# Processes controlling aqueous concentrations for riverine spills

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## Abstract

The aqueous concentrations of sparingly soluble compounds resulting from oil, fuel, or chemical spills onto rivers predicted by numerical spill models contain an inherent degree of uncertainty due to the inaccuracies, or bias, of the user supplied rate coefficients. Methods for estimating the values of spreading, evaporation, dissolution, volatilization, and longitudinal dispersion coefficients for a small sheltered river are reviewed, and the uncertainties associated with each coefficient are estimated. The uncertainties in the predicted aqueous concentrations are then computed using a concurrently developed riverine spill model for a simulated spill of 10,000 kg of jet fuel. The resulting aqueous concentrations were found to be most sensitive to the saturation concentrations and the dissolution rates, moderately sensitive to the evaporation rates and longitudinal dispersion coefficient, and nearly completely insensitive to the volatilization coefficient. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Riverine spills; Aqueous concentrations; Dissolution; JP-4 jet fuel

## 1. Introduction

Accidental releases of oils, fuels, and chemicals onto water bodies can be catastrophic events for the aquatic biota. Riverine spills can be particularly hazardous. Unlike spills onto oceans in which the water column is deep and is subjected to almost an infinite dilution, rivers are in comparison shallow, confined by the river bed and banks. Consequently, aqueous concentrations resulting from riverine spills can be several orders of magnitude higher than similar spills onto oceans.

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Spills of any sparingly soluble buoyant compound (grouped together and referred to generically as oil) initially form a slick on the water surface. The slick spreads across the water surface and drifts downstream as the various compounds in the slick evaporate and dissolve into the water column. To predict the impact of spills on the river biota, it is necessary to assess the concentration of compounds dissolved in the water column. Riverine spill models which simulate the processes that control the aqueous concentrations can be used to estimate the aqueous concentrations resulting from riverine spills. The predicted aqueous concentrations have an inherent level of uncertainty due to bias in the model input parameters. Since the user specified rate constants are seldom measured but are themselves often estimated from predictive relationships, these input parameters can often be in significant error. Depending upon the particular parameter, the uncertainty associated with each input parameter can range from a drastic to an insignificant impact on the predicted aqueous concentrations.

This paper presents the results of a series of model simulations of a JP-4 jet fuel spill described in detail in a companion paper [1]. The values of user supplied process rate constants and physical properties are varied one parameter at a time. The sensitivity of the model to changes in each parameter is then examined and inferences are drawn about which parameters and/or processes are the most important (i.e. which have the most influence over the aqueous concentrations).

## 2. Aqueous concentration model

The sensitivity analysis performed in this paper is conducted using an aqueous concentration model for riverine spills concurrently developed by the authors [1]. The model approximates the river as a series of completely mixed cells that are fixed in position, as shown in Fig. 1. The surface slick is approximated as a series of completely mixed cells that move across the water surface.

The slick is assumed to drift downstream at the velocity of the water surface, which is slightly greater than the mean velocity of the river [2]:

$$U_{\text{slick}} \approx 1.1\,U \tag{1}$$

where $U_{\text{slick}}$ is the streamwise velocity of the centroid of the slick and $U$ is the average
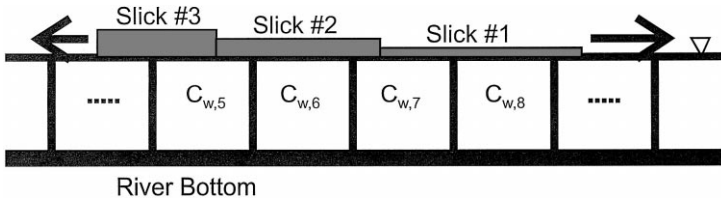


Fig. 1. Numerical approximation of the river and the surface slick.

streamwise velocity. The velocities of the leading and trailing edges of the slick are then calculated as:

$$U_{\text{leading}} = 1.1\, U + \frac{\mathrm{d}l}{\mathrm{d}t} \tag{2}$$

and

$$U_{\text{trailing}} = 1.1\, U - \frac{\mathrm{d}l}{\mathrm{d}t} \tag{3}$$

where $\mathrm{d}l/\mathrm{d}t$ is the spreading rate of the slick. The concentrations in the surface slicks are computed from a mass balance for each compound in each slick:

$$\frac{\mathrm{d}m}{\mathrm{d}t} = \int_{\substack{\text{length} \\ \text{of slick}}} \left[ -k_{\text{dis}} W \left( X_{\text{o}} C_{\text{w}}^{\text{sat}} - C_{\text{w}} \right) - k_{\text{evap}} W \left( \frac{X_0 P^{\circ} M_i}{RT} \right) \right] \mathrm{d}x + r \tag{4}$$

where $C_{\text{w}}$ is the aqueous concentration, $C_{\text{w}}^{\text{sat}}$ is the aqueous saturation concentration, $k_{\text{dis}}$ is the dissolution rate coefficient, $k_{\text{evap}}$ is evaporation rate coefficient for, $m$ is the mass of the compound in the slick, $M$ is the compound's molecular weight, $r$ is the release rate (i.e., rate at which the compound is spilled), $P^{\circ}$ is the vapor pressure of the pure compound, $R$ is the universal gas constant, $t$ is time, $T$ is the absolute temperature of the interface, $x$ is distance downstream, $X_{\text{o}}$ is the mole fraction in the slick, and $W$ is the width of the slick. This one dimensional model formulation assumes that a slick covers the water surface from bank to bank, therefore $W$ is also the width of the river. The concentration of each compound in the slick can then be expressed as a mole fraction:

$$X_0 = \frac{m(M)^{-1}}{\displaystyle\sum_{\substack{\text{all compounds}}} m(M)^{-1}} \tag{5}$$

The aqueous concentrations are computed from the one-dimensional advection–diffusion equation:

$$\frac{\partial(AC_{\text{w}})}{\partial t} + \frac{\partial(QC_{\text{w}})}{\partial x} = \frac{\partial}{\partial x}\left( AD_{\text{L}} \frac{\partial C_{\text{w}}}{\partial x} \right) + \phi\, k_{\text{dis}} W \left( X_0 C_{\text{w}}^{\text{sat}} - C_{\text{w}} \right)$$
$$- (1 - \phi)\, k_{\text{vol}} W C_{\text{w}} \tag{6}$$

where $A$ is the cross-sectional area of river, $D_{\text{L}}$ is the longitudinal dispersion coefficient, $Q$ is discharge, $k_{\text{vol}}$ is the volatilization rate coefficient, $\phi$ is a phase marker ($\phi = 1$ if there is a slick at location $x$; $\phi = 0$ otherwise).

## 3. Sensitivity analysis

In this section, we discuss what we believe to be the most applicable characterizations of the rate process parameters taken from the literature for small rivers which

Table 1
Input parameters used in sample application

| Properties | Toluene | Ethylbenzene | n-Butylbenzene | Tetralin | 1-Methyl-naphthalene | 1,4,-Dimethyl-naphthalene | Methyl-cyclohexane | Aliphatics[a] |
|---|---|---|---|---|---|---|---|---|
| $X$ (–)[b] | 0.04331 | 0.04785 | 0.03879 | 0.02922 | 0.02666 | 0.02613 | 0.2123 | 0.5759 |
| MW (g/mol) | 92.1 | 106.2 | 134.2 | 132.2 | 142.2 | 156.2 | 98.2 | 145.7 |
| $\rho$ (kg/m$^3$)[c] | 870 | 870 | 860 | 970 | 1002 | 1000 | 770 | 731 |
| $C_w^{sat}$ (mol/l)[c,d] | $10^{-2.50}$ | $10^{-2.80}$ | $10^{-3.97}$ | $10^{-3.47}$ | $10^{-3.67}$ | $10^{-4.22}$ | $10^{-3.77}$ | $10^{-6.52}$ |
| $P^o$ (atm)[c,e] | $10^{-1.42}$ | $10^{-1.90}$ | $10^{-2.86}$ | $10^{-3.27}$ | $10^{-4.07}$ | $10^{-4.60}$ | $10^{-1.23}$ | $10^{-2.77}$ |
| $D_{water}$ (m$^s$/s)[f] | $9.1 \times 10^{-10}$ | $8.2 \times 10^{-10}$ | $7.0 \times 10^{-10}$ | $7.6 \times 10^{-10}$ | $7.4 \times 10^{-10}$ | $6.8 \times 10^{-10}$ | $8.2 \times 10^{-10}$ | $6.2 \times 10^{-10}$ |
| $D_{oil}$ (m$^2$/s)[g] | $1.5 \times 10^{-9}$ | $1.4 \times 10^{-9}$ | $1.1 \times 10^{-9}$ | $1.2 \times 10^{-9}$ | $1.2 \times 10^{-9}$ | $1.1 \times 10^{-9}$ | $1.4 \times 10^{-9}$ | $1.0 \times 10^{-9}$ |
| $D_{air}$ (m$^2$/s)[h] | $8.1 \times 10^{-6}$ | $7.4 \times 10^{-6}$ | $6.4 \times 10^{-6}$ | $6.8 \times 10^{-6}$ | $6.6 \times 10^{-6}$ | $6.2 \times 10^{-6}$ | $7.7 \times 10^{-6}$ | $5.8 \times 10^{-6}$ |

*River properties*
$Q = 3$ (m$^3$/s)
$A = 10$ (m$^2$)
$W = 10$ (m)
$D_L = 25$ (m$^2$/s)
$U_{wind} = 2$ (m/s)
$k_{L\text{-}oxygen} = 2.47 \times 10^{-6}$ (m/s)
$T = 20°C$

*Rate constants*[i]
$k_{evap} = 5.27 \times 10^{-4}$ (m/s)
$k_{dis} = 1.50 \times 10^{-6}$ (m/s)
$k_{vol} = 1.20 \times 10^{-5}$ (m/s)

*Model parameters*
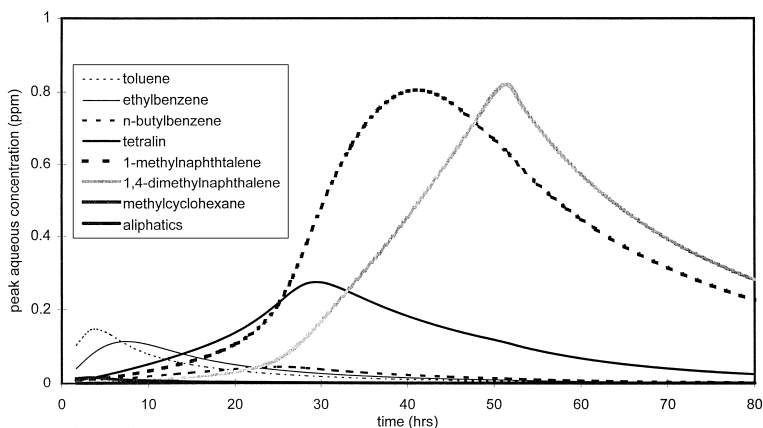$\Delta t = 60$ (s)
$\Delta x = 100$ (m)

Fig. 2. Results of jet fuel spill simulation: peak aqueous concentrations of compounds.

exhibit a fair degree of meandering and are often sheltered from the wind by the river banks and vegetation. Estimates of the uncertainty associated with each parameter are made. Finally, the sensitivity of the predicted aqueous concentrations to variations in the input parameters over their estimated range of uncertainty is presented.

The sensitivity analysis is performed on a hypothetical spill of 10 000 kg of a JP-4 jet fuel. The assumed flow characteristics and environmental conditions, as well as the composition and physical characteristics of the spilled fuel are listed in Table 1. The peak aqueous concentrations resulting from the spill are shown in Fig. 2. A more thorough analysis of the spill is presented by Hibbs et al. [1]. The estimated uncertainties in the user supplied parameters and the resulting variations in the highest aqueous concentrations are summarized in Table 2.

## 3.1. Longitudinal dispersion

Longitudinal dispersion accounts for the dilution of the cross-sectional average concentration of compounds dissolved in the water due to mixing in the streamwise

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Notes to Table 1:

[a] Average properties of the five aliphatic compounds in JP-4 fuel, Burris and MacIntyre [28].

[b] Burris and MacIntyre [28].

[c] Lide [29].

[d] Schwarzenbach et al. [23].

[e] Lyman et al. [24].

[f] Approximated using the method of Hayduk and Ladie [30].

[g] Approximated using the method of Wilke and Chang [31].

[h] Approximated using the method of Fuller et al. [32].

[i] Approximate values. Actual values determined for each compound based on wind speed, reaeration rate, and physical properties of individual compounds.

Table 2
Summary of sensitivity analysis

| User supplied parameter | Approximate uncertainty of input parameter | Resulting range of maximum aqueous concentration |
|---|---|---|
| $D_L$ | $\pm$ factor of 4 | $\pm$ 30% |
| $k_{evap}$ | $\pm$ factor of 4 | $\pm$ 50% |
| $k_{vol}$ | $\pm$ factor of 3 | $\pm$ 5% |
| $k_{dis}$ | $\pm$ factor of 20 | $\pm$ 2000% |
| $C_w^{sat}$ | $\pm$ factor of 3 | $\pm$ 300% |
| $dl/dt$ | $\pm$ factor of 2 | $\pm$ 10% |

Confidence interval of input parameters and resulting range of maximum aqueous concentrations are relative to the original values.

direction. The longitudinal dispersion coefficient, $D_L$, can be estimated as [3]:

$$D_L = \frac{0.011\, U^2 W^2}{h\,\sqrt{ghS}} \tag{7}$$

where $h$ is the average depth of river, $g$ is acceleration due to gravity, and $S$ is the slope of the water surface.

Fischer et al. [3] list numerous predictive equations for longitudinal dispersion, and perhaps not inconsequentially, estimates of $D_L$ from stream parameters are notoriously inaccurate. Fischer et al. state that the recommended relationship, i.e., Eq. (7), will generally predict $D_L$ only within a factor of four.

Fig. 3 shows the highest aqueous concentrations of four compounds that occur during the duration of the JP-4 jet fuel spill simulation, using the same parameters listed in Table 1. The highest aqueous concentrations are plotted as a function of $D_L$ over the range of uncertainty of the predicted value (i.e., from approximately 25% to 400% of the original value of $D_L = 25$ m$^2$/s). Higher values of $D_L$ tend to dilute the dissolved
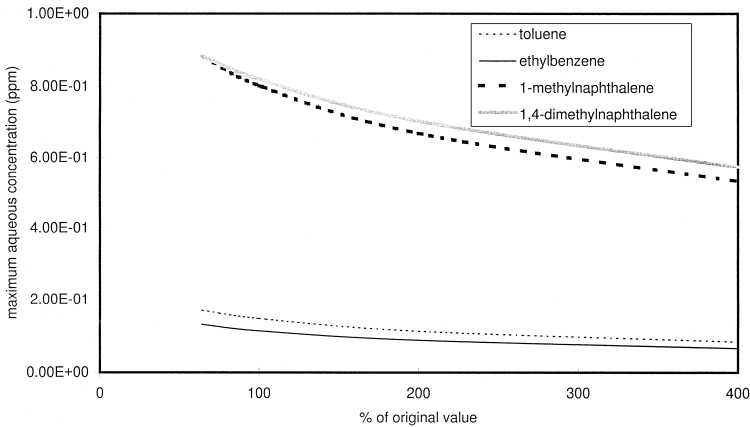


Fig. 3. Sensitivity analysis: effect of longitudinal dispersion on maximum aqueous concentration.

compounds in the streamwise direction, yielding lower maximum aqueous concentrations. Lower values of $D_L$ correspond to less dilution, and therefore higher aqueous concentrations. The maximum aqueous concentration of both the soluble/volatile compounds (toluene and ethylbenzene) and the relatively insoluble/nonvolatile compounds (1-methylnaphthalene and 1,4-dimethylnaphthalene) vary by approximately 30% from the high end value of $D_L$ to the low end. Therefore, longitudinal dispersion is a fairly significant process, and whenever possible, the value of $D_L$ should be measured by performing a dye study [3] on a river reach. Dye study measurements can also be used to precisely determine the value of $U$ [4].

## 3.2. Evaporation rate

Evaporation is generally described by a resistance in series model, commonly used to describe mass-transfer between phases. The overall transfer coefficient depends on the rate transfer coefficients on either side of the interface:

$$\frac{1}{k_{evap}} = \frac{P^\circ M_i}{k_{oa} RT\rho_o} + \frac{1}{k_G} \tag{8}$$

where $k_{oa}$ is the oil–film transfer coefficient at the oil–air interface, $k_G$ is the gas–film transfer coefficient, and $\rho_o$ is the density of the oil. For thick oil layers, the oil–film transport coefficient controls the evaporation of hydrocarbons due to their relatively high vapor pressures [5]. However, in most riverine spills the oil layer is so thin ($< 1$ mm) that the resistance to transfer in the oil–film is small, even if transport is assumed to be only by molecular diffusion, and $k_{evap}$ can be approximated by $k_G$ [6].

The gas-side mass transfer coefficient for compound $i$ can be estimated from the wind function coefficient by Ryan et al. [7] which relates evaporative heat flux to a vapor pressure difference:

$$k_G = f(w_z) b \left( \frac{Sc_i}{Sc_{water}} \right)^{-0.67} \tag{9}$$

where $k_G$ is the gas-side mass transfer coefficient for compound $i$ (m/s), $f(w_z)$ is the wind function (cal/cm$^2$ day mb), and $b$ is a coefficient relating the evaporative heat loss of water to the evaporative mass loss of water ($b = 2.67 \times 10^{-4}$ cm$^2$ day mb m/cal s). $b$ is a function of temperature and latent heat of vaporization of water, but is nearly constant for the range of temperatures typically seen in rivers. $Sc_{water}$ is the Schmidt number of water in air ($Sc_{water} = \nu/D$, where $\nu$ is kinematic viscosity of air and $D$ is diffusivity of water in air), and $Sc_i$ is the Schmidt number of compound $i$ in air. The ratio of Schmidt numbers in Eq. (9) converts the gas-side mass transfer coefficient for water vapor to an equivalent coefficient for compound $i$. The $-0.67$ power on the ratio of diffusivities has been used by several investigators including Mackay and Yeun [8], Mackay and Matsugu [9] and Goodwin et al. [10]. The function $f(w_z)$ is used to describe the influence of wind and waves on evaporation. The only

known experiments to characterize the wind function in a sheltered stream resulted in the following relationship by Gulliver and Stefan [11]:

$$f(w_z) = 3.21\, U_9 + 5.52(\Delta\theta)^{1/3} \tag{10}$$

where $U_9$ is the wind speed at a height of 9 m (m/s), and $\Delta\theta$ is the virtual temperature difference between the water surface and the air at a height of 2 m (°C).

Many existing spill models use a relationship for $k_G$ developed by Mackay and Matsugu [9] from pan evaporation and wind tunnels experiments. Values of $k_G$ used in this analysis are based on measurements taken in sheltered streams, and are typically 2 to 5 times lower than those for spills in open areas determined by Mackay and Matsugu. Regardless of the relationship used to predict the value of $k_G$, there is likely a large uncertainty due to its dependence on the local turbulence. Under similar wind velocities at a height of 10 m, the wind velocity profile over open water may be significantly different than the velocity profile over a river due to the topography and the vegetation on the river banks. Even on open lakes, the measured evaporation transfer coefficient can vary as much as $\pm 100\%$ for a given wind speed [12]. Thus, evaporation is a complicated and site-specific process. The confidence interval of the predicted evaporation-rate constant for rivers is estimated to be on the order of $\pm$ a factor of 4. The confidence interval for the value of $k_G$ is likely smaller for wide rivers in areas without significant vegetation or changes in topography.

Fig. 4 shows the highest aqueous concentrations of four compounds resulting from a series of JP-4 jet fuel spill simulations over the anticipated range of uncertainty in $k_G$. The maximum aqueous concentrations range from 130% to 60% of their original value as the value of $k_G$ is varied from 50% to 400% of its original value. The value of $k_G$ indirectly affects the aqueous concentrations by forcing changes in the composition of the slick. At low values of $k_G$, the compounds evaporate more slowly and remain in the slick for a longer time. In the slick they continue to dissolve, increasing the aqueous
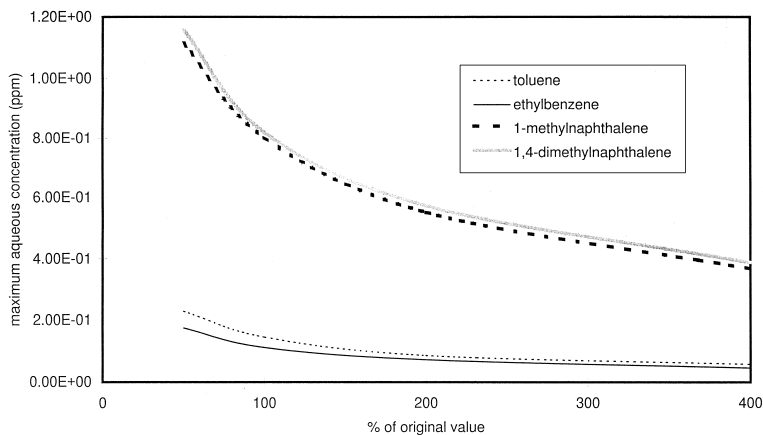


Fig. 4. Sensitivity analysis: effect of variations in evaporation rate on maximum aqueous concentration.

concentration. At high values of $k_G$, the compounds evaporate more quickly and are available to dissolve for less time, creating lower aqueous concentrations.

## 3.3. Volatilization rate

Volatilization is also generally described by a two-resistance model:

$$\frac{1}{k_{\text{vol}}} = \frac{1}{k_L} + \frac{RT}{Hk_G} \tag{11}$$

where $k_L$ is the liquid-side mass transfer coefficient for compound $i$, and $k_G$ is determined from Eq. (9). Values of $k_L$ used in the model are adapted from the stream reaeration coefficient of Cadwallader and McDonnell [13]:

$$k_{L\,\text{oxygen}} = 2.15 \times 10^{-3} (SU)^{0.5} \tag{12}$$

where $k_{L\,\text{oxygen}}$ is the liquid mass transfer coefficient for oxygen at 20°C (m/s), $S$ is the average slope of river, and $U$ is the average streamwise velocity (m/s). Several empirical relationships for reaeration coefficients were recently reviewed and tested by Moog and Jirka [14] who found that the form of the relationship given in Eq. (12) best characterized stream reaeration rates. A liquid mass transfer coefficient for each compound, $k_{li}$, can then be determined from a ratio of the Schmidt numbers [8]:

$$k_{L\,i} = k_{L\,\text{oxygen}} \left( \frac{\text{Sc}_i}{\text{Sc}_{\text{oxygen}}} \right)^{-0.5} \tag{13}$$

where $\text{Sc}_{\text{oxygen}} = \nu_{20}/D_{\text{oxygen}}$, $\text{Sc}_i = \nu/D_i$, $\nu$ is the kinematic viscosity of water at the modeled temperature, $\nu_{20}$ is the kinematic viscosity of water at 20°C, $D_{\text{oxygen}}$ is the diffusivity of oxygen in water and $D_i$ is the diffusivity of component $i$ in water.

Estimates of volatilization rates from stream parameters are also notoriously inaccurate. Moog and Jirka [14] found that even the best empirical relationships have a 95% confidence interval of greater than a factor of three. Values of $k_{\text{vol}}$ for a given river reach can be measured by conducting a gas tracer study when greater accuracy is desired [15,16].

Fig. 5 shows the highest aqueous concentrations resulting from a series of JP-4 jet fuel spill simulations over the anticipated range of uncertainty in the value of $k_{\text{vol}}$. The highest aqueous concentrations of all the compounds are essentially unaffected by variations in the value of $k_{\text{vol}}$ from 50% to 300% of its original value. The insensitivity of the aqueous concentrations to variations in $k_{\text{vol}}$ can be explained by examining the mass balance of the compounds dissolved in the water. From Eq. (6), the aqueous concentration of a compound is a function of both the dissolution flux rate and the volatilization flux rate. Even though the value of $k_{\text{vol}}$ is typically of the same order as $k_{\text{dis}}$, or larger, the concentration difference driving the mass transfer is usually much larger for dissolution than it is for volatilization. Due to the extremely low concentrations of most compounds dissolved the water after a spill, the volatilization flux is
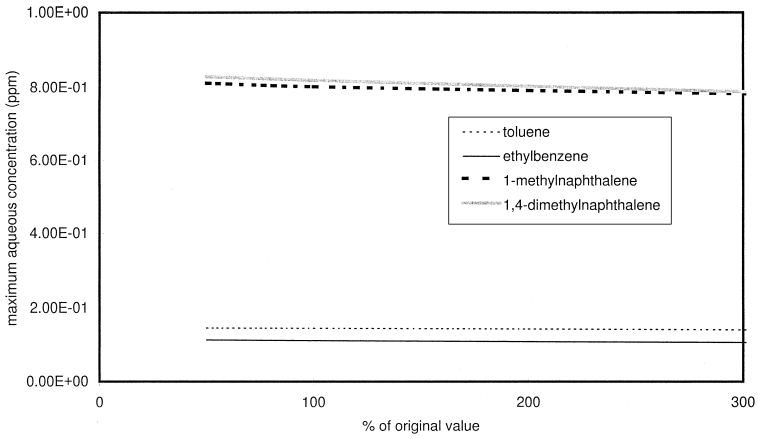
Fig. 5. Sensitivity analysis: effect of variations in volatilization rate on maximum aqueous concentration.

typically very small and the aqueous concentrations are fairly insensitive to variations in the volatilization rate.

### 3.4. Dissolution rate

Similar to evaporation and volatilization, dissolution is also commonly described by a two-resistance model:

$$\frac{1}{k_{\text{dis}}} = \frac{1}{k_w} + \frac{C_w^{\text{sat}} M_o}{k_o \rho_o} \tag{14}$$

where $k_w$ is the water film transfer coefficient, $k_o$ is the oil (slick) film transfer coefficient, $\rho_o$ is the density of the slick, and $M_o$ is the average molecular weight of the slick. In most instances, the resistance to transfer in the oil film can be ignored due to the small value of $C_w^{\text{sat}}$ for most hydrocarbons, such that $k_{\text{dis}} \approx k_w$. Values of $k_o$ and $k_w$ can be estimated from reaeration rates. Cohen et al. [17,18] measured dissolution rates of phenol from a surface slick and volatilization rates of benzene from the water to the atmosphere in a wind tunnel at wind speeds of 0 to 9 m/s. The measured water–film volatilization rate coefficients of benzene, $k_{L\text{ benzene}}$, were found to be roughly 8 times the water–film dissolution rate coefficients for phenol, $k_{w\text{ phenol}}$, at all but the highest wind speeds when it was thought that the oil slick had a significant dampening effect on the turbulence at the oil–water interface:

$$k_{L\text{ benzene}} = 8\, k_{w\text{ phenol}} \tag{15}$$

Since the molecular diffusivities of phenol and benzene in water are similar, the rate coefficients for phenol and benzene are nearly interchangeable:

$$k_{L\text{ benzene}} = 8\, k_{w\text{ benzene}} \tag{16}$$

Values of $k_w$ can then be estimated from values of $k_{L\,oxygen}$ by accounting for the differences in molecular diffusivities between benzene and oxygen using Eq. (13):

$$k_{w\,benzene} = \frac{k_{L\,oxygen}}{8} \left( \frac{Sc_{benzene}}{Sc_{oxygen}} \right)^{-0.5} \tag{17}$$

More generally, the water–film dissolution rate coefficient for any compound, $i$, can be estimated from the reaeration rate coefficient, again by correcting for the differences in molecular diffusivities:

$$k_{w\,i} = \frac{k_{L\,oxygen}}{8} \left( \frac{Sc_i}{Sc_{oxygen}} \right)^{-0.5} \tag{18}$$

Cohen et al. [17,18] also found the measured water–film volatilization rate coefficients of benzene to be roughly 20 times the measured water–film dissolution rate coefficients for phenol. Similarly, the oil–film dissolution rate coefficient for any compound, $i$, can be estimated as:

$$k_{o\,i} = \frac{k_{L\,oxygen}}{20} \left( \frac{Sc_i}{Sc_{oxygen}} \right)^{-0.5} \tag{19}$$

Values of $k_{L\,oxygen}$ can be obtained indirectly from stream parameters using Eq. (12), or more directly from volatilization measurements by conducting a gas tracer study [15,16].

Southworth et al. [19] related the water film dissolution coefficient to the aeration coefficient from studies in a stirred beaker:

$$k_{dis} = \alpha k_{L\,oxygen} + \beta \tag{20}$$

where $\alpha$ and $\beta$ are empirical coefficients ($\alpha \cong 0.5$ to $1.0$ and $\beta \cong 0$ to $0.5$, depending on the compound.)

The laboratory results of Southworth et al. are much different than the results of Cohen et al., thus there is no definitive relationship to use in the estimation of $k_{dis}$. Additionally, there are no known field studies from which to estimate the uncertainty in the value of $k_{dis}$ on rivers. Many existing oil spill models assume constant values for the film coefficients even though Lamont and Scott [20] have shown that the values of the individual film coefficients depend on the level of turbulence on either side of the oil–water interface. Shen and Yapa [21] used $k_{dis} = 1.0$ cm/h for all applications in their riverine oil spill model. Herbes and Yeh [22] used values of $k_o = 0.5$ cm/h and $k_w = 2.0$ cm/h for navigable rivers, which, for most compounds, gives $k_{dis} \cong 2.0$ cm/h. The relationships used in this analysis are based on laboratory experiments relating $k_{dis}$ to $k_{vol}$, but the dependence of $k_{dis}$ on $k_{vol}$ varies by more than a factor of eight. And as previously mentioned, predictive relationships for reaeration coefficients are usually only accurate to within a factor of three. Therefore, the overall uncertainty in the estimation of $k_{dis}$ is a factor of three times a factor of eight, or roughly a whopping factor of 20 to 30. In short, for a given application, modellers currently have almost no idea what the actual value of a dissolution rate coefficient is.

Fig. 6 shows the highest aqueous concentration resulting from a series of JP-4 jet fuel spill simulations with the value of $k_{dis}$ varied from 50% to 300% of its original value.
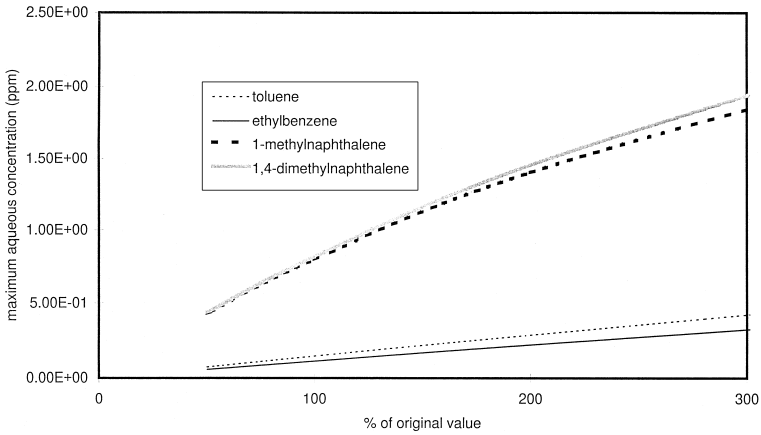
Fig. 6. Sensitivity analysis: effect of variations in dissolution rate on maximum aqueous concentration.

The slopes of the lines in Fig. 6 are nearly 1:1. Thus, over the estimated range of uncertainty in the value of $k_{dis}$, the maximum aqueous concentrations range can be expected to range from roughly 5% to 2000% of their original values, or over several orders of magnitude. This presents a serious problem for spill modellers. Not only are the aqueous concentrations of all compounds extremely sensitive to variations in the value of $k_{dis}$, but the value of $k_{dis}$ is very difficult to estimate.

### 3.5. Saturation concentration

Measured values of the aqueous solubility of pure compounds are available in the literature for most hydrocarbons of interest in the environment [23]. However, solubilities of compounds not available in the literature must be estimated. Depending on the compound, empirical relationships based on molecular structure can predict the aqueous solubility within ±25% to ±300% [24]. Additionally, for mixtures of structurally dissimilar compounds, Burris and MacIntyre [25] have shown that the aqueous solubilities can be 1.5 to 2.5 times higher due to increased activities in the hydrocarbon phase. In this analysis, the uncertainty in $C_w^{sat}$ is assumed to be ±a factor of three.

Fig. 7 shows the highest aqueous concentrations resulting from a series of JP-4 jet fuel spill simulations over the anticipated range of uncertainty in the values of $C_w^{sat}$. The slopes of the lines in Fig. 7 are nearly 1:1. As the values of $C_w^{sat}$ are varied from 50% to 300% of the original values, the resulting maximum aqueous concentrations range from roughly 50% to 300% of their original values. Thus, the aqueous concentrations of all compounds are extremely sensitive to variations in the saturation concentration.

### 3.6. Slick spreading velocity

Oils spread across a water surface due to density and surface tension differences between the slick and the water. Spreading is resisted by inertial and viscous forces.
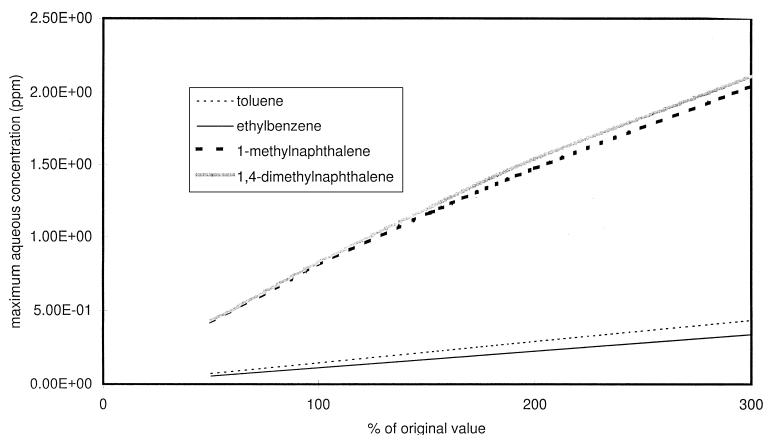
Fig. 7. Sensitivity analysis: effect of variations in saturation concentration on maximum aqueous concentration.

Except during the initial minutes following an extremely large spill, the extent of the slick due to spreading can be determined by the larger of an expression equating the surface tension and viscous forces [26]:

$$l = k_{lt}\left(\sigma^2 t^3 / \rho^2 \nu\right)^{0.25} \tag{21}$$

or an expression equating the gravitational and viscous forces [26]:

$$l = k_{lv}\left(\Delta g V^2 t^{1.5} / \nu^{0.5}\right)^{0.25} \tag{22}$$

where $l$ is the length of slick resulting from spreading in one direction, $k_{lt}$ is the spreading law coefficient for surface tension spreading ($k_{lt} = 1.33$ [27]), $k_{lv}$ is the spreading law coefficient for viscous spreading ($k_{lv} = 1.5$ [26]), $\sigma$ is the net surface tension ($\sigma = \sigma_{air-oil} + \sigma_{oil-water} - \sigma_{air-water}$), $\rho$ is the density of water, $\nu$ is the kinematic viscosity of water, $\Delta$ is the ratio of density difference between water and oil to density of water, $g$ is gravity, $t$ is time, and $V$ is the volume of slick per unit length normal to the direction of spreading (per unit width of the river).

Eqs. (21) and (22) were developed for constant volume, constant surface tension, and low viscosity spills on calm water. The effects of wind and currents on spreading rates is not well studied and is difficult to estimate. Therefore, the quantifiable uncertainty in the spreading rate lies in the estimation of the parameters used in Eqs. (21) and (22). The transition from a viscous spread (i.e. Eq. (22)) to a surface tension spread (i.e. Eq. (21)) occurs rapidly for most spills. Thus, the majority of the time the slick is present, the spreading rate is described by Eq. (21). Since the density and viscosity of water can be estimated fairly confidently, the majority of the uncertainty in the spreading rate likely lies in the estimation of the net surface tension, specifically, in the estimation of the air–oil surface tension and the oil–water surface tension.

There are two sources of uncertainty in estimating an interfacial surface tension for an oil slick. First, there can be a substantial error in estimating the initial value of the
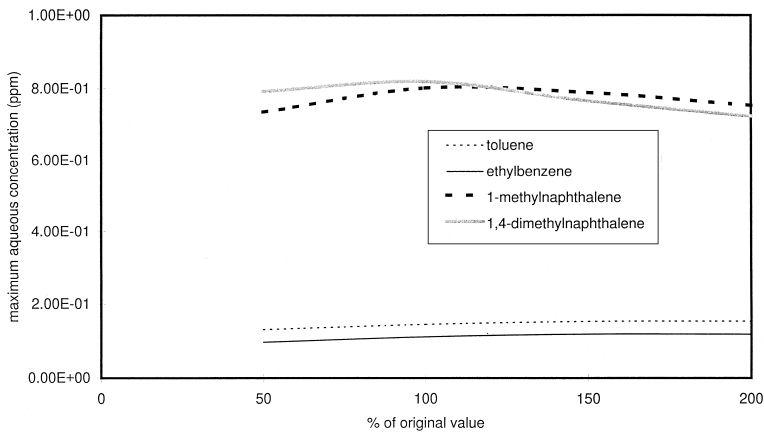
Fig. 8. Sensitivity analysis: effect of variations in spreading rate on maximum aqueous concentration.

surface tension. For most organic compounds, the air–oil surface tension can be predicted within ±20%, and the oil–water surface tension can be predicted within ±50% [24]. Second, the surface tension of a slick changes over time as the more volatile and more soluble compounds selectively evaporate and dissolve from the slick. However, the range of surface tensions for most organic compounds is fairly narrow. Values for the air–oil surface tension for most organics range from approximately 0.02–0.04 N/m, and for oil–water surface tension from approximately 0.020–0.035 N/m [24]. Therefore, it is estimated that the uncertainty in the interfacial surface tension, and also in the overall spreading rate, is roughly a factor of two.

Fig. 8 shows the highest aqueous concentrations resulting from a series of JP-4 jet fuel spill simulations over the anticipated range of uncertainty in the values of the spreading rate. Over the range of spreading rates simulated, the highest aqueous concentrations of all compounds are fairly insensitive to the spreading rates. Variations in the spreading rate ranging from 50% to 200% of its original value produce changes in the maximum aqueous concentration ranging from 90% to 110% of their original values. Higher spreading rates create a larger slick and more surface area for both dissolution and evaporation. A large rate of evaporation would tend to produce lower aqueous concentrations since the slick would be on the water surface for a shorter time. However, a larger dissolution rate would tend to produce higher aqueous concentrations. Perhaps the effect of slick size on dissolution and evaporation counteract each other, producing little net change in the highest aqueous concentration due to variations in the spreading rate.

## 4. Conclusions

The sensitivity of the aqueous concentrations to various parameters that control the aqueous concentration is particularly important in the modeling of riverine spills, where the water column is relatively shallow and high aqueous concentrations of many

contaminants are often seen. The aqueous concentrations of sparingly soluble compounds resulting from spills of hydrocarbons into rivers were found to be most sensitive to the values of the aqueous saturation concentrations and the dissolution rate coefficients, as shown in Table 2. Other parameters that control the aqueous concentration (in decreasing order of importance) are the evaporation rate coefficient, longitudinal dispersion coefficient, spreading rate of the slick, and volatilization rate coefficient. Not only is the dissolution rate coefficient one of the most important parameters for predicting the aqueous concentration, but conflicting studies of the dissolution rate coefficient lead to an extremely high uncertainty in the values the dissolution coefficient used in riverine spill models. Consequently, precise estimates of the aqueous concentrations resulting from riverine spills are impossible to obtain, and further investigation of the dissolution rate coefficient is needed.

## 5. Nomenclature

| | |
|---|---|
| $A$ | Cross-sectional area of river |
| $b$ | Coefficient relating the evaporative heat loss of water to the evaporative mass loss of water |
| $C_w$ | Aqueous concentration |
| $C_w^{sat}$ | Aqueous saturation concentration |
| $D_i$ | Diffusivity of compound $i$ in water |
| $D_L$ | Longitudinal dispersion coefficient |
| $f(w_z)$ | Wind function |
| $g$ | Acceleration due to gravity |
| $h$ | Average depth of river |
| $H$ | Henry's Law coefficient |
| $k_{dis}$ | Dissolution rate coefficient |
| $k_{evap}$ | Evaporation rate coefficient |
| $k_G$ | Gas–film transfer coefficient |
| $k_L$ | Liquid–film transfer coefficient |
| $k_{oa}$ | Oil–film transfer coefficient at the oil–air interface |
| $k_o$ | Oil–film transfer coefficient at the oil–water interface |
| $k_{vol}$ | Volatilization rate coefficient |
| $k_w$ | Water–film transfer coefficient |
| $k_{li}$ | Spreading law coefficient for surface tension spreading |
| $k_{lv}$ | Spreading law coefficient for viscous spreading |
| $l$ | Length of surface slick |
| $m$ | Mass of compound $i$ in the slick |
| $M$ | Molecular weight of compound $i$ |
| $M_o$ | Average molecular weight of oil |
| $P^o$ | Vapor pressure |
| $Q$ | Discharge in river |
| $r$ | Release rate of compound |
| $R$ | Universal gas constant |

| $S$ | Slope of the water surface |
| Sc | Schmidt number |
| $T$ | Temperature |
| $t$ | Time |
| $U$ | Mean river velocity |
| $U_{slick}$ | Streamwise velocity of centroid of slick |
| $U_{leading}$ | Streamwise velocity of leading edge of slick |
| $U_{trailing}$ | Streamwise velocity of trailing edge of slick |
| $U_9$ | Wind speed at 9 m height |
| $V$ | Volume of slick per unit length normal to $x$ |
| $W$ | Width of slick and width of river |
| $x$ | Distance downstream |
| $X_o$ | Mole fraction of compound in the slick |
| $\alpha$ | Empirical coefficient |
| $\beta$ | Empirical coefficient |
| $\Delta\theta$ | Virtual temperature difference between the air and water surface and the air at a height of 2 m |
| $\phi$ | Phase marker indicating the presence of a slick |
| $\Delta$ | Ratio of density difference between water and oil to density of water |
| $\rho$ | Density of water |
| $\rho_o$ | Density of oil |
| $\sigma$ | Net surface tension |
| $\nu$ | Kinematic viscosity |

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