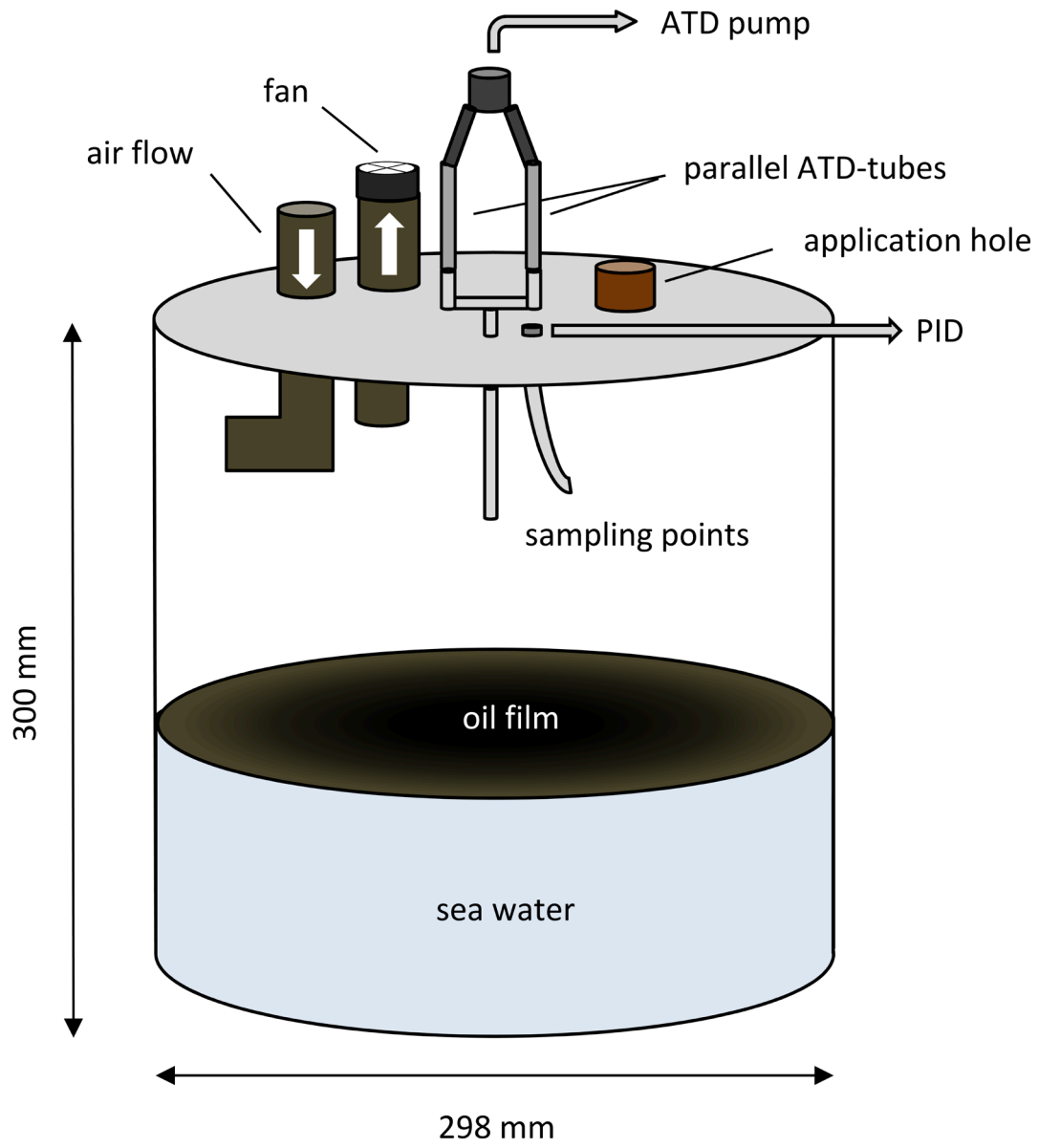


Figure 3. Schematic drawing of the experimental setup; a modified version of the Mackay weathering chamber.

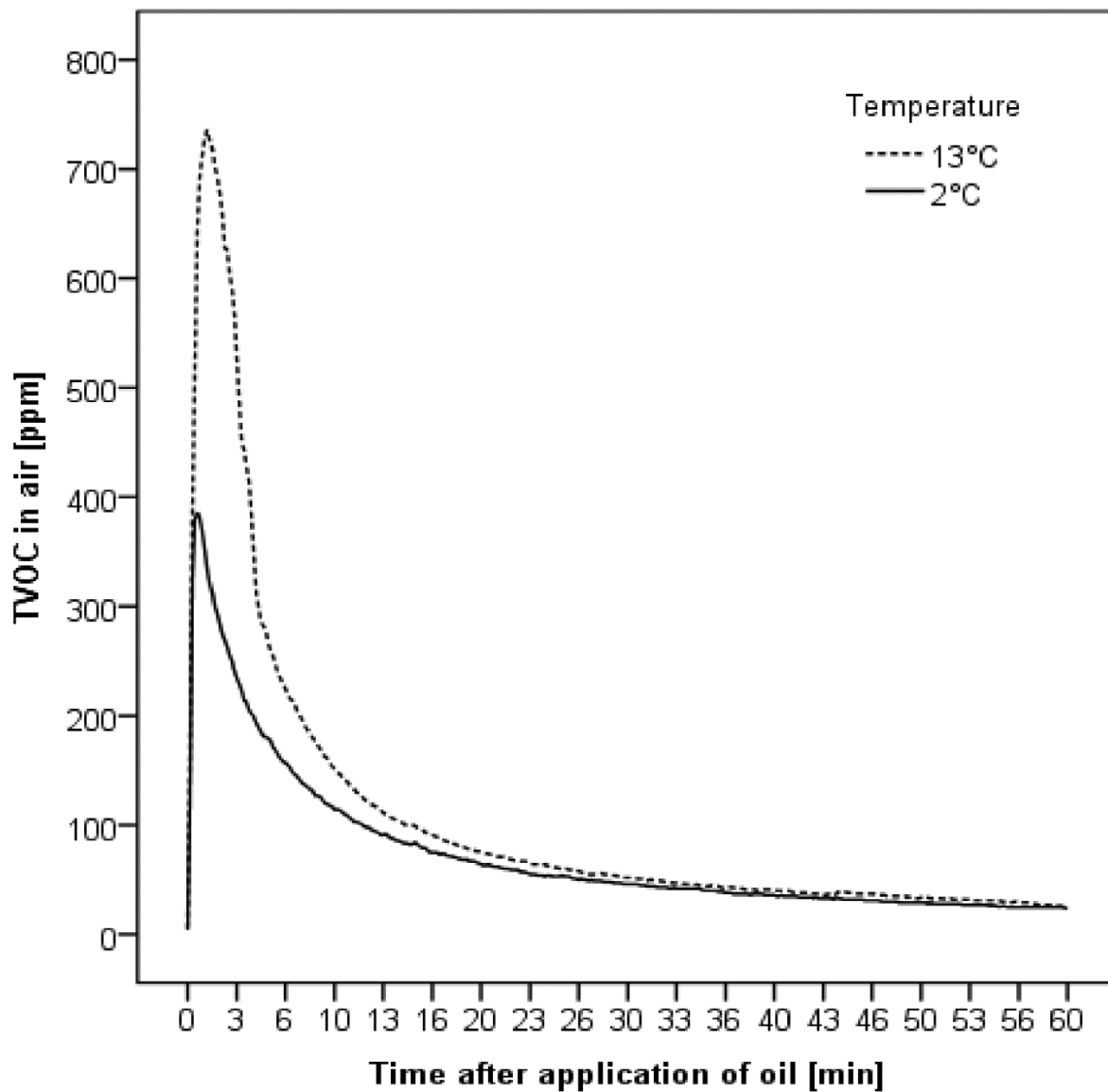


Figure 4. Arithmetic mean concentration of total volatile organic compounds (TVOC) in air with time for all oils at 13 °C (n = 9, black line) and 2 °C (n = 7, dotted line), measured with PID.

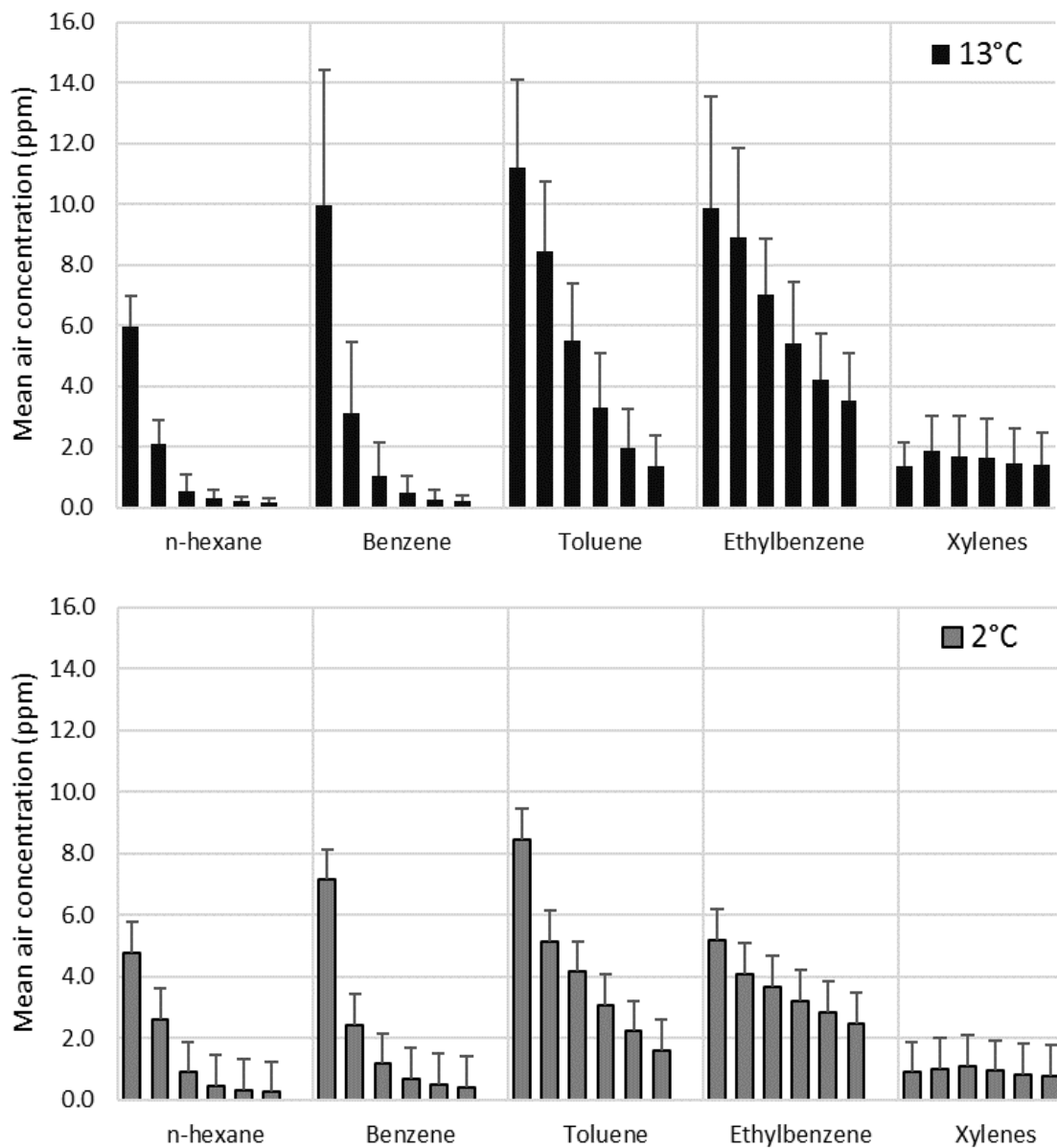


Figure 5. Arithmetic mean air concentration (ppm) and standard deviation of all oils for the selected compounds at 13 °C (top) and 2 °C (bottom). Each bar represents a 5 min TWA air concentration of the respective compound collected with ATD-tubes from release of oil and the following 30 min.

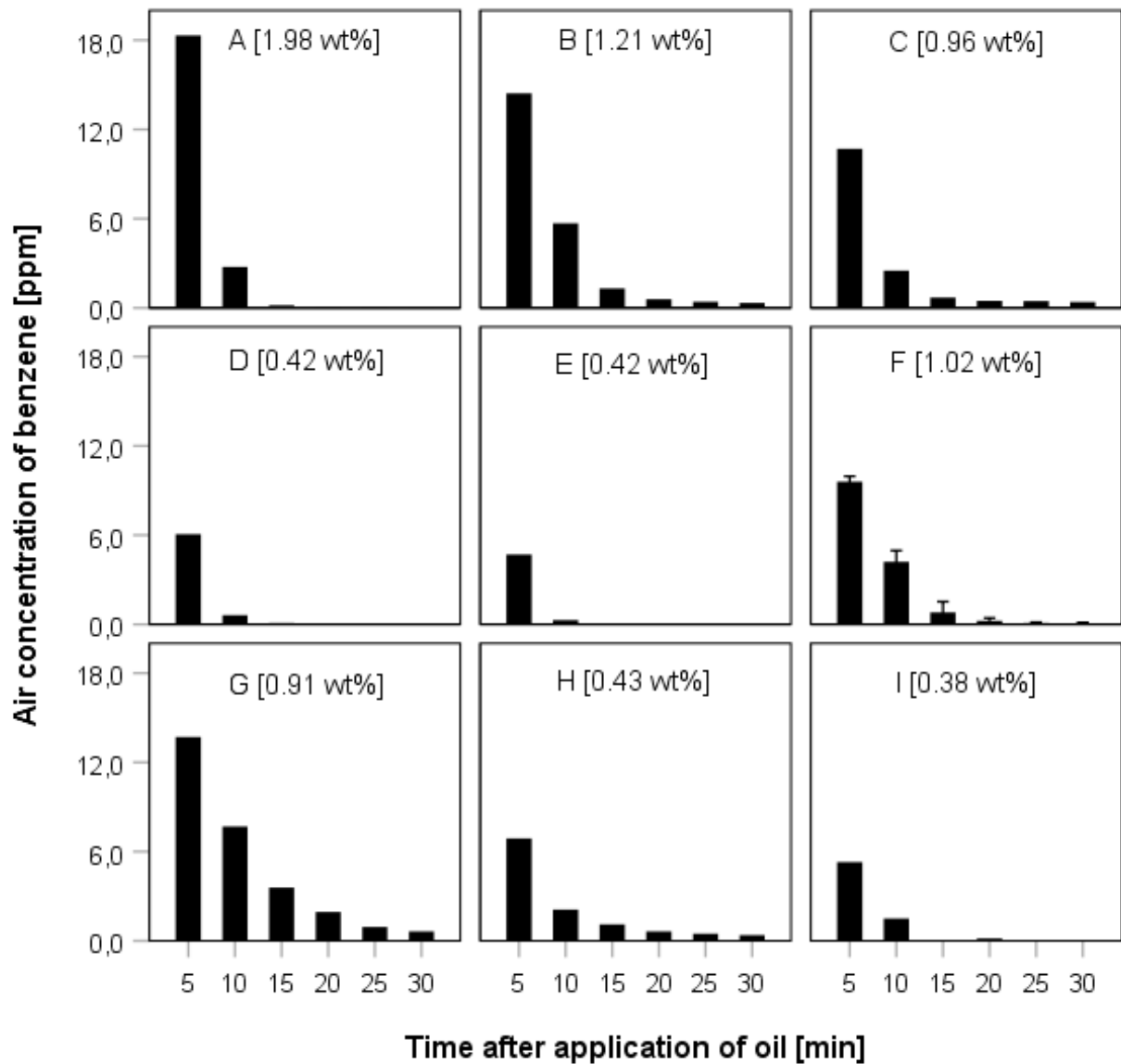


Figure 6. Measured air concentration (ppm) of benzene in 5 min periods for each oil (A–I) at 13 °C (n = 9). Weight % of benzene in the fresh oil is included in brackets. Standard deviation (SD) is included for oil F, which was tested three times.

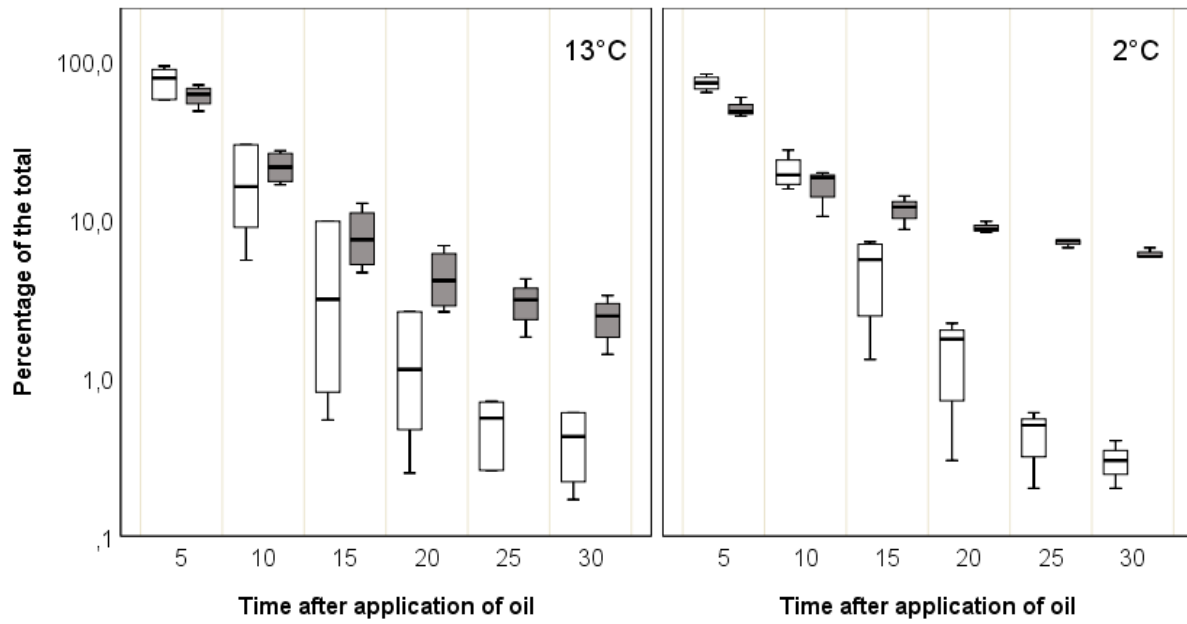


Figure 7. Box-plot of evaporated benzene (%) in 5 min TWA intervals on a log scale, calculated from the total amount of evaporated benzene in 30 min at 13 °C (left) and 2 °C (right). White boxes represents low pour point oils and grey boxes represents high pour point oils.

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

^aDensity, low: < 0.8 g/ml, medium: 0.8-0.85 g/ml

^bWax, low: < 2 wt%, medium: 2-5wt%

^cViscosity, low: < 3 mPa.s, medium: > 4 mPa.s (measured at 13 °C with a shear rate of 10s⁻¹)

^dPour point, low: < -33 °C, high: > -9 °C

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

Log benzene Effects model	First 5 min ppm		First 15 min ppm		Last 15 min ppm	
	Random β (SE)	Mixed-1 β (SE)	Random β (SE)	Mixed-1 β (SE)	Random β (SE)	Mixed-2 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 $p < 0.05^*$.