

# EFFECTIVENESS, BEHAVIOR, AND TOXICITY OF DISPERSANTS

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**ABSTRACT:** Three key issues must be addressed when deciding on the desirability of using chemical dispersants for mitigating the adverse effects of oil spills: (1) how effective a given dosage of dispersant will be on a given oil slick; (2) how the dispersed oil and dispersant diffuse into the water column, dissolve, volatilize, degrade, and interact with suspended and bottom sediments; and (3) what effects the dissolved and particulate oil and dispersant will have on water column and benthic biota. It is essential that the first two areas (physical and chemical studies) relate closely to the third (biological aspects) in order that bioassay exposure (in terms of concentration of dispersant, classes of and individual hydrocarbons, and duration) addressing the toxicity issue be realistic.

Here, we review the current status of a research program which addresses these issues. Under the program, attempts are being made to quantify dispersant effectiveness (including consideration of effectiveness testing using the Mackay-Nadeau-Steelman system for oils which have evaporated and/or formed water-in-oil emulsions to various extents), water column diffusion, and partitioning of specific hydrocarbons among water, oil, and suspended sediment as well as into the atmosphere. A procedure is described which has been used to quantify the acute toxicity of dispersants to copepods and which is being extended to apply also to the toxic contributions of dissolved and particulate oil. Hopefully, by assembling quantitative expressions for effectiveness, behavior, and toxicity, those situations in which dispersion is desirable can be better identified.

The use of chemical dispersants for oil spill treatment has received increasing attention in recent years for several reasons. Claims have been made that new dispersants are more effective and less toxic. Concentrations under dispersed spills may be quite low and may have relatively short durations, so that acute toxic effect levels are not reached for many marine organisms, especially at depths of more than five meters (m). Dispersed oil behaves quite differently from an oil slick when it reaches shore, possibly resulting in shorter or less impact and less expensive cleanup. Improved dispersant delivery systems have been developed and tested, especially those using aircraft. Finally, other countermeasures techniques, although steadily improving, have not yet demonstrated the capability of handling a significant fraction of a large marine spill. Despite the optimism surrounding dispersion, there remains concern about the use of potentially toxic chemicals to reduce the adverse effects of petroleum spills. Certainly, it is desirable to elucidate the transport and partitioning history of the dispersant and the oil so that the change in concentration and duration of the exposure due to the dispersant treatment is quantified and interpreted in the light of toxicity information about the oil and the dispersant.

The toxicological issue is complicated by the dual role which the dispersant plays. It is inherently toxic, but possibly more important, it alters the nature and extent of oil exposure to marine organisms. Thus the toxic effects of oil and dispersant cannot be combined directly.<sup>10</sup>

In a three-year research program we have investigated these issues experimentally and theoretically and have attempted to link the dis-

persed spill physical chemistry and toxicology using quantitative relationships wherever possible. The aim of this paper is to expose the principles and conceptual framework and give some illustrative data. More detailed accounts of the experimental component studies are being prepared for publication elsewhere.

## Dispersion

Figure 1 illustrates schematically the component processes which must be considered. First, is the dispersion process in which the surfactants penetrate the oil and reduce the oil-water interfacial tension thus promoting the formation of small oil drops. These drops may diffuse down into the water column, with some rising to the surface and reforming a slick, but most becoming incorporated into the water column.

Second, hydrocarbons and surfactant in the oil drops will partition into the water, approaching an equilibrium dependent on their partition coefficients and the oil-water volume ratios.

Third, the dissolved organics may volatilize from solution into the atmosphere.

Fourth, the dissolved and particulate oil will diffuse vertically and horizontally, yielding continuously changing concentrations with depth. As this occurs, the relative quantity of each hydrocarbon which partitions into the oil and the water will adjust accordingly.

Fifth, the oil particles may associate with mineral and organic particulate matter in the water column, and sediment to the bottom. Zooplankton may contribute substantially to this process. Sorption of dissolved hydrocarbons also may occur.

Finally, each organism in the water column of a given depth will be

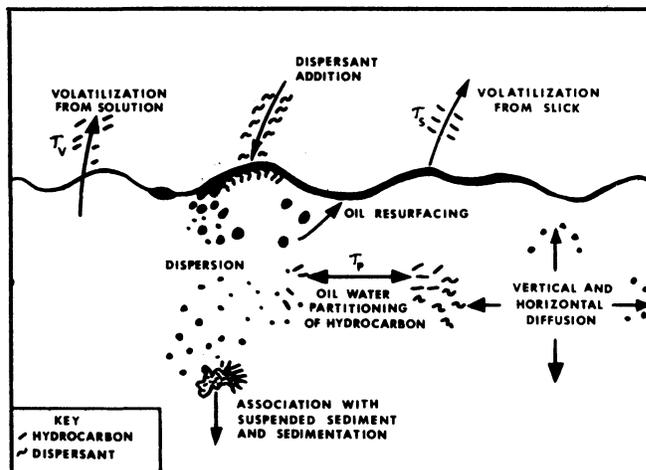


Figure 1. Dispersion processes

exposed to a pulse of dissolved and particulate hydrocarbon and dispersant and potentially will suffer a toxic effect.

The key questions appear to be: To what extent do the toxic effects of the oil slick on water column biota change as a result of dispersion? To what extent does dispersion change the amount of oil which reaches the bottom and thus change the nature and particularly the duration of the toxic effect on the benthos?

### The dispersion process

When dispersant is applied to an oil slick, a fraction of the oil is dispersed into the water column. This fraction depends on the nature of the oil and dispersant, their relative amounts, and the prevailing level of turbulence at the sea surface. Because of the difficulty and expense of quantifying the extent of dispersion at sea most results have been obtained using laboratory dispersant effectiveness tests. Hopefully, these laboratory and "at sea" results can be correlated and coefficients established describing the dependence of dispersant effectiveness on variables such as viscosity, and design equations which can be applied both to the laboratory test results and to those from at-sea experiments.

Our work with the Mackay-Nadeau-Steelman (MNS) test indicates that the primary determinants of effectiveness are:

- the nature of the dispersant formulation
- the oil viscosity ( $\mu$ ), density, and composition
- the dispersant-to-oil ratio
- the prevailing turbulence or mixing energy
- the water salinity
- the method of mixing oil and dispersant (e.g., spray droplet size or extent of dilution in water)

The dispersion process is a very complex, transient phenomenon and it is doubtful if accurate effectiveness equations ever will be developed. For example, high oil viscosity usually results in lower effectiveness but there may be regions (around 100 centipoise—cp) in which an increase in viscosity improves the retention of the dispersant by the oil and causes an increase in effectiveness. Different effectiveness results are obtained if the dispersant is premixed with the oil, added "neat" to the oil, or sprayed in water solution or suspension. Further, the dispersant droplet size alters the effectiveness.

It is clear that an ill-defined mixing process occurs between the oil slick and the dispersant in which only a fraction of the surfactant is present at the oil-water interface at any given time. There is a danger that dispersant formulations may perform well in laboratory tests but poorly at sea if the mixing process, as it occurs at sea, is not well simulated in the laboratory. For this reason we favor the MNS test in which there is some attempt to simulate the mixing process. It is very desirable, however, to establish the reliability of this and other tests by comparing performance in the laboratory with that at sea in boat spray tests or following actual treatment of slicks.

We believe that the effectiveness of a given treatment can be expressed by an empirical correlating equation of the form

$$F_D = 1 - \exp(-K_1 D^\alpha \mu^b) \quad (1)$$

Where:  $F_D$  = volume fraction of the oil dispersed  
 $K_1$  = a constant dependent on the dispersant, the turbulence level, the dispersant delivery method and to a limited extent on the oil  
 $D$  = ratio of dispersant to oil volumes  
 $\mu$  = oil viscosity  
 $\alpha$  = a constant with a value of approximately 1.5  
 $b$  = a constant with a value of  $-0.5$  to  $-0.8$

The equation probably breaks down at low viscosities (i.e.,  $\leq 100$  mPas) when very high effectiveness is predicted. An accurate fit of experimental data requires inclusion of another term to account for poor mixing of dispersant and low viscosity oils, which may be worsened by oil herding effects of the dispersants.

### Oil-water partitioning

If small drops of oil are present in water at a low concentration of  $C$  (in  $m^3$  of oil per  $m^3$  of water) water then a specific hydrocarbon

present at a total volume fraction in the original oil  $y_o$  will have a volume  $Cy_o$  ( $m^3$ ). It will partition between oil and water phases in such a way that its total volume is conserved, that is

$$C_o y_o = Cy + (1 - C)x$$

where  $y$  is the new, lower, volume fraction in the oil and  $x$  is the volume fraction in the  $(1 - C) m^3$  of water. We can assume that the total extent of the dissolution is so small that the oil volume does not fall as a result of dissolution, and thus  $C$  equals  $C_o$ .  $C$  is small, thus  $(1 - C)$  will be approximately unity. Further, if  $x$  and  $y$  are related by an oil-water volumetric partition coefficient  $K_v$  so that  $K_v = y/x$  then a mass balance gives

$$Cy_o = (CK_v + 1)x = \frac{(CK_v + 1)y}{K_v}$$

Now,  $K_v$  can be estimated from the hydrocarbon solubility ( $S$ ) which is normally expressed in mg/l. Assuming that the hydrocarbon forms an ideal solution in the oil,  $S$  in the water will be in equilibrium with  $\rho$  ( $kg/m^3$ ) or  $1,000 \rho$  (mg/l) in the oil, where  $\rho$  is the pure liquid hydrocarbon density (usually 700 to 900  $kg/m^3$ ).  $K_v$  is thus  $1,000 \rho/S$  and for a hydrocarbon such as toluene ( $S = 400$  mg/l) has a value of approximately 2,000. Alkanes such as octane have  $K_v$  values of approximately 1 million.

The fraction of the hydrocarbon in the oil is thus  $Cy/Cy_o$  or  $CK_v/(1 + CK_v)$  and that in the water is  $x/Cy_o$  or  $1/(1 + CK_v)$ . The critical group is thus  $CK_v$  and its magnitude relative to unity. If  $CK_v \gg 1$  most hydrocarbon will be in the oil, whereas if  $CK_v \ll 1$  most will be in solution in the water.

A convenient method of estimating  $y_o$  is to equilibrate a relatively small quantity of water with the original oil and measure the concentration of dissolved hydrocarbon,  $S_o$ , which will be approximately  $y_o S$ . For example, a hydrocarbon with a solubility ( $S$ ) of 100 mg/l and a density of 800  $kg/m^3$  will have a  $K_v$  of 8,000. If it is present in an oil so that the equilibrium water concentration  $S_o$  is 5 mg/l, then the volume fraction in the oil will be approximately  $S_o/S$  or 0.05.

There may be a kinetic limitation to dissolution corresponding to the time taken for the hydrocarbon to diffuse from the drop into solution. This "half time" ( $\tau_p$ ) has been estimated by Mackay *et al.*<sup>5</sup> to be approximately  $60 \times 10^6 d^2 K_v$  seconds, where  $d$  is the drop diameter (m). For drops of less than 10  $\mu m$  diameter, this time is quite short, except for very insoluble (high  $K_v$ ) hydrocarbons. A simple method of including this kinetic effect is to estimate that the fractional approach to equilibrium dissolution is

$$\left[ 1 - \exp\left(\frac{-0.69t}{\tau_p}\right) \right]$$

where  $t$  is time and  $\tau_p$  is estimated above (the quantity  $0.69/\tau_p$  is a rate constant). It follows that the fraction of the hydrocarbon which will be dissolved will be approximately

$$F_p = \left[ \frac{1}{(1 + CK_v)} \right] \left[ 1 - \exp\left(\frac{-0.69t}{\tau_p}\right) \right] \quad (2)$$

$F_p$  approaches  $1/(1 + CK_v)$  when  $t > \tau_p$  and tends to zero when  $t$  is zero or when  $CK_v$  is large. The fraction in the oil is thus  $(1 - F_p)$ . Clearly, as  $C$  falls due to diffusion  $F_p$  will increase and more hydrocarbon will dissolve. The absolute concentrations can be estimated by multiplying these fractions by  $Cy_o$ .

### Diffusion

When the oil slick is dispersed, an expanding cloud of small oil drops (believed to range from 1 to 50  $\mu m$  in diameter) form and diffuse horizontally and vertically. Some large drops may rise and reform a slick, but if dispersion is effective most will become mixed into the water column. The unsteady state equations describing the concentration-time-depth relationships are very complex, but by making some simplifying assumptions Mackay *et al.*<sup>5</sup> were able to estimate the oil concentration as a function of time and depth and obtain reasonable agreement with experimental spill observations. It was assumed in their derivation that a negligible fraction of the oil volatilized and there was no discrimination between dissolved and particulate (oil drop) form. The equation developed was

$$C = C_s \exp\left(-Z\sqrt{\frac{\pi}{4D_v t}}\right) \quad (3)$$

$C_s$ , the surface oil concentration (volume fraction), is given by

$$C_s = \frac{V_D \sqrt{\frac{\pi}{4D_v t}}}{A} \quad (4)$$

Where:  $V_D$  = dispersed oil volume  
 $Z$  = depth (m)  
 $D_v$  = effective vertical diffusivity ( $\text{m}^2/\text{s}$ ) in the water column  
 $A$  = horizontal area of the cloud (which may increase with time due to horizontal diffusion)  
 $V_d/A$  = thickness of the dispersed oil slick and will be the actual slick thickness ( $V_s/A$ ) multiplied by the volume fraction dispersed  $F_D$ .

From an examination of concentration data, Mackay *et al.* suggested that a typical value of  $D_v$  is  $0.0126 \text{ m}^2/\text{s}$ .

The area increase rate can be estimated from ocean diffusion correlations as reviewed by Okubo,<sup>9</sup> or a simple linear increase in area or diameter can be assumed.

### Volatilization from the slick

It is rarely possible, even in experimental spills, to apply dispersant immediately to the fresh oil; thus, much of the volatile material may be lost by evaporation prior to dispersion. Harrison *et al.*<sup>3</sup> measured half-lives of hydrocarbons in a slick and fitted a mathematical model to the data. This yields an expression for half life  $\tau_s$  as follows.

$$\tau_s = \frac{0.69 RTV}{K_G A P v}$$

Where:  $K_G$  = the evaporation mass transfer coefficient (approximately  $10^{-2} \text{ m/s}$ )  
 $A$  = slick area ( $\text{m}^2$ )  
 $V$  = slick volume ( $\text{m}^3$ )  
 $P$  = hydrocarbon vapor pressure (Pa)  
 $v$  = molar volume ( $\text{m}^3/\text{mol}$ )  
 $R$  = the gas constant ( $8.314 \text{ Pa m}^3/\text{mol K}$ )  
 $T$  = absolute temperature (K)

$V/A$  is the slick thickness  $h$  (m) and  $v$  is  $M/1000\rho$  where  $M$  is molecular weight (g/mol) and  $\rho$  is density ( $\text{kg}/\text{m}^3$ ). For nonane ( $P$  approximately 500 Pa),  $\tau_s$  for a 1 mm slick is approximately 2100 s or 35 minutes, in good agreement with experiment. This equation simplifies to

$$\tau_s = \frac{168 \times 10^6 h \rho}{PM}$$

Values of  $\tau_s$  are given later in Table 2 for 0.15 mm slicks for selected hydrocarbon groups.

### Volatilization from water solution

Volatilization of dissolved hydrocarbon can play a major role in depleting the water column of oil. It can be shown that a volatilizing hydrocarbon in a well mixed volume of water will experience a concentration decay expressed as<sup>2</sup>

$$x = x_o \exp\left(\frac{-K_{oL} t}{Z}\right)$$

Where:  $x_o$  and  $x$  = initial concentration at time  $t$   
 $Z$  = water depth

$K_{oL}$  is an overall liquid phase volatilization mass transfer coefficient ( $\text{m/s}$ ) given by

$$\frac{1}{K_{oL}} = \frac{1}{K_L} + \frac{RT}{HK_G} \quad (6)$$

Where:  $K_L$  = the water-side transfer coefficient (typically  $5 \times 10^{-5} \text{ m/s}$ )  
 $K_G$  = the air-side coefficient (typically  $10^{-2} \text{ m/s}$ )  
 $R$  = the gas constant ( $8.314 \text{ Pa m}^3/\text{mol K}$ )  
 $T$  = temperature (K)  
 $H$  = the hydrocarbon's Henry's Law constant ( $\text{Pa m}^3/\text{mol}$ )

$H$  is conveniently estimated as the ratio of vapor pressure  $P$  (Pa) to solubility in units of  $\text{mol}/\text{m}^3$  or  $MP/S$ , where  $M$  is the molecular weight in g/mol and  $S$  is solubility in  $\text{g}/\text{m}^3$  or  $\text{mg}/\text{l}$ . Mackay and Shiu<sup>4</sup> have recently reviewed  $H$  values for fresh water, but for saltwater  $S$  is usually 20-to-30 percent smaller and  $H$  correspondingly larger.

If the column is not well mixed, the diffusive resistance due to the water column can be added to give a modified  $K_{oL}$ :

$$\frac{1}{K_{oL}} = \frac{1}{K_L} + \frac{RT}{HK_G} + \frac{Z}{D_v} \quad (7)$$

The fraction of the dissolved hydrocarbon which will have volatilized will be  $(1 - x/x_o)$  which we term  $F_v$ .

It follows that a hydrocarbon of very low vapor pressure will have a large  $(RT/HK_G)$  value corresponding to a large air phase resistance;  $K_{oL}$  will be small and volatilization will be slow and  $F_v$  will remain close to zero. That is,

$$F_v = \left[1 - \exp\left(\frac{-K_{oL} t}{Z}\right)\right] = 1 - \exp\left(\frac{-0.69t}{\tau_v}\right) \quad (8)$$

where  $\tau_v$  is a volatilization half time equal to  $0.69Z/2K_{oL}$ , the 2 being included since the average depth will be half the final depth ( $Z$ ).

### Combined physical-chemical processes

In summary, if  $V_s \text{ m}^3$  of oil are dispersed over an area  $A$  ( $\text{m}^2$ ) with a fractional effectiveness  $F_D$  (equation 1), there will be a surface concentration of dispersed oil  $C_s$  (equation 4) underlain by lower concentrations  $C$  (equation 3) which will be functions of depth and time. A specific hydrocarbon ( $i$ ) of given aqueous solubility, density, and vapor pressure will have an oil-water partition coefficient  $K_i$  and will dissolve to the fractional extent  $F_p$  (equation 2). If no volatilization occurs it is thus possible to estimate the partitioning behavior of the hydrocarbon at any depth and time.

An estimate of the volatilization extent can be obtained from equation 8. If  $\tau_v$  is short compared to the time of interest appreciable volatilization is expected. Conversely if  $\tau_v$  is long most hydrocarbon will remain in the water.

Since the processes of dissolution and volatilization for an individual hydrocarbon are sequential it is erroneous to use each equation in isolation. It can be shown that rigorous solution requires setting up and solving two simultaneous differential equations, one each for the hydrocarbon concentration in the oil and in the water. The solution is inconveniently complex but a simpler, less accurate, yet reasonable equation can be obtained by inspecting the solution and making certain assumptions. The result, without detailed justification, is:

Initial amount present =  $C_y o$

Amount remaining in oil at time  $t$

$$= C_y o \frac{\exp\left(\frac{-0.69t}{\tau_o}\right) \left[CK_v + \exp\left(\frac{-0.69t}{\tau_p}\right)\right]}{CK_v + 1} \quad (9)$$

Amount in water at time  $t$

$$= C_y o \frac{\exp\left(\frac{-0.69t}{\tau_o}\right) \left[1 - \exp\left(\frac{-0.69t}{\tau_p}\right)\right]}{CK_v + 1} \quad (10)$$

Amount volatilized

$$= C_y o \left[1 - \exp\left(\frac{-0.69t}{\tau_o}\right)\right] \quad (11)$$

Where:  $\tau_p = 60 \times 10^6 d^2 K_v$   
 $\tau_v = \frac{0.69Z}{2K_{oL}}$   
 $\tau_o = \tau_p + \tau_v (1 + CK_v)$

It is important to note that the  $\tau$  values do not merely add; the factor  $CK_v$  must be included. The reason is that when  $CK_v$  is large, most hydrocarbon is in the oil phase and the volatilization rate is slowed since a relatively small fraction is in the water and thus accessible to volatilization. If  $\tau_v$  is small, volatilization is rapid and the dissolution rate controls the overall process.

It must be emphasized that these equations contain many assumptions and approximations, particularly those for  $F_v$  and  $\tau_v$ , but they are the most reasonable and simple expressions obtainable using the minimum number of adjustable parameters. They reduce to intuitively reasonable limits: for example, as vapor pressure and solubility approach zero all the hydrocarbon remains in the oil. The principal weakness is that in reality  $F_v$  depends on the oil's "life history" as it migrated from the surface and experienced a time-varying depth and surrounding concentration of dissolved hydrocarbon. This is not included in the equations. Our purpose here is thus not to derive accurate equations but rather to assemble a complete set in the hope that the entire process from dispersion to toxic effect can be quantified and component equations improved as they are demonstrated to be inadequate.

It is thus possible to estimate concentrations and their duration for specific hydrocarbons and total oil in the water column as a function of time. This exposure information can then be inserted into toxicity equations to examine the toxic effects of the various components on the organisms in question.

**Hydrocarbon groups**

Presumably, the physical-chemical condition and the toxicity of the dispersion are a combination of the individual properties and toxicities of the dispersant, the particulate oil, and the dissolved hydrocarbons. It is impractical to consider every hydrocarbon individually since the number is large and there is little possibility of obtaining toxicity data for each combination of hydrocarbon and organism. Further, little is known about the nature of the interaction of the toxicities. To simplify the situation yet retain some degree of fidelity to the real situation, we suggest that the hydrocarbons be classified into groups of broadly similar physical-chemical properties and behavior and, it is hoped, of similar toxicities. These groups (Table 1) are: the lower alkanes (which are quite volatile, have solubilities in excess of 10 mg/l, and generally lie in the C<sub>3</sub> to C<sub>7</sub> range including cycloalkanes); the higher alkanes (which are less volatile and soluble and have 8 or more carbons); the mono-aromatics (benzene and substituted benzenes); the naphthalenes; the higher polycyclic aromatics; and an inert residue. Typical group properties are given in

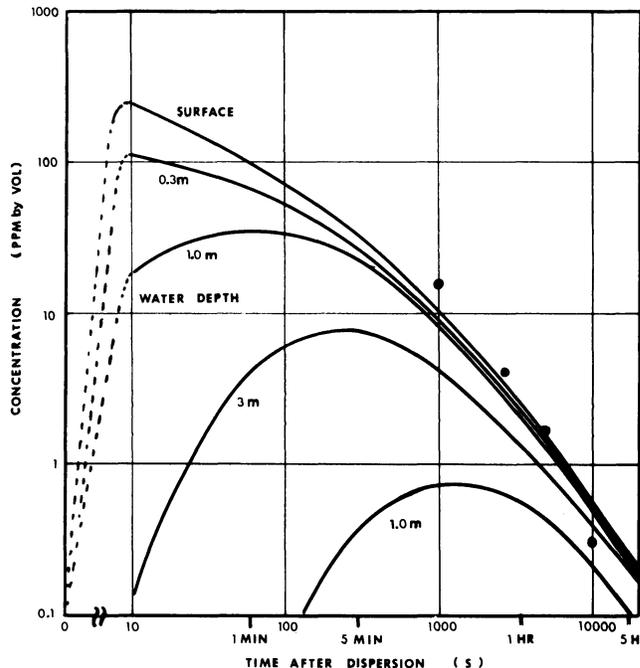


Figure 2. Illustrative plot of total concentration of oil under a slick at stated depths as a function of time—The points are from McAuliffe et al.<sup>8</sup>

Table 1, which can be used to calculate the partitioning characteristics of the group among oil, water, and air.

The values are calculated using a  $K_L$  value of  $5 \times 10^{-5}$  m/s and a  $K_G$  value of  $10^{-2}$  m/s. The Henry's Law constants are consistent with those reviewed by Mackay and Shiu.<sup>4</sup> The oil compositions ( $y_o$ ) appear reasonable, yielding a crude oil solubility of 26.5 mg/l. The dispersant properties are speculative, but seem to be sufficiently accurate for the present purposes, the value of  $K_v$  being supported by the work of Mackay and Hossain.<sup>7</sup>

**Acute toxicity**

Two approaches can be used to incorporate the toxicity information into an evaluation of acute toxicity: graphical and analytical.

In the graphical approach, a plot of concentration versus exposure time is prepared for each toxicant with lines of equal extent of mor-

Table 1. Suggested physical-chemical properties for hydrocarbon groups

Hydrocarbon	M Molecular weight (g/mol)	S Solubility (g/m <sup>3</sup> )	P Vapor pressure (Pa)	$\rho$ Density (kg/m <sup>3</sup> )	H Henry's Law constant (Pa · m <sup>3</sup> /mol)	$K_v$ Oil-water partition coefficient	$S_o$ (g/m <sup>3</sup> )	$y_o$	$K_{oL}$
Lower alkanes (caC <sub>5</sub> )	72	40	70,000	800	12,600	20,000	6	0.15	$5.0 \times 10^{-5}$
Higher alkanes (>C <sub>8</sub> )	120	0.8	2,000	800	300,000	1,000,000	0.08	0.10	$5.0 \times 10^{-5}$
Benzenes	100	200	1,500	800	750	4,000	20	0.10	$4.9 \times 10^{-5}$
Naphthalenes	160	20	5	800	40	40,000	0.4	0.02	$3.8 \times 10^{-5}$
Higher PNAs	200	0.1	0.003	800	6	8,000,000	0.002	0.02	$1.7 \times 10^{-5}$
Residue	—	0	0	800	0	$\infty$	0	0.61	0
Dispersant	300	100,000	0	1000	0	10	—	—	0

tality (or other effect). The oil spill exposure conditions can be plotted on this graph for a given water depth. This requires that a mean concentration and an exposure time be selected so that the gradual increase and decrease of concentration is simulated as illustrated in Figure 2. In effect, the actual bell-shaped exposure profile is replaced by a rectangular pulse. From the proximity of the exposure points or regions to the equal-effect lines it is possible to estimate the likely toxicity of this toxicant.

From plots of this type for each toxicant, the relative contributions can be estimated and if "additivity rules" are postulated, a total effect can be estimated.

To make real progress, however, toward elucidating the relative acute toxic contributions of dispersant components, and dissolved and particulate oil to marine organisms it is desirable to develop a mathematical or analytical framework which will express the individual and combined toxic effects. The only recent quantitative approaches are those of Anderson *et al.*<sup>1</sup> who proposed a toxicity index consisting of the product of oil concentration and time of exposure, and of Wells and Harris<sup>11</sup> who applied Marking's corrected sum-additive index method, with its recognized limitations. We propose here a more complex model which may have the capability of combining toxic effects from several components. The equation is a modification of the "one hit" equation.

$$S = 1 - E = \exp(-A_1 C_1^{n_1} t_1^{m_1} - A_2 C_2^{n_2} t_2^{m_2} - \text{etc.})$$

- Where:
- $E$  = fractional mortality (or other effect)
  - $S$  = fractional survival
  - $C_1, C_2, \text{etc.}$  = concentrations of each toxicant (dispersant, dissolved oil, particulate oil, etc.)
  - $t_1, t_2, \text{etc.}$  = times of exposure and are normally equal
  - $A_1, A_2, n_1, n_2, m_1, m_2, \text{etc.}$  = constants

Each term ( $AC^n t^m$ ) represents the effect of one toxicant. No claim is made that the equation correctly expresses the interactive effects of two or more toxicants. At this stage the equation is merely a working hypothesis. Experimental toxicity tests using, for example, dispersant alone provide estimates of the constants in one term, the equation reducing to

$$S = 1 - E = \exp(-AC^n t^m)$$

When  $n$  and  $m$  are unity, this reduces to Anderson's concentration-times-time toxicity index.

In principle, toxicity data in the form of a set of  $S, C,$  and  $t$  values can be used to obtain estimates for  $A, n,$  and  $m$  using a nonlinear regression technique. However, a simpler technique was devised as follows: acute toxicity data were plotted on probit graphs as fraction survival versus either log concentration or log time. A line was drawn through the points by eye using points between 16 and 84% effect and judgement of the relative accuracy of each point. The concentration  $C_1$  and  $C_2$  or the times  $t_1$  and  $t_2$  were then read off corresponding to 16 and 84% survival i.e.,  $S_1 = 0.16$  and  $S_2 = 0.84$ . It can be shown that  $n$  and  $m$  can be calculated from:

$$n = \ln\left(\frac{\ln S_1}{\ln S_2}\right) / \ln\left(\frac{C_1}{C_2}\right) = 2.35 / \ln\left(\frac{C_1}{C_2}\right)$$

$$m = \ln\left(\frac{\ln S_1}{\ln S_2}\right) / \ln\left(\frac{t_1}{t_2}\right) = 2.35 / \ln\left(\frac{t_1}{t_2}\right)$$

From the concentration and time to achieve 50 percent mortality ( $S = 0.5$ ), the constant  $A$  can be calculated:

$$A = \frac{-\ln S}{C^n t^m} = \frac{0.693}{C^n t^m}$$

We realize that this procedure has statistical weaknesses, but toxicity data generated with wild populations and static assays contain a high inherent variability. Judgement is necessary to avoid excessive weight being given to certain experiments in which the results are different in character. For example, mortality data at very long times (96 hours) are more variable than those at 24 h and are less relevant to oil spill treatment conditions.

Typical values of the constants for a dispersant test on marine copepods (*Pseudocalanus minutus*) were

$$A = 2.8 \times 10^{-8}, n = 4.0, m = 2.0$$

where  $C$  is in mg/l and  $t$  in hours. The equation corresponding to this line can be plotted on a concentration versus time graph with fractional mortality as a parameter as shown in Figure 3.

By conducting carefully designed experiments with dispersant, dispersant components, oil particles, and dissolved hydrocarbons (water soluble fraction) above and in combination it is possible to suggest values for the constants  $A, n,$  and  $m$  for each compound or group of compounds (as suggested in Table 1). The validity of the equation can be tested and if necessary the additivity rules inherent in it modified. The dominant toxicants should become immediately apparent and the toxicological implications of different dispersant application strategies can be explored.

### Illustration

To illustrate the overall approach, we consider treatment of a spill similar to that described by McAuliffe *et al.*<sup>8</sup> and Mackay *et al.*<sup>5</sup> in which Murban crude oil was treated with a concentrate dispersant. If the slick had a volume of 3 m<sup>3</sup>, an area of 20,000 m<sup>2</sup> (average thickness 0.15 mm), and is treated to achieve 67 percent dispersion (potentially calculable from Equation 1), then  $V_D$  is 2 m<sup>2</sup>. The area of the diffusing cloud may increase according to

$$A = 20,000 + 30t \text{ m}^2 \text{ (} t \text{ in seconds)}$$

The surface concentration can be calculated (equation 4) if a  $D_v$  of 0.013 m<sup>2</sup>/s is assumed as shown in Figure 2. The oil concentration at depths can be calculated using equation 3, as also shown in Figure 2.

If we consider the fate of specific hydrocarbon classes as listed in Table 1, the dissolution, volatilization, and total half-lives will be as given in Table 2 for selected depths. The concentrations of these hydrocarbons can be calculated using equations 9, 10, and 11.

Table 2. Estimated half-lives and partitioning of hydrocarbons between air, water, and oil phases

Hydrocarbon	$\tau_s$ (0.15 mm) (s)	$\tau_p$	$CK_V$	Equilibrium percent in water	$\tau_v$ at 1 m (s)	$\tau_o$ at 1 m (s)	Percent remaining after 1,000, at 1 m depth		
							oil	water	air
Lower alkanes	4	30	0.2	83	6,900	8,310	15	76	8
Higher alkanes	840	1,500	10	9	6,900	77,400	96	3	1
Benzenes	134	6	0.04	96	7,000	7,286	4	87	9
Naphthalenes	25,000	60	0.4	71	9,000	12,660	27	67	5
Higher PNAs	$33 \times 10^6$	12,000	80	1.2	20,000	$1.6 \times 10^6$	99.9	0.07	0.04
Dispersant	$\infty$	0.01	$10^{-4}$	$\geq 99$	$\infty$	$\infty$	0	100	0

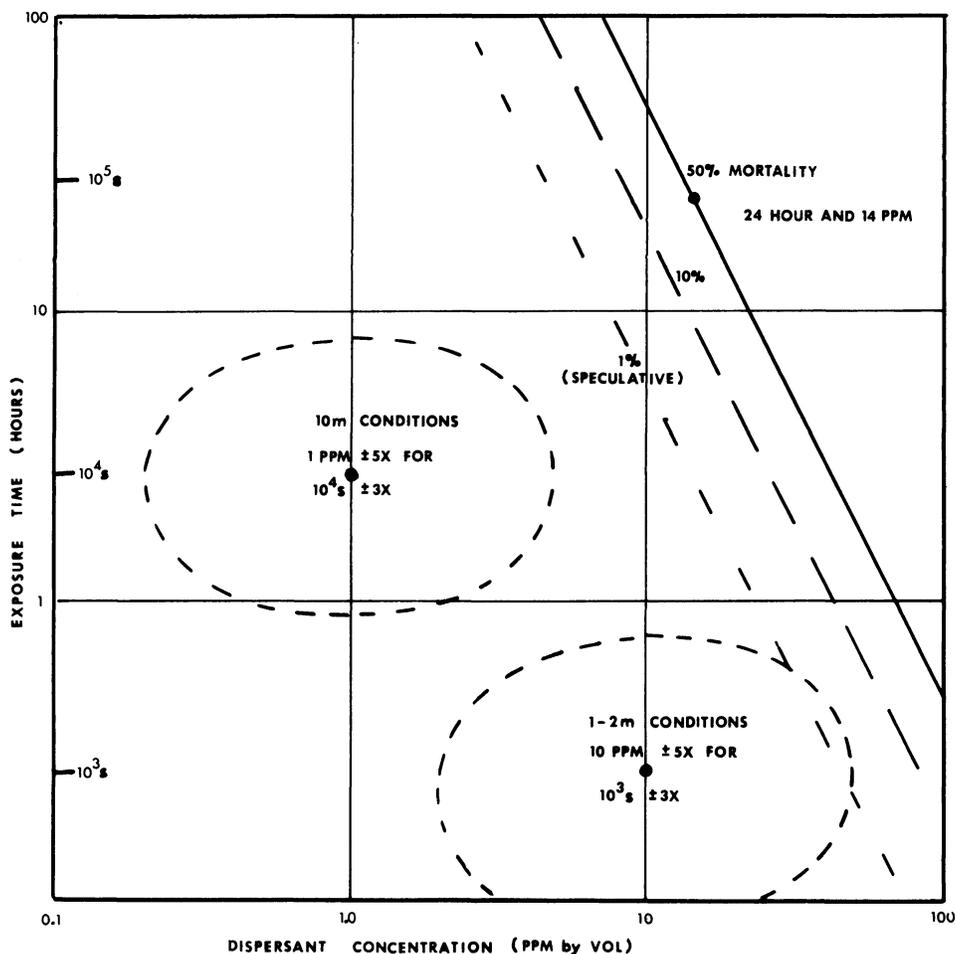


Figure 3. Illustrative toxicity plot of concentration of the dispersant Corexit 9527 versus time to median mortality for copepods (*Pseudocalanus minutus*) showing the relative location of spill exposure conditions

At a depth of 1 m the total oil concentration is an average of 20 ppm for approximately 1,000 s. At 3 m, the concentration pulse is approximately 5 ppm for 1000 s. An exposure of 10 ppm for 1,000 s is thus a reasonable figure for the top 3 m of water, but local exposures may vary above and below this figure by a factor of 5. Below 3 m, the corresponding exposure is 1 ppm for 10,000 s, plus or minus a factor of 5.

The fate of individual hydrocarbons can be estimated using the half life equations at a depth of 1 m and 10 ppm for 1000 s. Table 2 shows that dissolution is virtually instantaneous for dispersant (assuming a drop size of 5  $\mu\text{m}$ ) and is very fast for benzenes, naphthalenes, and lower alkanes. Higher alkanes and PNAs dissolve relatively slowly. The fraction which is dissolved at equilibrium ( $t = \infty$ ) is high for dispersant and benzenes, somewhat smaller for lower alkanes and naphthalenes, and very small for higher alkanes and PNAs. The volatilization half life is short for the alkanes and aromatics but longer for the others, especially the PNAs.

The overall half life in the water ( $\tau_o$ ) is very short for aromatics and lower alkanes because they are both volatile and water-soluble. The slick half-lives for these compounds are much shorter, thus most will be lost by volatilization prior to dispersion. Under certain conditions,  $\tau_s$  can exceed  $\tau_o$ , that is, volatilization from solution after dispersion will be faster than volatilization from the slick. This occurs when the slick thickness is large (say 1 mm) causing  $\tau_s$  to be large, the compound is very water-soluble (e.g., a benzene or naphthalene), and has a high Henry's Law constant. In Table 2 for example,  $\tau_s$  is longer than  $\tau_o$  for naphthalenes and it can be argued that chemical dispersion accelerates volatilization and thus reduces the potential for toxicity.

The percentage distributions in Table 2 illustrate the very different

behavior of the hydrocarbon classes. Lower alkanes will be lost mostly by evaporation from the slick, but those which are dispersed will tend to dissolve, then evaporate. Benzenes will behave similarly. Higher alkanes which are dispersed evaporate very slowly and tend to remain in the oil. Naphthalenes tend to partition 3:1, water to oil and evaporate only slowly. The PNAs remain in the oil. Dispersant dissolves almost totally in the water. From acute toxicity viewpoint the key compounds will probably be the benzenes and naphthalenes which can reach organisms by dissolution in water and partitioning into membranes.

It is thus possible to estimate the concentration-time behavior of each group and establish an exposure point or region on the toxicity diagram.

For example, if the dispersant quantity used was 10 percent of the oil, the concentrate would be approximately 1 ppm for 1000 s in the top 3 m. This point and the region (corresponding to a factor of 5 in concentration and 3 in time) is shown on Figure 3. The implication is that the dispersant will be responsible for <1 percent of the effect.

The experimental data obtained by McAuliffe *et al.*<sup>8</sup> are broadly consistent with these equations and half-lives. They observed that the lower alkanes were substantially depleted from the water samples. The benzenes also were substantially depleted, with there being a trend for the less volatile xylenes to be present in greater quantities. This suggests that slick evaporation was largely responsible, since water column volatilization would result in all benzenes being lost at equal rates because the overall rate is liquid phase diffusion controlled, not volatility controlled. Clearly, evaporation prior to or after dispersion can play an important mitigating role.<sup>8</sup>

Samples taken at 1 m depth, 18, 46, 72, and 110 minutes after

dispersion showed concentrations of 17.8, 3.8, 1.55, and 0.31 ppm. These points are plotted on Figure 2 and show the same general trend in which concentration drops rapidly and approximately in proportion to time.

The location of the spill exposure conditions for dispersant on the toxicity diagram (Figure 3) shows that the dispersant will have little acute toxic effect to the test organism. Similar diagrams should be prepared for the dispersed oil particles and the hydrocarbon groups (Table 1). This will permit the dominant source(s) of the toxic effects to be identified and quantified. This procedure could be repeated with different test organisms. Ultimately, when these relationships are expressed mathematically it becomes possible to compute the behavior of the entire set of processes, from dispersion to toxic effects.

## Conclusion

Equations have been proposed which potentially describe the entire set of processes at a dispersed slick: dispersant effectiveness, volatilization from the oil slick and from solution, diffusion in the water column (vertical and horizontal), oil-water partitioning kinetics and equilibria, and finally toxicity of the multiple toxicants present in the water column following dispersion.

We suggest that hydrocarbons be grouped for this analysis as in Table 1. The equations are consistent with the available data, but improvement is undoubtedly possible and is desirable. The contribution of this work is to establish the entire predictive framework in the expectation that experimental data will improve the component equations. It should be possible using such equations to identify the dominant sources of acute toxic effects in the laboratory and at sea, determine if more toxic and effective dispersants are acceptable, estimate the overall impact of dispersion using various dosages, oils, and dispersants, and suggest dispersion strategies which will remove oil from the sea surface and in which a full appreciation of the toxic effects on the water column biota is obtainable, thus enabling a subjective judgement of acceptability to be made.

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