

## ECOLOGICAL RISKS ASSOCIATED WITH BURNING AS A SPILL COUNTERMEASURE IN A MARINE ENVIRONMENT

by

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Following is a qualitative evaluation of the relative ecological risks associated with a burn/no-burn decision. The purpose of this evaluation is to assess risks from exposure to toxic chemicals in crude oil and the physical and physiological effects of the oil and its residue. The first step in conducting the risk evaluation is an exposure assessment, followed by a discussion of chemicals of concern (COCs) and the ecological risk evaluation.

### EXPOSURE ASSESSMENT

The various exposure pathways from the crude oil spill to ecological receptors under the burn/no-burn alternatives were evaluated to identify which pathways are complete. A complete exposure pathway generally requires five basic elements:

- A source of chemicals (e.g., the oil spill or one of the secondary sources);
- A mechanism of chemical release (e.g., weathering, burning);
- An environmental transport medium (e.g., water, air);
- An exposure point where receptors are present; and
- An intake route (e.g., ingestion, direct contact, inhalation).

If any one of the elements is missing, the pathway is not complete and exposure of the ecological receptors cannot occur.

Environment Canada. Arctic and Marine Oil Spill Program (AMOP) Technical Seminar, 17th Proceedings. Volume 1. June 8-10, 1994, Vancouver, British Columbia, Environment Canada, Ottawa, Ontario, 707-716 pp, 1994.

Schematic diagrams illustrating the processes involved in the dissipation of oil in the burn and no-burn scenarios are presented in Figures 1 and 2, respectively. Potentially complete exposure pathways are identified through the use of a conceptual site model (CSM), a schematic representation of the various exposure pathways from the source (i.e., crude oil spill) through the release mechanisms, secondary sources, and transfer mechanisms to the ecological receptor categories (e.g., plankton, finfish, waterfowl). Because three different marine environments are being evaluated (offshore, near-shore, and estuarine), three different CSMs (Figures 3 through 5) have been developed to assess exposures of the unique habitats and biota in each environment.

These CSMs are used by tracing the movement of the oil from the primary source (crude oil spill) through the release mechanisms (e.g., spill is burned), to the secondary sources (e.g., burn residue), through the transfer mechanisms (e.g., floats and moves onshore), to the ecological receptors. To illustrate one example of a CSM (Figure 3 -- offshore environment), plankton, shellfish, and finfish are "possibly" exposed to the burn residue when oil is burned, and the remaining ecological receptors are "unlikely" to be exposed. Tracing the movements of crude oil or its constituents through the other pathways and environments permits evaluation of the many potential exposure pathways.

Key considerations that should be kept in mind when using the three CSMs to compare the burn/no-burn alternatives include:

- Information presented in the CSMs considers relative quantities of oil or its components under the burn/no-burn alternatives.
- Burning of a crude oil spill typically removes more than 75 percent of the oil from the water and therefore reduces the likelihood of a complete exposure pathway for direct contact.
- The volume of the oil burn residue is approximately 25 percent of the original spill volume.
- Burning preferentially consumes the volatile and soluble fractions of a crude oil spill.

- Typical abundances and distributions of ecological receptors are assumed to be present in the three environments.
- The release mechanisms listed in the CSMs are considered to be the primary processes involved in the movement of spilled oil or constituents through marine habitats.
- The transfer mechanism "Collected" refers to that portion of the residue that is the object of physical recovery activities, which typically are less than 50 percent effective in removing spilled oil and residue.
- Results of the exposure assessment are presented in the CSMs in terms of likelihood of a complete, significant exposure pathway (i.e., "likely", "possible", "unlikely").
- In the offshore environment, movement of residues or particulate plumes "onshore" should be interpreted as movement toward shore and shallower water but not onto the shoreline.
- In both the near-shore and estuarine environments, some portion of the sinking residues will likely wash into the intertidal zone.
- In the estuarine environment, movement "offshore" should be interpreted as movement toward open water of the estuary (e.g., center of a bay) and away from fringing marshes and other intertidal habitats.

Following is a summary of the numbers of potential exposures of ecological receptors for each exposure probability, alternative, and marine environment as illustrated in the three CSMs:

## SUMMARY OF CONCEPTUAL SITE MODEL RESULTS

Alternative:	Offshore			Near-Shore			Estuarine			Totals		
	L	P	U	L	P	U	L	P	U	L	P	U
Spill is not burned	0	24	32	14	32	10	26	26	4	40	82	46
Spill is burned	0	10	38	0	25	23	5	26	17	5	61	78

Exposure Probability: L - Likely; P - Possible; U - Unlikely

Some of the observations that can be made regarding ecological exposure pathways under the burn/no-burn alternatives are:

- Because burning an oil spill reduces the spill volume by at least 75 percent, the probability of a complete exposure pathway is substantially lower for the remaining burn constituents than for unburned spill constituents for essentially all receptors in all environments;
- The greatest number of "likely" complete pathways would occur as the soluble fraction and weathered oil spill residue move onshore; and
- The greatest number of "unlikely" complete pathways would be found between the smoke (i.e., particulates and other pollutants) and the ecological receptors.

The following conclusions can be drawn regarding the exposure pathways under the burn/no-burn alternatives:

- Regardless of the alternative (burn or no-burn), a crude oil spill offshore results in less likely exposure of ecological receptors to the oil, its residues, and constituent chemicals than spills in the near-shore or estuarine environment (this confirms the observations of impacts from several previous oil spills as reported by Freedman [1989]).

- For all of the environments (offshore, near-shore, or estuarine), the burn alternative results in less likely exposure of ecological receptors to crude oil, its residues, and smoke than does the no-burn alternative (total of 66 likely or possibly complete exposure pathways if the spill is burned versus 122 likely or possibly complete pathways if the spill is not burned).

## CHEMICALS OF CONCERN

The potentially toxic constituents of crude oil, its residues and combustion products are similar to those of concern for human health. Of the many compounds and elements present in crude oil (Table 1), two classes of chemicals, PAHs and metals (nickel and vanadium), are considered more toxic to ecological receptors than the alkanes or cycloalkanes. However, both the PAHs and metals are in relatively low concentrations in crude oil and are not in a form that can be readily metabolized (not bioavailable) by ecological receptors.

Several of the individual PAHs are recognized as potent carcinogens while other PAHs can adversely affect survival and growth of organisms. PAHs vary widely in their toxicity to aquatic organisms, with toxicity generally increasing with increased molecular weight (Eisler 1987). However, Neff (1979) reports that in most cases even the most heavily polluted waters have PAH concentrations that are several orders of magnitude lower than acutely toxic concentrations.

Individual PAHs are in low concentrations in crude oil and have limited mobility in an aquatic setting. Although there can be 2 to 25 percent aromatic hydrocarbons in crude oil (Table 1), most of these aromatics are comprised of lighter weight benzenes and naphthalenes (Table 2). Recognized carcinogenic or toxic PAHs such as benzo[a]pyrene and pyrene are typically found at concentrations less than 5 mg/kg. Low concentrations of the lighter PAHs can be found in water beneath oil spills, but most PAHs have low solubilities in water and high partition coefficients ( $K_{ow}$ s) that limit the mobility of PAHs from oil into the water. The following table lists the solubilities and Log  $K_{ow}$ s for some of the PAHs found in crude oil.

**SOLUBILITIES AND PARTITION COEFFICIENTS FOR  
POLYCYCLIC AROMATIC HYDROCARBONS**

PAH	Solubility in Water (mg/l)	Log $K_{ow}$
Naphthalene	31	3.4
Pyrene	0.13	5.3
Anthracene	0.06	4.4
Benzo[a]anthracene	0.014	5.6
Benzo[a]pyrene	0.004	6.0
Benzo[g,h,i]perylene	0.0003	7.2

Sources: Eisler (1987); Varanasi (1989); Callahan et al. (1979)

An example of the limited mobility can be illustrated for benzo[a]pyrene. This PAH has a reported concentration of 2.8 mg/kg in Kuwait crude oil (Table 2). The Log  $K_{ow}$  for benzo[a]pyrene is 6.0 ( $K_{ow} = 1 \times 10^6$ ), which describes the log of the concentration in oil divided by its concentration in water. In other words:

$$1 \times 10^6 = 2.8 \text{ mg/kg benzo[a]pyrene in oil} / \text{concentration in water (mg/l)}$$

Therefore, the concentration of benzo[a]pyrene in water immediately beneath an oil spill could be up to  $2.8 \times 10^{-6}$  mg/l. This is four orders of magnitude less than the concentration of benzo[a]pyrene reported by Neff (1979) as toxic ( $LC_{50}$ ) to the sandworm (*Neanthes arenceodentata*). An  $LC_{50}$  is the concentration that is lethal to 50 percent of the test organisms.

For pyrene (4.5 mg/kg in crude oil; Log  $K_{ow}$  of 5.3), the highest concentration expected in water directly beneath a spill would be  $2.3 \times 10^{-5}$  mg/l. This is three orders of magnitude less than the concentration reported by Verschueren (1983) as toxic to the mosquitofish (*Gambusia affinis*).

For naphthalene, the PAH with the lowest Log  $K_{ow}$  (3.4), the highest concentration expected in water directly beneath a spill having 400 mg/kg naphthalene would be 0.16 mg/l. This concentration of naphthalene may be toxic to zooplankton (depending on exposure duration and other factors) but is not expected to be toxic to fish or shellfish, which have toxicities ( $LC_{50}$ s) of 0.92 mg/l for pink salmon to 150 mg/l for mosquitofish (Eisler 1987).

The primary metals found in crude oil, nickel and vanadium, are found in concentrations of 1 to 20 mg/kg, but may be present at concentrations up to 200 mg/kg nickel and 1,200 mg/kg vanadium in some crude oils (WHO 1989). These metals occur primarily as organometallic complexes known as porphyrins (Costantinides and Arich 1967) which can be distilled at temperatures above 500°C (WHO 1989), and are therefore stable at ambient temperatures. Because these metals are complexed in porphyrins, they are unlikely to represent a risk to ecological receptors.

Because PAHs and metals in crude oil are in low concentrations and have limited bioavailability in water, the risk to ecological receptors is likely more closely related to the probability of direct exposure to oil and its physical and cumulative toxic effects than to the individual chemicals found in the oil. One of the most important adverse effects of oil on birds and marine mammals is fouling of feathers and fur (Freedman 1989). This fouling causes a loss of the properties of insulation and buoyancy and leads to death by drowning or extreme heat loss (hypothermia). Sea otters and other furred marine mammals are especially vulnerable to oil spills because of their reliance on fur rather than blubber for insulation (Stoker et al. 1992). Birds and marine mammals can also suffer toxic effects by ingesting or inhaling oil while in direct contact with the spill or during attempts to clean feathers or fur by preening. There continues to be long-term chronic effects in fish and waterfowl resulting from direct contact with oil spilled from the Exxon Valdez as reviewed by Schneider (1993).

#### **RELATIVE RISK EVALUATION**

The relative risk evaluation discusses which alternative, burning or not burning spilled crude oil, presents fewer risks to ecological receptors in the offshore, near-shore, and estuarine habitats. Because the relative risks to ecological receptors is more directly related to the probability of direct exposure to crude oil and its constituents than to the individual compounds in the oil, the results of the risk evaluation closely parallel those of the exposure evaluation:

- Because burning a crude oil spill reduces the spill volume by at least 75 percent, the overall probability of ecological risk is substantially less for burn residue than for the spilled oil or unburned spill residue in all three marine environments.
- Because burning effectively eliminates the volatile/soluble fraction of a crude oil spill, two potential exposure pathways and their related risks are eliminated.
- The greatest risk to ecological receptors under both burn and no-burn alternatives would occur as the soluble fraction (no-burn alternative) and oil spill residue move onshore in response to winds and currents.
- Because of the low number of "likely" or "possible" complete exposure pathways, the least likely risk would be due to inhalation of smoke (i.e., particulates and other pollutants) and direct contact by the ecological receptors, most of which are under water.

## CONCLUSION

It appears, based on the results of the ecological risk evaluation, that under practically all combinations of physical conditions (e.g., winds and currents) and ecological receptors, the preferred decision would be to burn a crude oil spill rather than not to burn. A decision not to burn the spill may possibly represent less overall risk to ecological receptors only if the most sensitive and important (e.g., threatened or endangered species) receptors are physically isolated from the marine/estuarine waters yet are close enough to the potential burn site that they would be exposed to the fire or soot (particulates and other airborne pollutants). Such a unique situation may exist if significant terrestrial receptors were located onshore directly downwind from a crude oil spill and there were only limited receptors in the near-shore habitats. Because this exposure pathway is potentially complete but highly unlikely, it was not included in the near-shore or estuarine CSM.



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