Acta Oceanol. Sin., 2019, Vol. 38, No. 9, P. 113–119
https://doi.org/10.1007/s13131-019-1479-8
http://www.hyxb.org.cn
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Flammability risk assessment for oil spill response operations

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Received 17 January 2018; accepted 27 August 2018

Abstract

Immediately following a spill at sea, released oil—ranging from diesel to light crude and diluted bitumen, will initially weather through evaporation, resulting in an elevated concentration of light hydrocarbons in the air. As part of oil spill response operations, first responders use hand-held devices to monitor airborne concentrations when approaching a spill. The feasibility of using numerical modelling as an additional tool to assess potential flammability and plan response operations in the spill area was explored in this study. The Lower Explosive Limit (LEL) is defined as the minimum concentration of a gas in air, in this case a mixture of evaporated hydrocarbons, which can produce a flash fire in the presence of an ignition source. This ignition source could be triggered by the vessel itself or by spill response operations. A framework was put into place, utilizing a three-dimensional hydrodynamic model (H3D), an oil spill model (SPILLCALC), and an air dispersion model (CALPUFF) to assess the risk of possible ignition of the hydrocarbon vapour in the event of a spill. The study looked at a hypothetical credible worst case tanker spill (16 500 m^3) of diluted bitumen (cold lake winter blend) occurring at Arachne Reef in Haro Strait, British Columbia, Canada. SPILLCALC provided one-minute averaged vapour fluxes from the water surface for each of 17 modelled pseudo-components which were used as inputs to CALPUFF. Using the predicted airborne concentrations of each pseudo-component, time-scaled to one-second averages, the flammability potential in the immediate spill area was determined at each grid point using Le Chatelier's mixing equation. The approach describe here was developed as a proof of concept, and could be established as a real-time system, bringing valuable information in addition to hand-held devices during a spill response, or during a response exercise. This modelling study was conducted as part of Kinder Morgan's Trans Mountain Pipeline Expansion Project. There are a number of commercially available oil spill models but few if any are equipped with the ability to model air dispersion and forecast hazardous conditions as discussed in this paper.

Key words: oil spill, response operations, modelling, Salish Sea

Citation: Hospital Aurelien, Miguez Travis, Stronach James. 2019. Flammability risk assessment for oil spill response operations. Acta Oceanologica Sinica, 38(9): 113–119, doi: 10.1007/s13131-019-1479-8

1 Introduction

The use of oil spill modelling has grown over the years and its applications have diversified. Major applications include environmental impact assessments for the permitting process, human health risk assessments and enhancement of mitigation strategies. A modelling framework assessing the flash fire risk of evaporated hydrocarbons during an oil spill was developed as part of the Trans Mountain Expansion Project in British Columbia (BC), western Canada. This framework combines three-dimensional hydrodynamic modelling, weathering and Lagrangian trajectory spill modelling and three-dimensional air dispersion modelling. This framework can be used to develop a reliable tool, which can then be used by first responders in case of an accident, in addition to hand-held devices, to assess the potential risk of flammability.

The area of interest, shown on Fig. 1, is located in the Haro Strait, British Columbia, part of the Salish Sea, in western Canada. Coastal fjords and estuarine regions, such as Haro Strait, are complex systems to model: temperatures and salinities are primarily governed by estuarine processes with, in this case, the Fraser River entering as surface waters and oceanic waters from the Pacific entering as a deep inflow. Along the shipping route between the Pacific Ocean and Vancouver BC, this location has been statistically determined to have a higher risk of an incident resulting from a powered grounding and/or a collision. It is emphasized that the modelled spill is hypothetical and for study purposes only and that the probability of an accident at this location is extremely low.

Although the dominant currents affecting an oil spill are the surface currents, the best way to obtain realistic surface currents is to use a three-dimensional model. In this way, processes such as wind-driven currents, river plumes and large-scale estuarine circulation, including inflow from the ocean, are correctly included in the calculation of surface currents. The use of an oil spill tracking model which simulates weathering of the oil and advection based on three-dimensional currents is therefore the most appropriate tool to conduct a realistic assessment of the full fate and behaviour of a spill.

To assess the issue of potential flammability, a high-resolution (20 m grid cell size) spill simulation was conducted at the Arachne Reef (pink dot in Fig. 1) to assess impingement of airborne hydrocarbon concentrations on flammability thresholds in and around the immediate spill area. The coupling of a three-dimensional hydrodynamic model providing surface currents to a spill model, which then computes evaporation and provides evaporated hydrocarbon fluxes to an air dispersion model rep-

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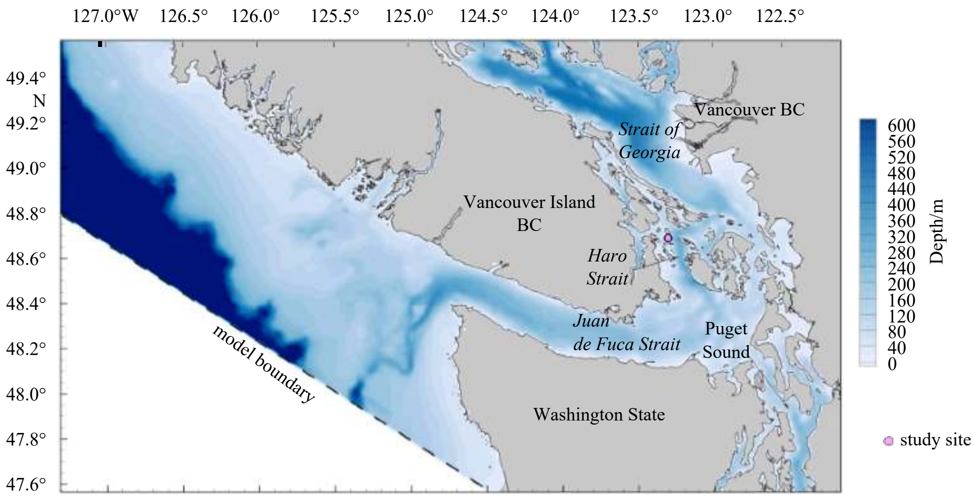

Fig. 1. Domain of study.

resents the core of this framework. Flammability of the hydrocarbon vapour over the spill area was assessed as a percentage of the Lower Explosive Limit (LEL).

2 Framework and models

2.1 *Method*

The framework developed for this study is as follows:

(1) The creation of a high-resolution (20 m spacing) oil spill model grid around Arachne Reef. The 3D hydrodynamic model H3D (model bathymetry shown in Fig. 1) directly provides surface current information to the spill model at 10 minute intervals. The spill model SPILLCALC was used for this study. A diluted bitumen, Cold Lake Winter Blend, was the hypothetical spilled oil.

(2) Evaporation curves for pseudo-component constituents of the oil determine evaporation fluxes from the water surface. Fluxes are provided as one-minute averages over a grid resolution of 20 m over a domain of approximately 3 km×3 km. Fluxes within the grid cell are assumed to be homogeneous, i.e. the variance within a 20 m×20 m area is below the resolution of the model.

(3) The meteorological grid is a subset of a larger 200 km regional grid with 1 km spacing. Hourly averaged winds are assumed i.e., the modelling excludes meandering within one hour intervals.

(4) Evaporated hydrocarbon fluxes are used as inputs in the air dispersion model CALPUFF.

(5) Airborne concentrations are predicted at the surface over a receptor grid with 20 m spacing. The spatial distribution of met data as well as the model grid resolution result in little difference between airborne concentrations near the surface and at nominal human height.

(6) The theoretical LEL of the hydrocarbon vapour is calculated at each grid cell, based on the constituent hydrocarbon vapour concentrations.

(7) Predicted hydrocarbon concentrations are assessed against the LEL as a percentage to characterize flammability risk on a minute-by-minute basis.

2.2 *Hydrodynamic model: H3D*

Surface currents for this paper were hindcast using Tetra Tech's in-house three-dimensional hydrodynamic model, H3D. This model is derived from GF8 (Stronach et al., 1993) developed for Fisheries and Oceans Canada, which has had numerous applications to the European continental shelf (Duwe et al., 1983; Backhaus and Maier-Reimer, 1983), Arctic waters (Kampf and Backhaus, 1999; Backhaus and Kämpf, 1999) and deep estuarine waters (Stronach et al., 1993). H3D is a three-dimensional time-stepping numerical model which computes the three components of velocity (u, v, w) on a regular grid in three dimensions (x, y, z), as well as scalar fields such as temperature and contaminant concentrations. The model uses the Arakawa C-grid (Arakawa and Lamb, 1977) in space, and uses a two level semi-implicit scheme in the time domain. H3D uses a semi-implicit scheme, allowing relatively large time steps, and does not separately solve the internal and external models. H3D has been used in several studies along the BC coast, including the Enbridge Northern Gateway Project, the Vancouver Airport Fuel Facility Terminal Project and the Trans Mountain Pipeline Expansion Project. An extensive application of an operational version of this model to the St. Lawrence Estuary is described in Saucier and Chassé (2000).

H3D has been extensively validated in the study area (Strait of Georgia, Juan de Fuca Strait and Fraser River). Details on the validation of the model can be obtained in the Trans Mountain Expansion Project Application and in the CWRA conference proceedings (Hospital et al., 2015). The following key points provide further information on the hydrodynamic characteristics of the model.

(1) Tidal constituents from Topex Poseidon (Schrama and Ray, 1994) were used to provide water level data at the oceanic boundary of H3D;

(2) Wind forcing is derived from interpolations of coastal Meteorological Service of Canada (MSC) stations, National Oceanic and Atmospheric Administration (NOAA) stations and Fisheries and Oceans moored buoys;

(3) River inputs from 50 rivers and creeks throughout the model domain were incorporated;

(4) Meteorological data is used to compute heat fluxes into the waterbody and thus its temperature structure (Zaremba et al., 2005);

(5) Turbulence modelling is based on the Smagorinsky shear-dependent formulation in the horizontal and Mellor and Yamada Level 2 in the vertical;

(6) Oceanic boundary conditions for salinity and temperature were available via models maintained by the Alaska Ocean

Observing System (AOOS); and

(7) H3D was implemented on a 1 km×1 km grid, rotated to align with the major axis of the Strait of Georgia.

2.3 *Spill trajectory and weathering model: SPILLCALC*

SPILLCALC is a proprietary oil spill model developed by Tetra Tech Canada. SPILLCALC is a time stepping model that computes the motion and weathering of liquid hydrocarbon spills on water. A description of the model and weathering processes can be found in Hospital et al. (2015). For this paper, only the evaporation module is described, since the risk of flammability is the focus of this study.

Evaporation is one of the main mechanisms of weathering. The representation of diluted bitumen components is crucial in modelling correctly the evaporation process. However, most crude oils contain over 100 pure components. A more practical approach is to split the diluted bitumen into pseudo-components. Each pseudo-component is an aggregation of several pure components, all with similar physical and chemical properties.

The pseudo-component description was based on the Canada Wide Standard Approach (Canadian Council of Ministers of the Environment (CCME), 2008) (14 pseudo-components) with the addition of three hydrocarbon fractions: light fraction volatiles (C_1 – C_5) and heavy fraction resins and asphaltenes. This pseudo-component approach was supported by a detailed chemical analysis of a diluted bitumen sample (Engineering Tetra Tech EBA Consultants, 2013). The final two pseudo-components, resins and asphaltenes, account for about 28% of the oil mass, but have limited solubility and very high boiling points, hence limited evaporability. However, they represent a significant part of the molar composition of the oil and influence the evaporation and dissolution rates of the lighter fractions through Raoult's Law. These two heavier fractions figure prominently in the formation of tar balls and are therefore important to the overall simulations. Table 1 shows the 17 pseudo-components used in the study.

In SPILLCALC, two processes determine the rate of evaporation. The first one is the standard bulk aerodynamic process, which calculates the mass flux from the surface slick based on wind speed, temperature, equilibrium pressure for each of the pseudo-components and molar concentration of the pseudo-component in the total product, as shown in Eq. (1).

$$E = \frac{k_{\rm term} \cdot W^{\frac{7}{9}} \cdot M_{\rm f} \cdot ppi \cdot M_{\rm v} \cdot A}{R \cdot T}, \tag{1}$$

where

E: amount of oil that evaporates (m³/(s·m²));
$k_{\rm term}$: mass transfer coefficient, calculated in Eq. (2);
W: wind speed (m/s);
$M_{\rm f}$: mole fraction;
ppi: vapor pressure of the pure product (Pa);
$M_{\rm v}$: molar volume (m³/mol);
A: area of the cell, here 20 m×20 m = 400 m²;
R: gas constant, 8.314 4 J/(mol·K);
T: temperature in Kelvin degrees.

$$k_{\rm term} = 0.029\,2 \cdot L^{\frac{-1}{9}} \cdot Sc^{-2/3}, \tag{2}$$

where

Sc: Schmidt number (Thibodeaux, 1979);
L: representative length, 20 m.

Table 1. Modelled pseudo-components

Pseudo-component	Description
VOL	volatile
AR1	benzene
AR2	TEX
AR3	aromatics $>C_8$–C_{10}
AR4	aromatics $>C_{10}$–C_{12}
AR5	aromatics $>C_{12}$–C_{16}
AR6	aromatics $>C_{16}$–C_{21}
AR7	aromatics $>C_{21}$–C_{32}
AL1	aliphatics $>C_6C_8$
AL2	aliphatics $>C_8C_{10}$
AL3	aliphatics $>C_{10}$–C_{12}
AL4	aliphatics $>C_{12}$–C_{16}
AL5	aliphatics $>C_{16}$–C_{21}
AL6	aliphatics $>C_{21}$–C_{32}
RES	F4 ($>C_{34}$–C_{50}) +
RES2	resins
ASP	asphaltenes

SPILLCALC also includes an additional mechanism to account for the effect of the slow rate of molecular diffusion within diluted bitumen (Stronach and Hospital, 2014).

2.4 *Air dispersion model: CALPUFF*

The airborne transport of the portion of each pseudo-component that evaporated from the spill was modelled over a 4 km×4 km domain centred on the spill location, using CALPUFF. CALPUFF is an advanced, multi-layered, multi-species, non-steady-state Gaussian puff air dispersion modelling system that can simulate the effects of time- and space-varying meteorological conditions on pollutant transport and is recommended by the BC Ministry of Environment for long-range transport studies in general and for short-range transport studies in complex, non-steady state meteorological situations such as over-water and coastal settings.

The main components of the CALPUFF modeling system are CALMET (a diagnostic three-dimensional meteorological model), CALPUFF (an air quality dispersion model), and a post-processing package (CALPOST). In addition to these components, there are numerous other processors that are used to prepare geophysical (land use and terrain) and meteorological data (surface, upper air and buoy data).

2.5 *Determination of flammability*

Flammability of the hydrocarbon vapour over the spill area was assessed as a percentage of the LEL over the duration of the 14 h simulation, corresponding to the largest evaporation fluxes. The LEL is an empirically derived value which defines the lowest concentration, or volume percentage in air, of a gas or mixture of gases that can ignite and result in a flash fire when an ignition source (such as a spark) is encountered. Concentrations of a vapour below the LEL are too lean to burn.

The LEL of a mixture of gases is determined by Le Chatelier's mixing equation:

$$\mathrm{LEL_{mix}} = \frac{1}{\sum \frac{x_i}{\mathrm{LEL}_i}}, \tag{3}$$

where

x_i: the volume fraction of each species in the mixture;

LEL_i: the respective lower explosive limit of each species.

The characteristics of the pseudo-components being modelled in SPILLCALC and CALPUFF are a representative surrogate for the major species within that pseudo-component with the exception of benzene, which is treated as a pure component.

Using Eq. (3), a representative LEL was determined for each aliphatic pseudo-component using the volume fractions of pure species within that pseudo-component (or isomers of species) obtained through liquid hydrocarbon analysis of the Cold Lake bitumen sample (Tetra Tech EBA). For the aromatic carbon chains for which detailed analysis was not provided, representative species within a particular carbon number range typically associated with petroleum were taken from "Toxicological Profile for Total Petroleum Hydrocarbons" (ATSDR, 1999). Volume fractions of individual species for aromatics were assumed to be equal. The LEL properties of pure components were taken from the Pure Component Technical Databook published by the Petroleum Refining branch of the American Petroleum Industry (American Petroleum Industry (API), 2013).

Within each pseudo-component, there is minimal variability in LEL between each species therefore an exact representative volume fraction for each constituent of a pseudo-component is not critically important to the analysis. Table 2 lists the species used to determine representative LELs for each pseudo-component and the LEL used in the flammability analysis.

Table 2. LEL determined for pseudo component groupings in Cold Lake Bitumen

Pseudo component	Surrogate species	Repre-sentative LEL
Volatiles	methane, ethane, propane, iso-butane, n-butane, iso-pentane, n-pentane	1.39%
Benzene	benzene	1.30%
TEX	toluene, ethyl benzene, o, m, p-xylenes	1.07%
Aliphatics $>C_6$–C_8	hexanes, heptanes, octanes	1.05%
Aliphatics $>C_8$–C_{10}	nonanes, decanes	0.70%
Aliphatics $>C_{10}$–C_{12}	unedecanes, dodecanes	0.63%
Aliphatics $>C_{12}$–C_{16}	tridecanes, tetradecanes, pentadecanes, hexadecanes	0.50%
Aliphatics $>C_{16}$–C_{21}	heptadecanes, octadecanes, nonadecanes, eicosadecanes	0.40%
Aromatics $>C_8$–C_{10}	isopropylbenzene, n-propylbenzene, methyl-ethylbenzenes, trimethylbenzene isomers, branch chain butylbenzenes	0.87%
Aromatics $>C_{10}$–C_{12}	n-butylbenzene, n-pentylbenzene, naphthalene, mono-methyl naphtalenes, p-cymene (alkylbenzene), methylindene	0.82%

Overall, LEL is inversely proportional to the length of the carbon chain and has little variation for the hydrocarbons species within a pseudo-component of interest, ranging between 1.4% and 0.4%.

Once knowing the LEL of each pseudo-component, the next step consists in determining the LEL of the modelled vapour. The vapour cloud may ignite when concentrations exceed the LEL. The relative concentration of each pseudo-component in the hydrocarbon vapor (volume fraction) as predicted by CALPUFF varies spatially and temporally based on the migration of the spill, the evaporation curves, and the dispersion conditions. The concentration time series outputs from CALPUFF were converted to ppm for each pseudo-component using Eq. (4):

$$Conc_{\text{ppm}} = \frac{Conc_{\text{mg/m}^3} \times 24.45}{mol_{\text{wt}}}, \qquad (4)$$

where

24.45: molar volume in L at 1 atm and 25°C;

mol_{wt}: the representative molecular mass determined for each pseudo-component from the Cold Lake Winter Blend analysis in g/mol.

This procedure enabled volume fractions to be determined at each grid point and subsequently produced a spatially and temporally varying time series of LEL for the hydrocarbon vapour over the entire grid. The concentration time series was then divided by the LEL to determine the percentage of the LEL of the vapour over the entire grid.

2.6 *Scenario*

Year 2012 was selected as a representative year from a wind condition and Fraser River flow rate perspective. Details on this selection are available in the Trans Mountain Expansion Project Application (EBA, A Tetra Tech Company, 2013). The month of August, in particular August 17 and 18, was selected for this study. On August 17, 22:00, a credible worst-case spill of 16 500 m^3 was simulated for the study with a release duration of 13 h. The credible worst-case scenario corresponds to the loss of one tank of a partly loaded Aframax tanker. It is emphasized again that the modelled spill is hypothetical and for study purposes only. The release was completed on August 18, 11:00, i.e., 13 h after the hypothetical incident started. 25% of the overall amount spilled was released in the first hour of the simulation with the remaining 75% of the product released over the final 12 h at a constant rate.

Figures 2 and 3 show the wind and current conditions, respectively. The top panel of Fig. 2 shows the wind stick plot and the bottom shows the wind speed, with an average of about 4 m/s.

3 Results

3.1 *Model results*

Evaporation during the first 14 h follows the expected trend: lighter hydrocarbons evaporate in greater proportion than heavier chains. Figure 4 shows the modelled rate of evaporation for the major pseudo-components. Most of the volatiles and aliphatics (C_6–C_{16}) evaporate at the beginning of the simulation. Note that the evaporation rate for volatiles (VOL) and the different classes of aliphatic (AL C_6–C_{16}) is shown on the left axis, whereas Benzene, TEX and aromatic (AR C_8–C_{12}) are shown on the right axis.

Figure 5 presents snapshots of the slick and the associated vapor cloud at various times over the simulation, illustrating the variability of the slick and vapor cloud trajectories. The top panel shows August 17 at 23:00, or one hour after the initial release. The middle panel shows August 18 at 02:00, or four hours after the initial release. The bottom panel shows August 18 at 06:30, or

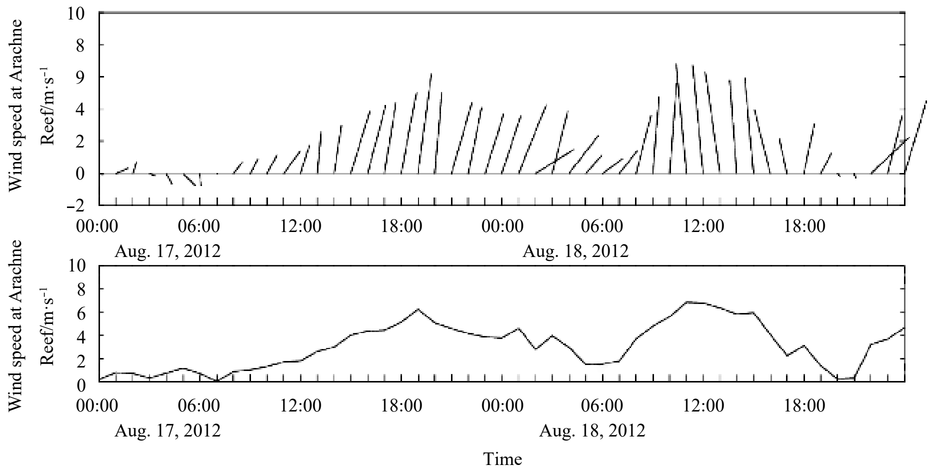

Fig. 2. Wind conditions.

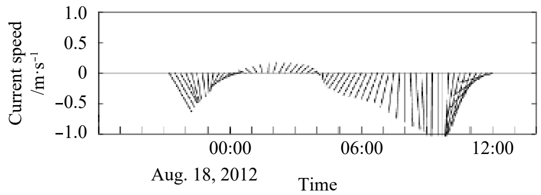

Fig. 3. Surface current conditions.

seven and a half hours after the initial release. Each panel contains information on the oil on water (left side of the panel) and the evaporated hydrocarbons (right side of the panel). The oil on water is characterized by its thickness, in microns, and the hydrocarbon vapour is characterized by its potential flammability, calculated as a percentage of the LEL. Note that a reduced domain with high resolution was considered in this study, the purpose being to present the framework, hence the clipped nature of the plots.

At the beginning of the simulation, at hour 23:00 on August 17, (top panel, Fig. 5) currents are heading southeastward, whereas there is a south-southwesterly wind. In this situation, the currents are dominant in determining the trajectory of the oil and results in the slick migrating towards the southeast. The dispersion of the associated vapor plume however, is entirely determined by the wind conditions, and is transported to the northeast. The evaporation flux is dominated by lighter hydrocarbon fractions (Fig. 4), which have a higher LEL (Table 2). As a result, the LEL of the vapour plume is in the range of 1.0% to 1.4%. Surface level concentrations in the air over the slick are in the range of 5% to 10% of the LEL, while towards the northeast dispersion of the plume results in concentrations below 5% of the LEL.

Four hours following the initial release, on August 18, 02:00, currents are heading towards the north, resulting in migration of the slick northward. South-southwesterly winds continue to transport the plume to the northeast. As the ratio of evaporation of heavier fractions increases over older portions of the slick, the LEL of the vapour plume becomes less spatially homogeneous, generally exceeding 1.0% with pockets between 0.4% and 1.0%. Surface level concentrations in air are below 5% of the LEL.

Eight and a half hours following initial release, on August 18, 06:30, the current had reversed two hours prior, pushing the oil southward. The mean wind speed had decreased below 2 m/s, resulting in more stable conditions which are less conducive to lateral and vertical dispersion, resulting in higher surface level concentrations over the spill area which reach 37% of the LEL.

Figure 6 shows the maximum predicted one-second averaged vapour concentration at sea-level as predicted by CALPUFF, as a percentage of the LEL. Unlike Fig. 5, it is not an illustration at a given time, rather it is a conglomerate of the maximum at all grid points over the entire duration of the 14-h simulation.

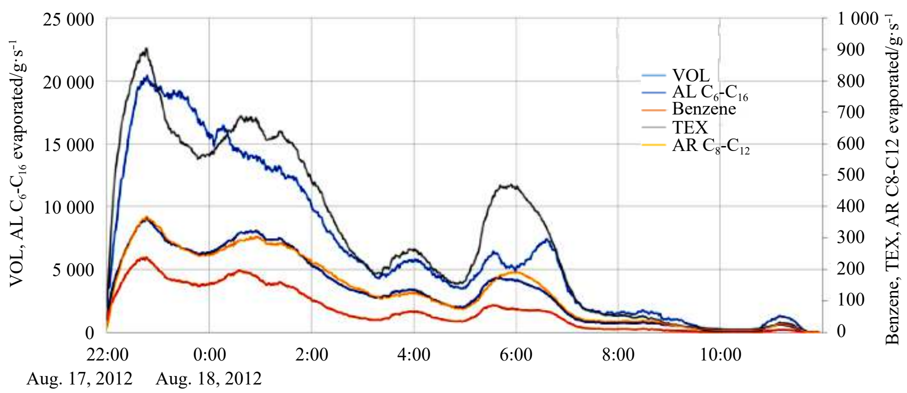

Fig. 4. Modelled rate of evaporation for major pseudo-components.

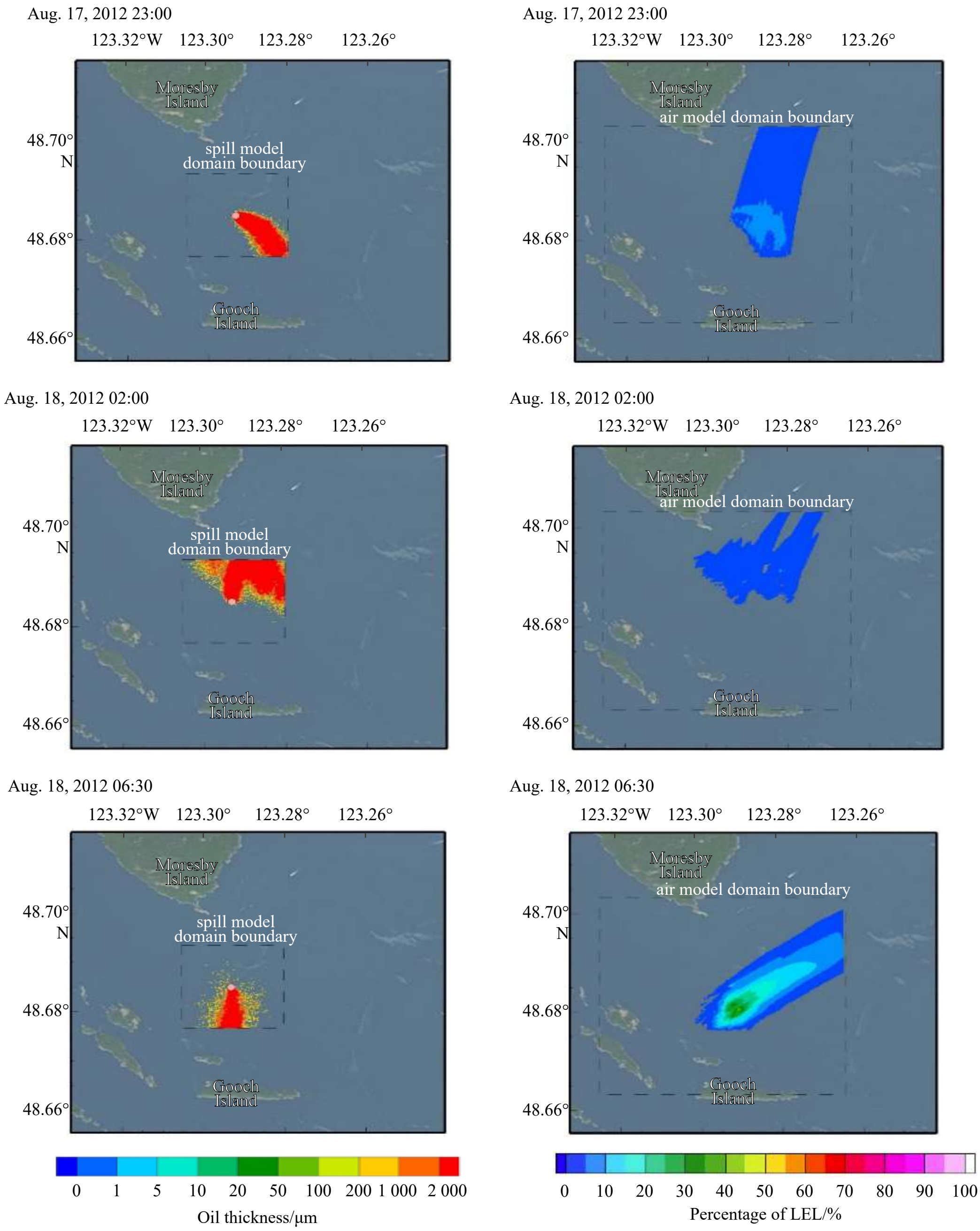

Fig. 5. Snapshots of spill extent and vapor cloud.

The areas over the active spill area reach a concentration which approach closest to the LEL as indicated by the yellow and green shading. As alluded to above, these higher vapour concentrations occur towards the end of the simulation when winds are calmer and therefore less conducive to dispersion, and when the vapour is composed of a higher percentage of heavier fractions, lowering the LEL of the hydrocarbon vapour mixture. The maximum concentration over the entire simulation, in terms of flammable potential, reached 54% of the LEL.

3.2 *Impact on first responders*

The vapour cloud may ignite when concentrations exceed the LEL. Concentrations exceeding LEL were not met during the simulation. However, since surface currents and winds are vastly different from day-to-day, this modelling framework offers maps of flammability risk on an hourly or daily basis, which can be used by first responders, in addition to hand-held hydrocarbon concentration monitoring devices, as part of the mitigation strategy. It should be noted that even if the vapour concentration is well below the LEL, vapour concentrations could still pose a health risk to humans, especially responders. Values of LEL above 50% should be indicative of careful monitoring as they may be a potential threat to first responders.

4 Conclusion

A modelling framework was developed to assess the risk of a vapour flash fire presenting significant risks to first responders during an oil spill. Tools supporting this framework included a three-dimensional hydrodynamic model (H3D), a trajectory and weathering oil spill model (SPILLCALC) and an air dispersion

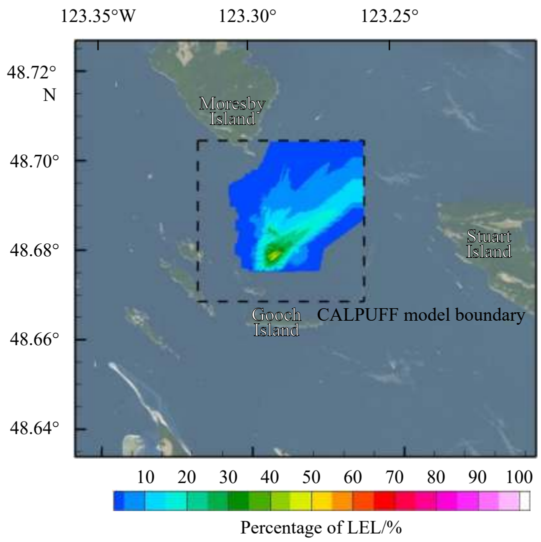

Fig. 6. Maximum predicted 1s-averaged vapour concentration.

model (CALPUFF). A hypothetical credible worst case spill of Cold Lake Winter Blend was simulated to take place on August 17, 2012: 16 500 m^3 of oil was released over a 14 h period.

The determination of the LEL for the vapor cloud at each cell of the model for various times, as well as the concentration of each pseudo-component, allowed an assessment of the risk of an explosion.

The model results presented in this report are based solely on the modelled scenario under the assumptions associated with the composition of each pseudo-component and indicate that under this scenario, ignition of the vapor cloud would not occur. The simulation is specific to the meteorological conditions occurring during the simulation and the oceanographic conditions existing at the spill location during the selected time. At no time was the LEL reached over the course of this simulation. A maximum of 54% of the LEL was reached, corresponding to calmer winds and a higher percentage of heavier fractions composing the vapour, hence lowering the LEL of the hydrocarbon vapour mixture. It should be noted that in areas where the vapour concentration is below the LEL, pockets of higher concentrations may exist which could exceed flammable levels and may ignite.

The results described in this paper are not inclusive whatsoever of conditions which may be encountered with a tanker spill at sea and the results herein are not intended to be interpreted as an encompassing assessment of safety for first responders. Other scenarios or other spilled oil products may very well result in concentrations exceeding the LEL.

Such a tool could be used in a real time oil spill dispersion and forecasting system and would provide additional inputs to first responders in addition to hand-held hydrocarbon monitoring devices for mitigation strategy.

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