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Release of Volatile Liquid Hydrocarbons from Spilled Petroleum

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The extensive shipping of crude oil over the world's oceans has produced increased concern over the effects of the accidental spillage of petroleum on the marine environment. Ca. 2.1 x 10^6 tons of the total 6.1 x 10^6 tons of oil added to the oceans annually from all sources (National Academy of Science 1975) come from spilled petroleum. One portion of the petroleum released to the oceans that is of particular interest environmentally are the toxic, volatile liquid hydrocarbons (VLHs). VLHs are defined empirically as all compounds with boiling points between those of n-C_6 and n-C_{14}. Although VLHs can constitute a major fraction of crude oil (ca. 20-40%), little information is available on VLHs associated with oil spills. Hydrocarbons within this range include normal and branched alkanes, monocycloalkanes, aromatics, and alkyl-sub-stituted analogues. The light aromatics (benzene → naphthalene) are considered to be one of the most immediately toxic components of petroleum other than the carcinogenic polycyclic aromatics (Blumer 1971). Studies have suggested that the toxicity of an oil is due primarily to the water soluble fraction (Rice *et al.* 1977). Refined products are usually more toxic than crude oils due to the higher concentrations of soluble aromatic hydro-carbons. The fate and mode of incorporation of VLHs into the water column during a petroleum spill is important both to the controlling of the spill and in assessing its environmental impact. For example, Figure 1 shows a gas chromatogram of VLHs in seawater around the IXTOC-I oil spill in the Gulf of Mexico (Brooks *et al.* 1981).

METHODS AND MATERIALS

Volatile hydrocarbon solution studies were conducted in a 68.5 L, glass rectangular tank with a surface area of 2250 cm^2 (Figure 2). Each experiment was run with 10-L (9 cm deep) of Gulf of Mexico seawater with a salinity of approximately 32 ppt. A laminar flow hood with two axial fans was used to vary the wind speed in the tank headspace and reduce the "herding" of oil along the sides of the tank. The tank was covered with a plexiglass sheet. Slow stirring of the water column with magnetic stirring bars was used to ensure that water samples were representative of the entire water volume. Without stirring the precision among

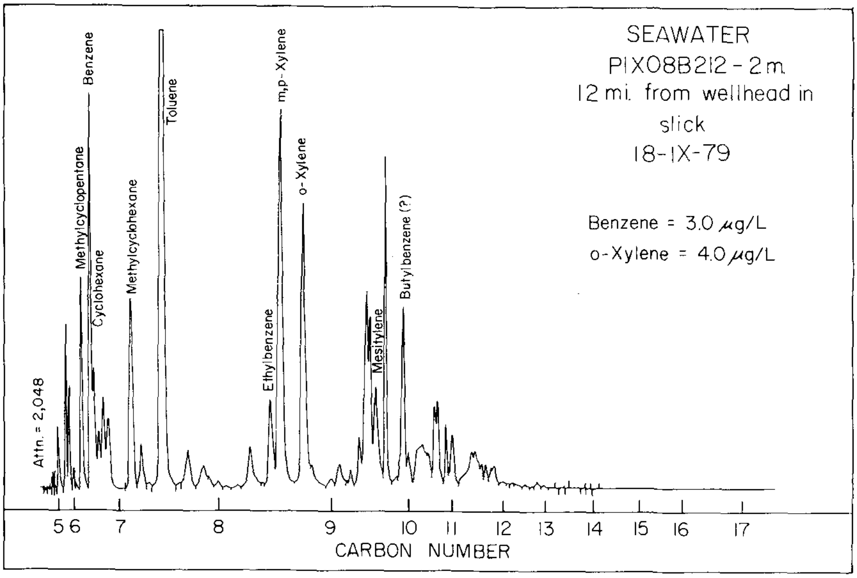

Figure 1. VLHs in the water column associated with the IXTOC-I oil spill in the Gulf of Mexico.

Table 1. Parameters and variables in the oil solution tank studies.

Parameter	Variables	
Temperature	5°C	25°C
Light	Simulated day/night	
Crude Oils	Arabian Light; Swanson R.; So. Marsh	
Wind Velocity	Fan speed 50 (≅0.17 m/s)	Fan speed 75 (≅0.25 m/s)

replicate samples was unacceptable. The temperature of the tank was maintained at 5° ± 1°C or 25° ± 3°C. These two temperatures were chosen because the majority of oil exploration and shipping are in arctic and temperate waters. Table 1 is a list of the conditions used during the study.

The oil (50 ml) was slowly added to the surface of the water column through an injection tube, parallel to and at the water/air interface. This method of introduction reduces immediate evaporation to the atmosphere and reduces the addition of oil to subsurface waters (McAuliffee *et al.* 1980).

Aliquots of water (5 ml) were removed from the sampling tank through an underwater sampling port 4.5 cm below the water sur-

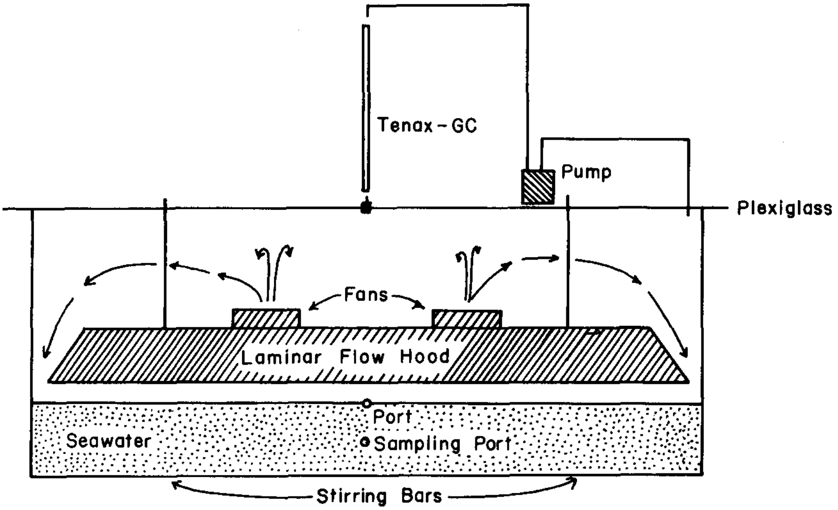

Figure 2. Representation of system used for solution tests.

face in the center of the water column. The water samples were analyzed for volatile hydrocarbons using a modified Tekmar ALS-LSC-II automated purge and trap concentrator system, interfaced with a Hewlett-Packard 5830A gas chromatograph. The water samples were stripped with helium for 20 minutes and the volatile hydrocarbons were trapped on a 50/60 mesh Tenax-GC column at ambient temperature. Tenax-GC a solid polyphenol ether adsorbent which has excellent retention characteristics for volatile hydrocarbons, retains very little water, and exhibits negligible column bleed at temperatures under 300°C (Butler and Burke 1976). After stripping, the Tenax-GC was heated to 200°C to desorb the volatile hydrocarbons into the gas chromatograph as a plug for separation and analysis. Sample components were separated on a 0.3 cm x 305 cm stainless steel column packed with 10% SP-2100 on 80/100 mesh Supelcoport. The chromatographic oven was maintained at 50°C for 10 min., temperature programmed from 50 to 180°C at a rate of 4°C/min., and held at a final temperature of 180°C for 20 min.

RESULTS AND DISCUSSION

A number of experiments were conducted to aid in developing an understanding of the influences of physical and chemical parameters on the solubility and incorporation of VLHs into the water column associated with the spillage of crude oil. Results will be presented in two sections, one dealing with the factors effecting the total amount of volatile compounds incorporated into the water column and a second dealing with the observed distributions of individual compound types. A separate report (McDonald *et al.* 1983) details the effects of chemical dispersants on VLH incorporation into the water column.

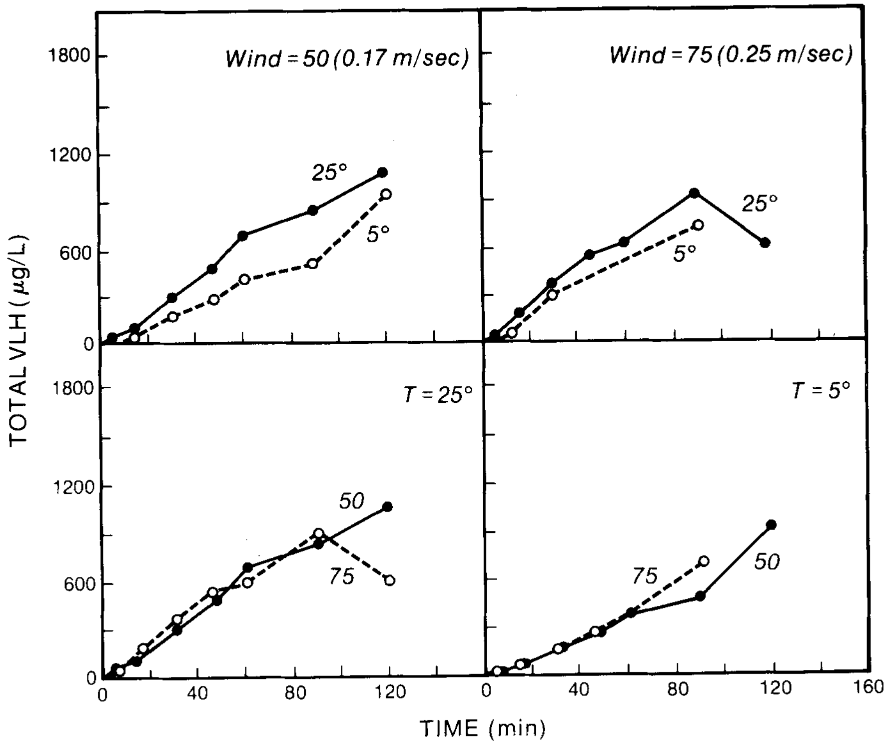

Figure 3. Effects of wind and temperature on incorporation of Arabian Light oil total VLHs into the water column during a 2 hr. experiment.

Experiments conducted at 25° and 5°C with other variables held constant showed that a decreased amount of volatiles are incorported into the water column at lower temperatures (Figure 3). VLHs were released from the slick to the water column at a slower rate at the lower temperature. Dispersive processes effected by temperature include solution, diffusion, and evaporation, which all vary directly with temperature. Vapor pressures decrease ca. 5 % per degree centigrade (McAuliffee 1977). Up to twice the concentration of VLHs were detected in the water at 25°C as at 5°C.

Wind speed had very little effect on VLH incorporation into the water column within the limitations of the experimental design (Figure 3). Increased wind has been shown in previous studies to accelerate weathering of oil (McAuliffee *et al.* 1980). Only two wind speed were tested in this experiment and the change in wind speeds was not large enough to cause a measurable difference in VLHs incorporation. It would be expected that as wind speed increased, accompanied by the break up of the oil slick, that both evaporation and solution of VLHs would be increased.

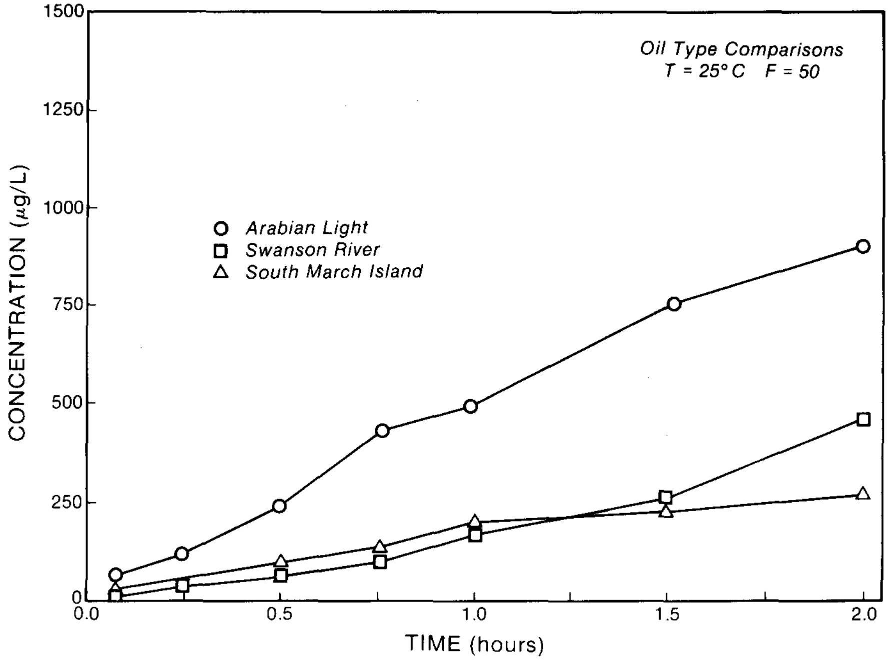

Figure 4. Incorporation of VLHs into the water column for 3 oils.

The chemical composition and physical properties of the tested oils exerted an important influence on the concentrations of VLHs detected in the water column (Figure 4). Maximum concentrations of Arabian Light, Swanson River and South Marsh Island oils at 2 hours were 1068, 539, and 336 µg/L, respectively. Maximum VLH concentrations in the tank were generally reached at ca. two hours after oil introduction with concentrations decreasing to less than 10% of the maximum concentration within 24 hours. The more viscous oils (e.g., Swanson River and South Marsh Island) produced a reduced amount of VLHs in the water column. This is in part due to the lower amounts of VLHs in the more viscous oils as compared to higher API gravity oils. The lower API gravity oils contain substantial amounts of compounds that are less soluble in water (i.e., asphaltenes). Of the oils tested, the Arabian Light oil introduced the greatest amount of VLHs into the water column.

Due to the variable reactivities, solubilities, and toxicities of the VLHs, a number of representative model compounds were independently monitored during the study (Table 2). These compounds include n-alkanes, aromatics, cycloalkanes, and branched alkanes; each representative of a major class of VLHs found in oils. The majority of VLHs detected were accounted for by the chosen model compounds. The VLHs in the water column were generally dominated by the aromatics, in particular benzene and toluene. Due to this fact, the aromatic distribution mirrored the behavior of the total volatile compounds very closely in most cases. Wind and temperature effects were the same for the aromatics as for the total VLHs. An approximate two fold decrease of aromatic VLH concentration in the water column accompanied a reduction in temperature from 25°C to 5°C.

Table 2. Compound types and groups monitored for each experiment.

n-Alkanes:	C_6-C_{14} n-alkanes	Cycloalkanes:	methylcyclopentane [MCP] methylcyclohexane [MCH] cyclohexane [CHX] dimethylcyclohexane
Aromatics:	benzene [BZ] toluene [TOL] ethylbenzene xylene (m,p&o) cumene mestiylene cymene butylbenzene	Branched Alkanes:	3-methylpentane 2,3-dimethylpentane 2,2,4-trimethylpentane 3-methylhexane 3-methylheptane

Table 3 gives the maximum concentrations by compound type for the three oils. The Swanson River oil incorporated less than half the VLHs into the water column as the Arabian Light oil (Figure 4), although more n-alkanes were incorporated. In these experiments, the aromatics were by far the dominant compounds found in the associated water (Table 3). Benzene and toluene were the dominant aromatic compounds and hexane was the dominant n-alkane (except for the Swanson River oil). Measurable, though low, amounts of n-alkanes and cycloalkanes were also detected.

A number of parameters affecting the solution of VLHs from an oil spill into a water column were evaluated. At 5°C less VLHs were incorporated into the water column than at 25°C. The decrease is due to the lower solubilities. Wind speed, within the experimental limits, did not significantly affect VLH incorporation into the water column. Greater incorporation should occur at higher wind speeds due to greater turbulent mixing, more efficient break up of the oil slick and increased evaporation. The incorporated VLHs were dominated by the more soluble compounds such as benzene and toluene. The total amount and composition of incorporated VLHs are initially controlled by the composition of the oil since the original oil composition defines the pool of VLHs available.

VLHs associated with dispersed oil slicks were most directly affected by the original composition of the oil. VLH concentrations measured in the water directly below an oil spill reached

Table 3. Maximum concentration by compound type and the two most concentrated compounds (in descending order) for each compound type group at the time of maximum VLH incorporation for a 2 hr. experiment; temperature @ 25°C and fan speed @ 50.

Oil	Aromatics	n-Alkanes	Cyclo-alkanes	Branched Alkanes
Arabian Light Oil				
Max. Conc. (μg/L)	849	21	0.7	0
Most Concentrated Compounds	BZ;TOL[1] (5/9)*	n-C_6;n-C_7 (2/9)	MCH;- (1/4)	- (0/5)
Swanson River Oil				
Max. Conc. (μg/L)	344	33	57	0
Most Concentrated Compounds	TOL;BZ (7/9)	n-C_{12};n-C_{13} (4/9)	CHX;MCP (4/4)	- (0/5)
South Marsh Island Oil				
Max. Conc. (μg/L)	257	4	0.6	0
Most Concentrated Compounds	BZ;TOL (5/9)	n-C_6;- (1/9)	MCH;- (1/4)	- (0/5)

[1] See Table 2 for abbreviations in brackets of compounds.

*Indicates the number of model compounds detected (i.e., 5 out of the 9 model aromatic compounds were detected).

their maximum concentration within a few hours and were reduced by a third to a tenth of their maximum values in 1 - 2 days. Factors which exerted a lesser influence (under the given test conditions) were wind speed and temperature.

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