IS OVEREXPOSURE TO BENZENE LIKELY DURING CRUDE OIL SPILL RESPONSE?[1]

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ABSTRACT: *This article examines the potential for benzene exposure during crude oil spill response. Literature review found that under normal conditions benzene is lost from an oil slick within 40 minutes to 8 hours. A correlation between benzene and API gravity is presented graphically. This information was used to develop worst-case scenarios. Results of a preliminary field investigation indicate that benzene overexposure may be possible during "ideal adverse" conditions. Four generic crude oil spills are described along with rationale for the suggested level of self protection.*

In December 1987 the Occupational Safety and Health Administration lowered the benzene permissible exposure limit (PEL) from 10 parts per million (ppm) to 1 ppm as a time weighted average. This new standard caused widespread concern throughout the U.S. Coast Guard. Most attention focused on marine safety programs. It was felt that the greatest potential for overexposure occurred among personnel who worked within the marine safety industry or who were engaged in various environmental response functions. Examples of such activities include internal inspection of marine vessels, cargo transfer monitoring, and hazardous chemical cleanups.

The purpose of this paper is to examine another potential source of benzene overexposure—open water crude oil spills. The authors take a two-pronged approach to this problem. First, a worst-case scenario is described. Second, the results of a preliminary field investigation conducted with the assistance of Amoco Oil Company is reported. Based on this work, precautionary measures for four generic oil spills are suggested.

Development of the worst-case scenario

The benzene content of crude oil averages 0.2 percent (2,000 ppm),[3] although fractions as high as 0.64 percent (6,400 ppm) were noted in some North American crudes.[5] Exact values of benzene in specific crudes are not commonly available. The quantity of low boiling components increases with the geologic age of the oil.[2] However, benzene concentrations appear less dependent on maturation than on the amount and type of organic matter with the source rock.[5] One laboratory found a relation between specific dispersion of each distillate fraction and the percent benzene within the crude.[5] It was also able to correlate the volume percent of all aromatic compounds within the crude with the amount of benzene and toluene present. The drawback of these methods of estimating benzene is the difficulty of obtaining specific dispersion or the quantity of aromatic compounds within a given crude oil.

The API gravity of oil is more easily obtainable. In fact, API gravity is the only data an agent may be able to supply during the initial stages of an oil spill. The authors plotted percent benzene by volume against API gravity for 30 foreign and domestic crude oils.[1] Results of this work are shown in Figure 1. Although a definitive linear relationship is not seen, an upward trend of increasing benzene concentration with increasing API gravity is apparent. The linear least-squares regression analyses or best fit line allows a quick estimate for a given crude oil. The 95 percent upper confidence limit provides a more conservative figure. This graph will be used in the ensuing discussions of hypothetical worst-case scenarios.

Because of benzene's high vapor pressure (100 mm Hg at 26.1°C) and low boiling point (80.1°C, 176°F), it evaporates rapidly from crude oil. In addition, black crude oil slicks efficiently absorb radiant energy, raising the oil temperature and subsequently the vapor pressure for benzene in the oil. The authors' field work showed that sunlight, even on a mild breezy day, could increase the temperature of crude oil more than 17°C (32°F) above ambient temperatures. This rise in temperature more than doubles the benzene vapor pressure. In a summary of six field observations and two laboratory studies, Jordan and Payne found that volatile hydrocarbons were lost from oils on the water surface within 40 minutes to 8 hours.[6] McAuliffe reported near total benzene loss for an oil slick within the first hour.[7] Thus, it appears that if work close to the oil spill can be avoided for the first few hours then exposure to benzene would be negligible. However, this conclusion assumes the ability of the oil slick to spread in thin layers over the water surface, allowing the benzene substrate immediate contact with the atmosphere.

During an experimental spill of crude oil in the North Sea 0.5 metric tons (4.25 barrels) of Ekofisk crude oil created a slick area of 0.025 km^2 (0.01 mi^2).[4] Assuming the specific gravity of this crude was initially 0.74, then the slick thickness can be calculated at 0.027 mm. This thin crude layer allows the benzene substrate immediate access to the atmosphere. If the benzene component is estimated to be 0.30 percent by volume (from Figure 1), then approximately 1.8 kg (4.0 lb) of benzene evaporate during the first hour. Given the large slick area, small amount of benzene, and open ocean conditions, potential overexposure to benzene vapor during the first hour would appear to be slight, and nonexistent at any time after a few hours.

Under adverse conditions the potential for benzene overexposure is greater. If the same Ekofisk crude is placed in calm, protected waters with no wind, then a hypothetical benzene concentration can be calculated using the following formula:

$$\text{ppm} = \frac{10^6\,(w/mw)(v)}{V}$$

1. The views and opinions presented in this paper are those of the authors solely and do not necessarily represent views or policy of the U.S. Coast Guard.
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Where: ppm = benzene vapor concentration in parts per million
w = weight of benzene evaporating (1,800 g for hypothetical use)
mw = molecular weight (benzene 78.11 g per mole)
v = volume in 1 mole of vapor (24.45 L or 0.02445 m^3 at 25°C)
V = volume of air over the slick (area times height)

Since benzene vapor is heavier than air, with a vapor specific gravity of 2.8 under zero wind conditions this aromatic vapor would likely remain within 2 m above the slick surface. Returning to the basic formula:

$$\text{ppm} = \frac{10^6(1{,}800 \text{ g Bz}/78.11 \text{ g/mole})(0.02445 \text{ m}^3\text{/mole})}{0.025 \text{ km}^2(10^6 \text{ m}^2/\text{km}^2)(2\text{m})} = 11.25$$

Granted, it is unreasonable to assume no air circulation or overturn above the slick for an entire hour. It is reasonable, however, to envision the same sized spill in a more restricted area. A narrow canal with steep banks would create a thicker slick with slower evaporation and more efficient containment of dense benzene vapors. For example, consider 0.50 t of Ekofisk crude spilled into a canal 200 m long and 40 m wide. Using the above formula and assumption, evaporating benzene could theoretically create an exposure level of 50 ppm within 2 m of the oil surface.

Field and laboratory investigations

One barrel (158 L) of crude oil was poured over water in an open fire pit (Figure 2). This crude oil was a blend of Oguendjo (West African) and Ninian (North Sea) oils, with an API gravity of 36.0. The water surface on which the crude was poured was 15.6 m^2 (167.7 ft^2). The resulting oil thickness was 1.0 cm (0.4 in.). Air temperature averaged 25.5°C (77.9°F) Relative humidity was 71 percent. The test was conducted under clear and sunny skies with winds from 8 to 24 km/h (5 to 15 mph). Air velocity at the slick surface ranged from 0.9 to 2.75 km/h (0.5 to 1.7 mph). During the two-hour sampling period, the crude oil absorbed radiant energy and quickly reached an equilibrium temperature of 43°C (110°F) or 17.5°C 32°F) above ambient temperature. Air sampling for benzene was conducted using personal sampling pumps and activated charcoal collection tubes. Standard NIOSH procedures for sampling were employed.[8] The sampling tubes were positioned to draw air 2.5 cm (1 in.) above the oil surface (Figure 3). Sampling tubes were changed frequently to pinpoint periods of maximum benzene volatilization. After collection, the charcoal sampling tubes were analyzed by gas chromatography.

Benzene concentrations at 2.5 cm above the oil surface ranged from 80.5 ppm to 3.5 ppm. The background concentration was less than 0.1 ppm. As expected, the highest concentrations were measured during the first hour after the oil was poured. Benzene concentrations ranged from 68 ppm to 23 ppm during the first hour. The two-hour time-weighted average was 15.8 ppm.

A second experiment was conducted the same day. This trial attempted to gain some idea of the benzene concentration at heights above the oil surface and nearer human breathing zones. Five and one-quarter gallons (19.75 L) of the same crude were poured into a 1.5 m^2 (16 ft^2) fire pan. Vapors were collected for a one-hour period

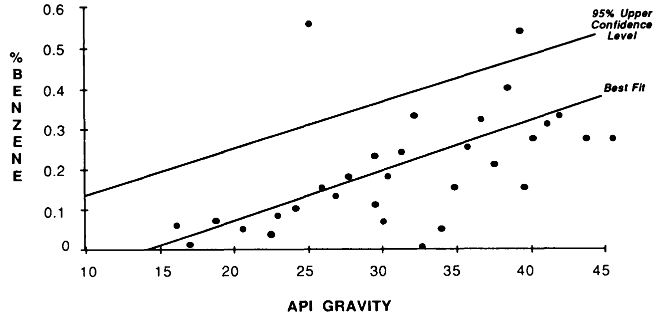

Figure 1. Percent benzene vs API gravity for 30 crude oils—Source: *Oil & Gas Journal,* April 11—December 19, 1983

Figure 2. One barrel of light crude oil was poured into an open fire test basin to test for benzene vapor.

at levels from 0.125 m (5 in.) to 0.71 m (28 in.) above the oil surface. During the sampling period efforts were made to achieve near zero wind conditions through the use of barricades. Sampling instruments and analytical methods remained the same as in the first trial. Average benzene concentrations during this hour ranged from 26.6 ppm at 0.125 m above the oil surface to 8.3 ppm at 0.71 m above the oil surface.

Significant amounts of other hydrocarbons were collected on the sampling tubes during these tests. As a result, benzene concentrations

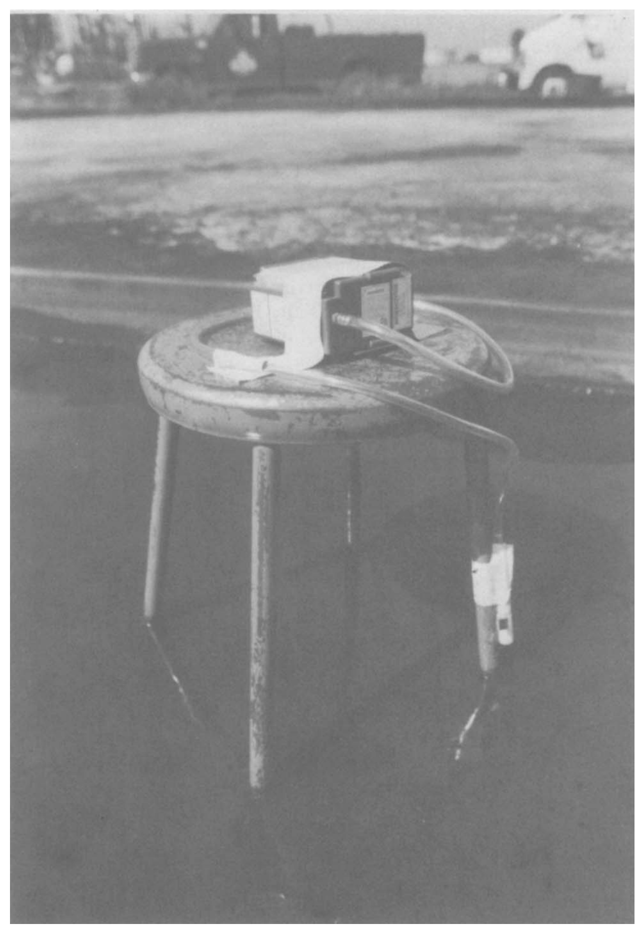

Figure 3. In the first trial, air was sampled 2.5 cm from the oil surface.

determined through gas chromatography may be over-reported due to interference. At the time of this writing, the authors are preparing for a more rigorous study using mass spectrometry.

Conclusions and recommendations

In theory, benzene overexposure may be possible during "ideal adverse" conditions. In addition, field investigations showed that under the worst conditions tested (sampling within 2.5 cm of the crude oil surface, with near zero wind) ambient benzene concentrations may be above 1 ppm. This preliminary work is unable to support the contention that benzene overexposure is likely under normal work conditions for oil spill recovery. It does suggest that further investigation is necessary.

Literature review shows benzene will evaporate almost entirely within one to eight hours. Thus, benzene exposure is best avoided by staying away or upwind from a crude oil spill for the first few hours. Unfortunately, this strategy is sometimes contrary to the most effective response actions. For example, quick boom deployment might result in effective spill mitigation, but deploying containment boom usually demands work downwind from the spill. Even with low levels of benzene exposure (less than 1 ppm) the presence of other volatile hydrocarbons causes concern. Any interaction of various volatile components of crude to create toxic effects is not yet understood or reported in the literature.

The following crude oil spill scenarios cover most oil spill response conditions. The intent is to provide general recommendations. At present they lack the support of thorough scientific study. For specific spills the potential for benzene overexposure should be evaluated by a professional in occupational health. However, the authors do feel the scenarios are useful. They serve as a practical alert to potentially hazardous atmospheres in an activity previously assumed to be relatively benign.

Situation 1. A crude oil spill has an API gravity of less than 25.

Recommendation: It is likely that benzene exposure is negligible. Normal precautions apply, especially if the oil has weathered for more than a few hours.

Situation 2. An open water spill of crude oil has an API gravity above 25. The day is overcast or the water temperature is below 15°C (59°F).

Recommendation: Benzene will volatilize slowly from the liquid. Some benzene will also dissolve in the water. However, it is unclear how long benzene takes to evaporate completely. Liquid samples should be analyzed for benzene. For work close to the oil, the counsel of an occupational health professional should be sought.

Situation 3. An open water spill of crude oil has an API gravity above 25. The day is sunny or the water temperature is above 15°C (59°F).

Recommendation: This spill will spread and most of the benzene will probably evaporate within the first hour. Monitoring and the counsel of an occupational health professional are indicated for the first few hours after the oil spill.

Situation 4. A crude oil spill has an API gravity above 25, and is in protected or restricted waters (an inlet, bayou, canal, ditch, or more commonly, between vessels or a vessel and a wharf). The wind velocity at the oil surface is near zero.

Recommendation: These are optimal conditions for benzene overexposure. The dense vapor will seek low areas and pocket. Restricted waters create thicker layers of oil, slowing benzene evaporation and prolonging the period for the risk of overexposure. Monitoring and use of an occupational health professional to define the level of protection required are both advisable.

Acknowledgments

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References

1. Aalund, L. R., 1983. Assay series. *Oil & Gas Journal,* April 11—December 19
2. Biederman, E. W., 1965. *World Oil,* December, p78
3. Cheremisinoff, P. N. and A. C. Morresi, 1979. Benzene—Basic and Hazardous Properties. Marcel Dekker, New York, and Basel.
4. Fingas, M. F., et al., 1970. Basics of Oil Spill Cleanup. Environment Canada, Minister of Supply and Service, Canada, p24
5. Grizzle, P. L. and H. J. Coleman, 1979. Gas chromatographic determination of benzene and toluene in crude oils. *Analytical Chemistry,* v51, n6, pp602–608
6. Jordan, R. E. and J. R. Payne, 1980. Fate and Weathering of Petroleum Spills in the Marine Environment. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, p20
7. McAuliffe, 1980. *in* Fate and Weathering of Petroleum Spills in the Marine Environment, R. E. Jordan and J. R. Payne, eds. Ann Arbor Science Publishers, Inc., Ann Arbor, Michigan, p21
8. National Institute of Occupational Safety and Health, 1984. NIOSH Manual of Analytical Methods, Method 1501. Cincinnati, Ohio