MODELED EXPOSURES TO FRESHLY SPILLED CRUDE OIL

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ABSTRACT: *Understanding initial oil spill responder's exposures is essential for planning purposes and a safe operation; however, there is little relevant information in the literature. Potential oil components of concern include hydrogen sulfide and benzene.*

This paper uses three dispersion models to evaluate and discuss these potential responder health exposures. Key parameters addressed include the effects of the thickness of the spill and the component concentration in the crude oil. Determination of the amount of time needed for site concentrations to fall below the relevant health guidelines is an important outcome. Model results are compared with available exposure data in the literature. Implications for response planning are discussed.

Introduction

There is very little data in the literature regarding exposures that might be encountered during the initial stages of crude oil spills. For the purposes of this paper, "first responders" refers to those who will be the first personnel working in the area of freshly spilled crude oil. Modelers such as Hanna (1993), the Marine Spill Response Corp (MSRC, 1993), and the Western States Petroleum Association (WSPA, 1997), estimate maximum benzene vapor concentrations in the range of 5–200 parts per million (ppm). Exposure values vary significantly depending on the computer input parameters used. This variability makes comparisons difficult. There is even less data regarding hydrogen sulfide concentrations. WSPA (1997) indicated levels of 0.0004 ppm could be expected 30–45 minutes after the spill.

Actual data, which is only available from simulated spills, has been reported by Delikat (1992), Eley (1989), and Jones (1992). Maximum benzene concentrations range from 7–90 ppm with the higher maximums possibly due to sampling very close to the oil surface (a parameter that is very difficult to model). Hydrogen sulfide measurements taken during crude oil spills or simulations were not found in the literature.

Methods

Based on the paucity and the variability of the data that is reported, it was decided to model benzene and hydrogen sulfide concentrations in crude oil spills by focusing on two key parameters: (1) their concentrations in the crude oil, and (2) the thickness of the crude oil on the water. In addition to maximum airborne concentrations, the time to reduce vapor concentrations to non-toxic levels was also investigated.

To more realistically model the spill scenarios, an oil spill trajectory and fate model, Oilmap v. 2.4 (ASA, 1998) was used to estimate general evaporation rates and oil film thicknesses of a typical crude oil. Three scenarios were selected to represent the range of conditions for a 10,000 barrel medium crude oil spill: a boomed scenario where the oil remains relatively thick (12 mm) and two un-boomed scenarios where oil spreads freely to two thicknesses (4mm and 0.1 mm). Wind and current speeds were set to represent a worse case scenario (calm winds, 1 knot currents). Air and water temperatures were typical of the southern United States (air 80°F, water 70°F).

Benzene and H2S emission rates were estimated by coupling the Oilmap output (which provides total hydrocarbon emissions) to the Liquid Spill Model (LSM90, Cavanaugh, 1994) which estimates constituent-specific emission rates from hydrocarbon mixtures. LSM accepts a mixture of up to 10 constituents from which a "model" crude oil is developed. Table 1 summarizes the "model" crude for three different cases: low, medium, and high benzene and H2S concentrations.

Table 1. Composition of "model" oil used in the liquid spill model for three concentration scenarios.

Constituent	Low (wt %)	Medium (wt %)	High (wt %)
Benzene	0.01	0.2	2.1
H2S	0.0001	0.002	0.035
Propane	0.42	0.42	0.42
n-Butane	1.08	1.08	1.08
n-Pentane	1.9	1.9	1.9
n-Hexane	5.46	5.46	5.46
n-Heptane	9.49	9.49	9.49
n-Nonane	16.4	16.4	16.4
n-Hexadecane	65.24	65.048	63.12

This composition was based on the actual composition of a light to medium crude oil (Jacks Creek) with the benzene and H2S concentrations modified to create ranges typical of high, medium and low values.

The LSM model is also capable of considering the effect of oil thickness on evaporation rates. Input conditions were set to match those outlined by the Oilmap modeling. The result of the LSM model is the composition (in wt %) of the evaporating cloud. Composition will vary significantly over time as those chemicals with the higher vapor pressures "boil" more quickly than the less volatile components. Thus, even though the initial weight percents of benzene and in particular H2S are very low, these more volatile compounds could represent a significant portion of the vapor cloud. Benzene and H2S-specific volatilization rates were

calculated by multiplying the total hydrocarbon emission rates (from Oilmap) and the cloud concentrations of benzene and H2S. The result is time-varying emission rates. This also narrows the time window of interest. For example, in all cases H2S was released within 4 minutes of the spill, after which estimated vapor concentrations drop to zero. Benzene, which is less volatile, continued to emit for up to 6 hours of the spill for the thick oil spill scenarios.

Air concentrations (in ppm-v) were estimated by applying a simplified air dispersion model, ALOHA (USEPA, 1995), to the chemical-specific emission rates under conservative meteorology. ALOHA is a dense gas and Gaussian dispersion model that calculates footprints of concentration greater than a specified concentration limit. In this case the Gaussian option was applied as the chemicals were assumed to be mixed in the air (consistent with WSPA, 1997). Also, maximum concentrations at a specific location can be determined as well. ALOHA was specifically chosen for its ease of use and clear graphical output.

Results

Figures 1, 2 and 3 show the ALOHA results for the different benzene modeling scenarios in which oil thickness and benzene concentration in the crude were varied. The results are consistent and reasonable in that the thinner oil spill results in higher initial concentrations, but for shorter durations. Area impacted also seems reasonable in that the distance in which benzene concentrations exceed 1 ppm (OSHA permissible exposure limit) vary with time and distance (Figures 4, 5, and 6).

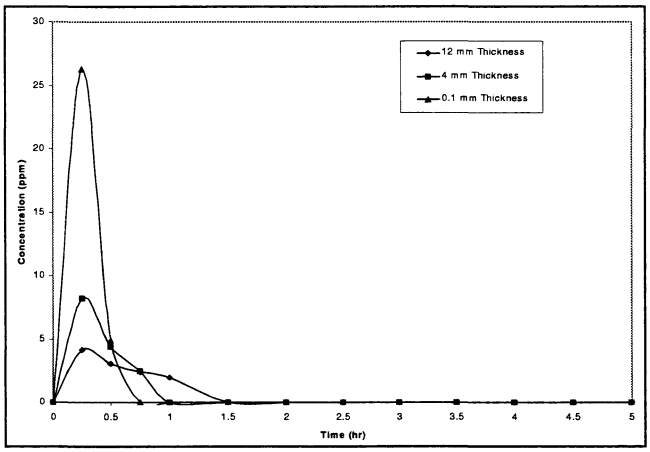

Figure 1. Estimated concentrations of benzene over time for three oil thicknesses initial benzene concentration in crude = 0.01 wt %.

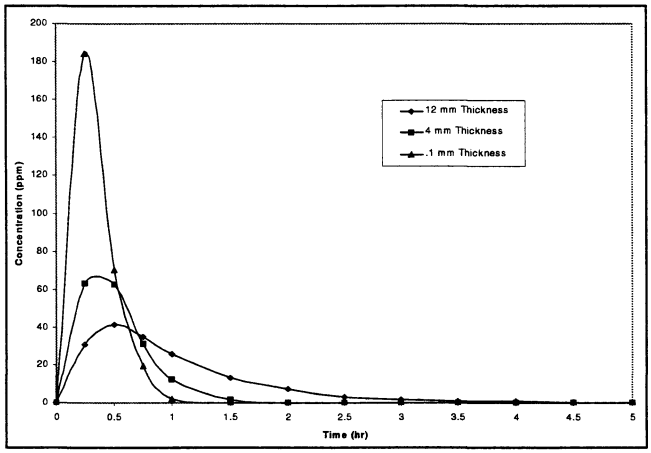

Figure 2. Estimated concentrations of benzene over time for three oil thicknesses initial benzene concentration in crude = 0.2 wt %.

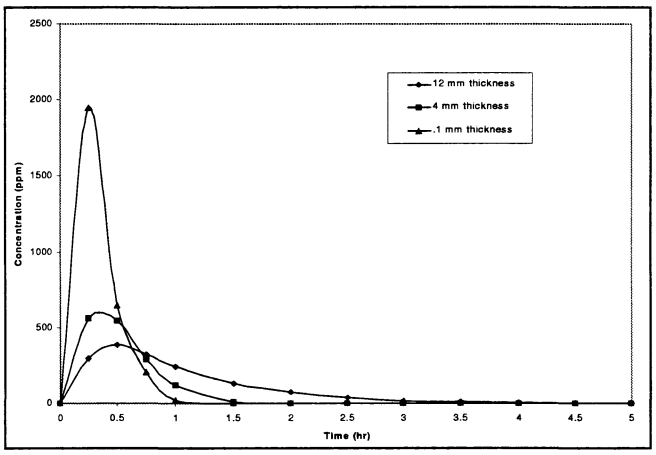

Figure 3. Estimated concentrations of benzene over time for three oil thicknesses initial benzene concentration in crude = 2.1 wt %.

It can be seen that for thin films, the benzene flashes off quickly resulting in high peak exposures that dissipate rapidly. Conversely, for thick films, the surface is insulated from the warm water, thus evaporating more slowly. However, since there is more total benzene present, vapor clouds containing greater than 1 ppm benzene last for a longer period of time. These results were compared to similar scenarios presented in WSPA (1997) and MSRC (1993). For those scenarios that were most similar, estimated benzene concentrations were within a factor of two of each other.

As stated above, hydrogen sulfide modeling predicted that the H2S would be emitted very rapidly (less than 4 minutes). This results in high concentrations for very brief periods of time. Figure 7 presents the worst-case H2S modeling results for two initial H2S concentrations (.035 wt % and .002 wt %).

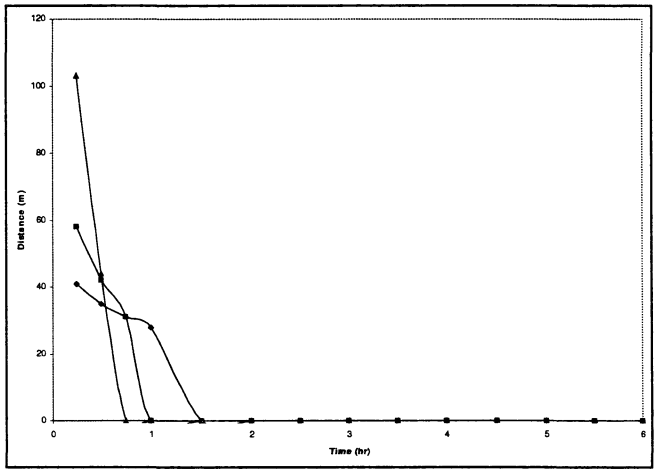

Figure 4. Maximum distance impacted by concentrations of benzene > 1 ppm initial benzene concentration in crude = 0.01 wt %.

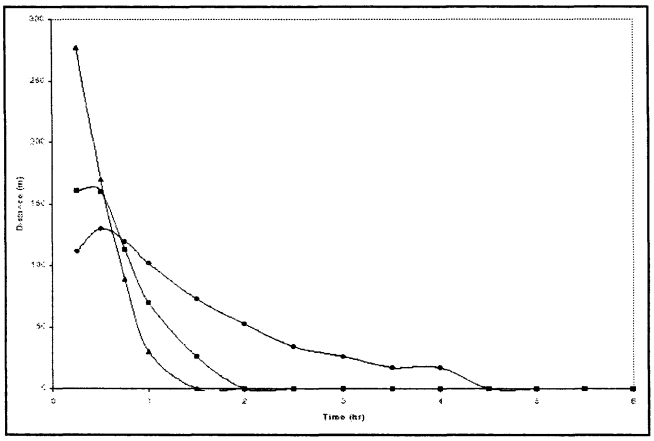

Figure 5. Maximum distance impacted by concentrations of benzene > 1 ppm initial benzene concentration in crude = 0.2 wt %.

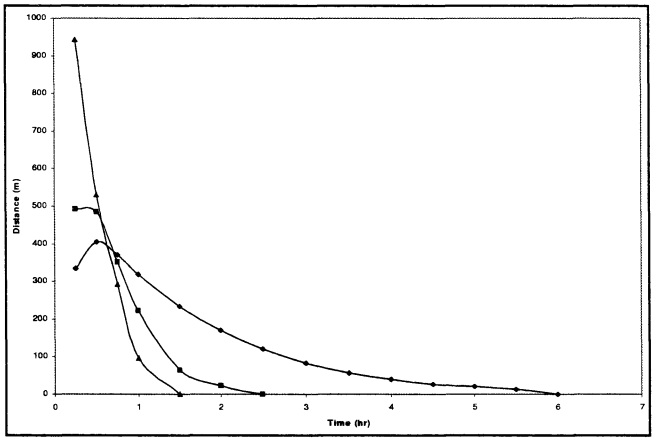

Figure 6. Maximum distance impacted by concentrations of benzene > 1 ppm initial benzene concentration in crude = 2.1 wt %.

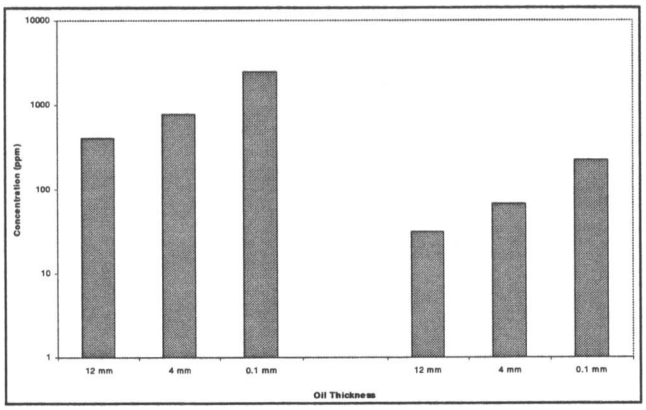

Figure 7. Estimated concentrations of h2s for three oil thicknesses initial H2S concentrations in crude = 0.035 wt% and 0.002 wt %time of exposure < 4 minutes.

The maximum area impacted is less than 400m, as predicted by ALOHA. No values were estimated for the low H2S concentration scenario (0.0001 wt %) due to poor resolution in the LSM model (inadequate significant digits). WSPA (1997) also modeled H2S but did not estimate concentrations in the initial minutes of the spill. Result for after 30 minutes were consistent (0 ppm versus 0.0004 ppm).

Discussion/conclusions

As can be seen from Figures 1–6, modeled benzene vapor concentrations are very sensitive to concentration in crude oil, time, and spill thickness. In reviewing these and the other results discussed in the Introduction, several generalizations or rules-of-thumb can be made regarding benzene concentrations resulting from a crude oil spill:

- Initial concentrations can be well over 1 ppm
- Initial concentrations decrease rapidly over the first hour
- Concentrations should drop to below 1 ppm within 6 hours (even with calm winds)
- Take appropriate protective measures and monitor concentrations if there is any uncertainty regarding potential worker overexposure

Regarding hydrogen sulfide, Figure 7 indicates high H2S crude oils can create modeled concentrations that might be immediately dangerous to workers in the area due to respiratory paralysis. H2S odors (rotten eggs) may not provide adequate warning due to olfactory fatigue. However, even under worst case conditions, modeled exposures would drop to non-toxic levels in less than 4 minutes. Again, if uncertain about potential exposures, taking appropriate protective measures and monitoring are recommended.

Typically, even initial responders do not arrive at spill sites immediately, and oil spill response teams follow after some interval. Therefore, unless there were a continuous spillage of crude oil, hydrogen sulfide exposures would not be expected to be a concern, and any concern about benzene exposures would diminish rapidly. However, where uncertainty exists, monitoring should be conducted at specific spill sites to confirm these findings.

Biography

Evan C. Thayer has a M.S. degree in Industrial Hygiene and Air Pollution Control from Harvard University. He has been responsible for numerous industrial hygiene programs/activities including Asia and Africa operations and international shipping. His duties currently include coordinating occupational health activities for Exxon's oil spill research group.

References

1. Applied Science Associates, 1998. *Oilmap version 2.4*. Narragansett, RI.
2. Cavanaugh, T. A., J. H. Seigell, and K. W. Steinberg, 1994. Simulation of Vapor Emissions form Liquid Spills. Journal of Hazardous Materials, v38, PP41–63.
3. Delikat, D. S., M. A. Zustra, C. P. Rennix, D. L. Matthews, and J. J. Ocken, 1992. Benzene exposure levels during a simulated crude oil spill. Poster Session, Paper 401, 53rd Annual American Industrial Hygiene Conference, June 1992, Boston, MA.
4. Eley, W. D., R. J. Morris, L. L. Hereth, and T. F. Lewis, 1989. Is overexposure to benzene likely during crude oil spill response? Proceedings: 1989 Oil Spill Conference (API, EPA, and USCG).
5. Hanna, Steven R., and Peter J. Drivas, 1993. Modeling VOC emissions and air concentrations from the Exxon

Valdez oil spill. Journal of Air and Waste Management Association, v43, PP298–309.
6. Jones, Robert K., James Farr, Debra Simecek-Beatty, Kenneth Carney, David Roques, Charles Henry, and Edward Overton, 1992. The evaporation of benzene and a series of alkanes from crude oil. Hazardous Materials Response and Assessment Division, Office of Ocean Resources Conservation and Assessment, National Oceanic and Atmospheric Administration, Report HMRAD 92–5.
7. Marine Spill Response Corporation, 1993. Occupational health implications of crude oil exposure: literature review and research needs. Technical Report Series 93–007.
8. U.S. Environmental Protection Agency and National Oceanic and Atmospheric Administration, 1995. *ALOHA version 5.2*. Distributed by the National Safety Council, Washington, DC.
9. Western States Petroleum Association, 1997. Development of respiratory protection criteria for initial response to marine oil and petroleum spills. Final Report, August 22, 1997.