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# An aqueous concentration model for riverine spills

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## Abstract

A numerical model is developed to predict the aqueous concentrations of sparingly soluble compounds resulting from oil, fuel, or chemical spills onto rivers. The model computes the concentration of compounds both in the slick phase and in the aqueous phase by simulating the processes that affect the fate of the spilled compound. Processes simulated by the model include spreading and drifting of the surface slick, evaporation from the slick, dissolution from the slick into the water, volatilization from the water, and longitudinal dispersion in the river. The model is used to simulate a hypothetical spill of jet fuel, demonstrating that the concentration of a compound in the aqueous phase is strongly linked to its concentration in the slick phase. The most soluble and most volatile compounds exhibit the highest aqueous concentrations in the early stages of the spill, but ultimately the less soluble and less volatile compounds reach the highest aqueous concentrations. Streamwise concentration gradients in the slick due to the rapid evaporation of the more volatile compounds are shown to have an effect on the aqueous concentration. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Riverine spills; Evaporation; Aqueous phase

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## 1. Introduction

Accidental releases of oils, fuels, and chemicals into rivers can be catastrophic events for the river biota. Spills of any sparingly soluble buoyant compound (grouped together and referred to generically as oil) will initially form a slick on the water surface. The

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slick spreads across the water surface and drifts downstream as the various compounds in the slick evaporate and dissolve into the water column. Most of the compounds are typically lost from the slick through evaporation, due to the low solubility of most hydrocarbons. However, it is the small concentration of compounds that dissolve in the water that is particularly hazardous to the river biota. Fish absorb toxins by gill-water contact and by ingestion of tainted food from lower trophic levels. Exposure to even low levels of many dissolved compounds can be toxic. Therefore, assessing the concentration of compounds dissolved in the water column is necessary to predict the impact of spills on the river biota.

Several riverine spill models reviewed by Yapa and Shen [1] compute the position and extent of the surface slick, but do not compute the concentrations of the individual compounds dissolved in the water column. Other riverine spill models assume that the spilled product is completely soluble and compute the downstream propagation of the contaminant pulse in the water [2–4]. Since the aqueous concentration is largely controlled by the concentration in the overlying slick, the composition of both the slick and the water need to be computed when a slick forms and the aqueous concentrations are of interest. To our knowledge, the only other riverine spill model that uses the composition of the slick to compute the aqueous concentration is that of Herbes and Yeh [5].

The riverine spill model developed herein improves on the model of Herbes and Yeh by adding volatilization to the list of processes modeled. Additionally, unlike Herbes and Yeh's model, which treats the slick as a single compartment, the slick in this model is treated as a series of control volumes on the water surface, each with its own composition. The model is one-dimensional, and it therefore assumes a well-mixed cross-section. Cross-sectional concentration gradients often seen in wide, poorly-mixed rivers cannot be accounted for using this model. Additionally, this model assumes the spilled product is either dissolved in the water column or floating on the water surface in the form of a slick. The model does not account for the breakup or entrainment of small droplets of the slick that may occur if the slick passes over a spillway, or is subjected to strong wind waves. The model was developed primarily for application to smaller, non-navigable rivers where the assumptions of a cross-sectionally well mixed water body are usually valid. The rate coefficients used in an example spill later in this paper, and discussed in detail a companion paper [6], are most applicable for smaller rivers which exhibit a fair degree of meandering and are often sheltered from wind by the river banks and vegetation.

## **2. Model development**

The model is established on an Eulerian coordinate system. The river is approximated as a series of completely mixed cells (typically 10–1000 m in length) fixed in position, as shown in Fig. 1. The slick is approximated as a series of completely mixed cells that move across the water surface. This treatment of the slick as a series of cells allows for spatial variation in the concentration of the slick.

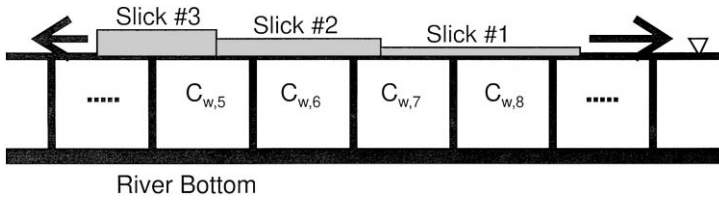


Fig. 1. Numerical approximation of river cross-section with multiple surface slicks.

### 2.1. Movement of the surface slick

The movement of the slick on the water is largely a function of the velocity of the water surface and the direction and magnitude of the wind:

$$U_{\text{slick}} = \alpha_{\text{vel}} U + \alpha_{\text{drift}} U_{\text{wind}} \quad (1)$$

where  $U_{\text{slick}}$  is the streamwise velocity of the centroid of the slick, and  $U$  is the average streamwise velocity,  $U_{\text{wind}}$  is the streamwise component of the wind speed vector,  $\alpha_{\text{vel}}$  is the velocity profile correction factor ( $\alpha_{\text{vel}} \cong 1.1$ , Ref. [7]), and  $\alpha_{\text{drift}}$  is the wind drift coefficient ( $\alpha_{\text{drift}} \cong 0.03\text{--}0.04$ , Ref. [8]). For smaller rivers which are often tortuous and sheltered, the wind drift term in Eq. (1) is dropped, and the velocities of the leading and trailing edges of the slick are:

$$U_{\text{leading}} = 1.1 U + \frac{dl}{dt} \quad (2)$$

and

$$U_{\text{trailing}} = 1.1 U - \frac{dl}{dt} \quad (3)$$

where  $dl/dt$  is the spreading rate of the slick. While the oil is spilling onto the water surface, the leading edge of the slick is allowed to drift and spread downstream at a velocity determined from Eq. (2) and the trailing edge of the slick is assumed to be fixed in position. The oil is added to the trailing end of the overall slick, i.e. into the upstream-most individual slick. This treatment of the spilling process reasonably simulates the behavior of a slick forming on a river. During the early stages of a riverine spill,  $dl/dt$  is on the order 0.1 m/s. Thus, the spreading velocity is less than typical water surface velocities, and the slick is not likely to spread upstream from the point of spilling. Once the spilling stops, the trailing edge of the slick is released to drift and spread at a velocity determined from Eq. (3). The position of the leading and trailing edges of the overall slick are determined from Eqs. (2) and (3) and the boundaries of the individual slicks are interpolated from the spreading rate of the leading edges based on their distance from the midpoint of the overall slick.

Table 1  
Input parameters used in sample application

Properties	Toluene	Ethyl- benzene	<i>n</i> -Butyl- benzene	Tetralin	1-Methyl- naphthalene	1,4,-Dimethyl- naphthalene	Methylcyclo- hexane	Aliphatics <sup>h</sup>
$X^a$	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 <sup>3</sup> ) <sup>b</sup>	870	870	860	970	1002	1000	770	731
$C_w^{\text{sat}}$ (mol/l) <sup>b,c</sup>	$10^{-2.50}$	$10^{-2.80}$	$10^{-3.97}$	$10^{-3.47}$	$10^{-3.67}$	$10^{-4.22}$	$10^{-3.77}$	$10^{-6.52}$
$P^o$ (atm) <sup>b,d</sup>	$10^{-1.42}$	$10^{-1.90}$	$10^{-2.86}$	$10^{-3.27}$	$10^{-4.07}$	$10^{-4.60}$	$10^{-1.23}$	$10^{-2.77}$
$D_{\text{water}}$ (m <sup>2</sup> /s) <sup>e</sup>	$9.1 \times 10^{-10}$	$8.2 \times 10^{-10}$	$7.0 \times 10^{-10}$	$7.6 \times 10^{-10}$	$7.4 \times 10^{-10}$	$6.8 \times 10^{-10}$	$8.2 \times 10^{-10}$	$6.2 \times 10^{-10}$
$D_{\text{oil}}$ (m <sup>2</sup> /s) <sup>f</sup>	$1.5 \times 10^{-9}$	$1.4 \times 10^{-9}$	$1.1 \times 10^{-9}$	$1.2 \times 10^{-9}$	$1.2 \times 10^{-9}$	$1.1 \times 10^{-9}$	$1.4 \times 10^{-9}$	$1.0 \times 10^{-9}$
$D_{\text{air}}$ (m <sup>2</sup> /s) <sup>g</sup>	$8.1 \times 10^{-6}$	$7.4 \times 10^{-6}$	$6.4 \times 10^{-6}$	$6.8 \times 10^{-6}$	$6.6 \times 10^{-6}$	$6.2 \times 10^{-6}$	$7.7 \times 10^{-6}$	$5.8 \times 10^{-6}$
<i>River properties</i>								
$Q = 3$ (m <sup>3</sup> /s)								
$A = 10$ (m <sup>2</sup> )								
$W = 10$ (m)								
$D_L = 25$ (m <sup>2</sup> /s)								
$U_{\text{wind}} = 2$ (m/s)								
$k_{\text{L-oxygen}} = 2.47 \times 10^{-6}$ (m/s)								
$T = 20^\circ\text{C}$								
<i>Rate constants<sup>i</sup></i>								
$k_{\text{evap}} = 5.27 \times 10^{-4}$ (m/s)								
$k_{\text{dis}} = 1.50 \times 10^{-6}$ (m/s)								
$k_{\text{vol}} = 1.20 \times 10^{-5}$ (m/s)								
<i>Model parameters</i>								
$\Delta t = 60$ (s)								
$\Delta x = 100$ (m)								

## 2.2. Mass balance for the slick phase

The mass of the slick decreases over time as the compounds dissolve into the water phase and evaporate into the atmosphere. A mass balance for each compound in the slick is written as:

$$\frac{dm}{dt} = \int_{\text{length of slick}} \left[ -k_{\text{dis}} W (X_o C_w^{\text{sat}} - C_w) - k_{\text{evap}} W \left( \frac{X_o P^\circ M_i}{RT} \right) \right] dx + r \quad (4)$$

where  $C_w$  is the aqueous concentration,  $C_w^{\text{sat}}$  is the aqueous saturation concentration,  $k_{\text{dis}}$  is the dissolution rate coefficient,  $k_{\text{evap}}$  is the evaporation rate coefficient,  $m$  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,  $X_o$  is the mole fraction in the slick, and  $W$  is the width of the slick. This one dimensional model formulation assumes the slick covers the water surface from bank to bank, therefore  $W$  is also the width of the river. The product  $X_o P^\circ$  represents the vapor pressure of a compound at the slick–air interface based on Raoult's Law. The mass flux rate is integrated over the length of the slick since  $W$  and  $C_w$  can vary as a function of distance. The concentration of each compound in the slick can then be expressed as a mole fraction:

$$X_o = \frac{m(M)^{-1}}{\sum_{\text{all compounds}} m(M)^{-1}} \quad (5)$$

## 2.3. Transport equation for aqueous phase

The concentrations of compounds dissolved in the water change over time and distance as the compounds dissolve from the slick into the water, volatilize from the

Notes to Table 1:

<sup>a</sup>Burris and MacIntyre [11].

<sup>b</sup>Lide [12].

<sup>c</sup>Schwarzenbach et al. [13].

<sup>d</sup>Lyman et al. [14].

<sup>e</sup>Approximated using Hayduk and Ladie [15].

<sup>f</sup>Approximated using Wilke and Chang [16].

<sup>g</sup>Approximated using Fuller et al. [17].

<sup>h</sup>Average properties of the five aliphatic compounds in JP-4 fuel, Burris and MacIntyre [11].

<sup>i</sup>Approximate values. Actual values determined for each compound based on wind speed, reaeration rate, and physical properties of individual compounds.

water to the atmosphere, and disperse in the river. The one-dimensional advection–diffusion equation for each compound is written as:

$$\frac{\partial(AC_w)}{\partial t} + \frac{\partial(QC_w)}{\partial x} = \frac{\partial}{\partial x} \left( AD_L \frac{\partial C_w}{\partial x} \right) + \phi k_{\text{dis}} W (X_o C_w^{\text{sat}} - C_w) - (1 - \phi) k_{\text{vol}} W C_w \quad (6)$$

where  $A$  is the cross-sectional area of river,  $D_L$  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). When the surface slick is present at location  $x$ , there is an exchange between the slick and the water. When the surface slick is not present at location  $x$ , there is an exchange between the water and the atmosphere.

The approximation of the river as a series of discrete well-mixed cells introduces additional dispersion into the model. Even if a value of  $D_L = 0$  is input, some dispersion will still be predicted by the model. Banks [9] developed a mixed cell model which may be used to quantify this numerical dispersion:

$$D_{L-\text{num}} = 0.5 U \Delta x \quad (7)$$

where  $\Delta x$  is the length of the river control volume. Eq. (7) is based on an infinite number of cells and is approximately valid as long as roughly 10 or more cells are used in the model [10]. Since Eq. (6) is often approximated as a linear partial differential equation where superposition applies, the numerical dispersion and the user specified dispersion are nearly additive. Thus, the value of longitudinal dispersion that should be specified in the model to obtain the true dispersion,  $D_L$ , can be estimated from the expression:

$$D_{L-\text{model}} = D_L - D_{L-\text{num}} \quad (8)$$

where  $D_{L-\text{model}}$  is the longitudinal dispersion coefficient that is supplied to the model in Eq. (6).

#### 2.4. Solution algorithm

Eqs. (2)–(6) form the basis of the model. A formulation of Eq. (6) is needed for each compound that is to be modeled. A pair of Eqs. (4) and (5) are needed for each compound and for each individual slick used in the simulation. No direct solution for the equation set is available, so the equations are solved numerically. At each time step, the extent and location of the oil slick is determined from Eqs. (2) and (3). The mass of each compound in the oil phase is then determined by an explicit time integration of Eq. (4), i.e. the values of  $C_w$  and  $X_o$  are taken from the previous time step. The mole fraction of each compound in the slick is then determined from Eq. (5). Next, the aqueous concentration of each compound at each location in the river is determined by a fully implicit time integration of Eq. (6), i.e. the current values of  $C_w$  and  $X_o$  are used in the calculation.

### 3. Sample application

As an example of the capabilities of the model, consider a spill of 10 000 kg of JP-4 jet fuel released onto a river of the scale typical of a tributary to a navigable river over a period of 10 min. The approximate composition of the fuel, the physical properties of the compounds, the river flow data, and the model parameters for the simulation are listed in Table 1. A majority of the jet fuel is comprised of several relatively insoluble long-chain aliphatics [11]. For simplicity, these aliphatic compounds were grouped and modeled as a single compound with properties averaged from the individual aliphatic compounds.

The results of the jet fuel spill simulation are shown in Figs. 2–5. Fig. 2 shows the aqueous concentrations of two compounds, ethylbenzene and 1-methylnaphthalene, plotted vs. distance downstream at times of 10, 20, 40, and 60 h after the spill occurred. The concentration profiles are nearly Gaussian in shape, typical of pulse loadings in rivers. The profiles tend to broaden over time due to the streamwise mixing in the river, approximated by the longitudinal dispersion term in Eq. (6). Notice that the concentration profiles are slightly skewed to the downstream direction. Since the slick is drifting downstream at a rate slightly higher than the mean river velocity, the compounds in the slick are constantly dissolving into the river slightly downstream of the aqueous concentration peak, creating a skewed profile.

The peak aqueous concentrations of all eight compounds in the jet fuel are plotted vs. time in Fig. 3. The peak aqueous concentrations of the more volatile compounds (e.g. toluene and methylcyclohexane) reach maximums within the first 10 h, then decrease as these volatile compounds rapidly evaporate from the slick and are no longer available to dissolve into the water. The aqueous concentration of each compound continues to rise until that compound has evaporated from the slick. Once a compound has been removed from the slick, the peak aqueous concentration of that compound decreases as its concentration is diluted by longitudinal dispersion and as it volatilizes from the water to the atmosphere. In this example, the least soluble compounds also are least volatile, and

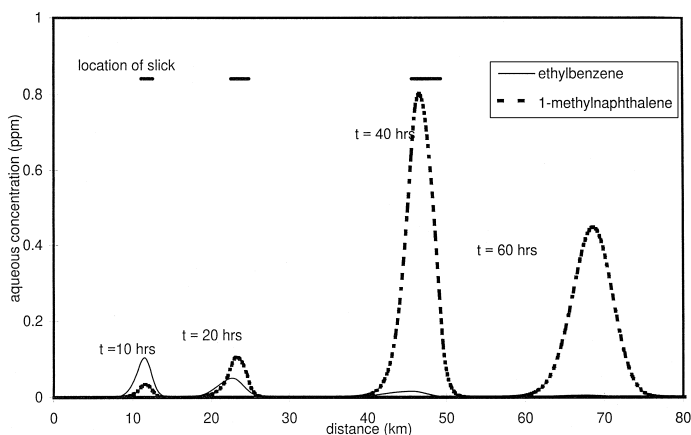


Fig. 2. Results of jet fuel spill simulation: Aqueous concentration profiles for ethylbenzene and 1-methylnaphthalene.

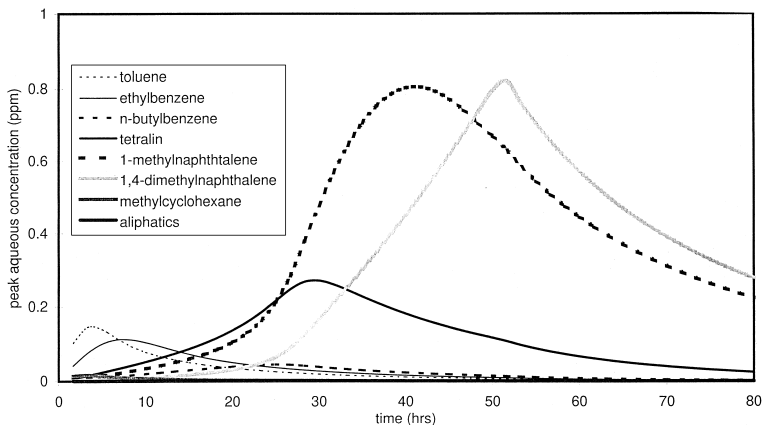


Fig. 3. Results of jet fuel spill simulation: Peak aqueous concentrations of compounds.

therefore they tend to remain in the slick for a longer time and continue to dissolve into the water column, resulting in higher aqueous concentrations. Consequently, the highest aqueous concentrations resulting from this spill are not for the most soluble compounds, but rather for some of the least soluble and least volatile compounds (e.g. 1-methylnaphthalene and 1,4-dimethylnaphthalene). This surprising behavior warrants experimental verification and/or investigation.

Fig. 4 shows the mass of each compound in the slick as a function of time. Fig. 5 shows the mole fraction of each compound in the slick plotted vs. time. For simplicity, this simulation was run using only one slick. The composition of the slick changes drastically with time. Notice that the evaporation and dissolution flux rates of compounds from the slick, as inferred from the slopes of the lines in Figs. 4 and 5, increase as a compound's mole fraction in the slick increases. This behavior exemplifies the fact that the dissolution and evaporation rates are governed not only by environmental

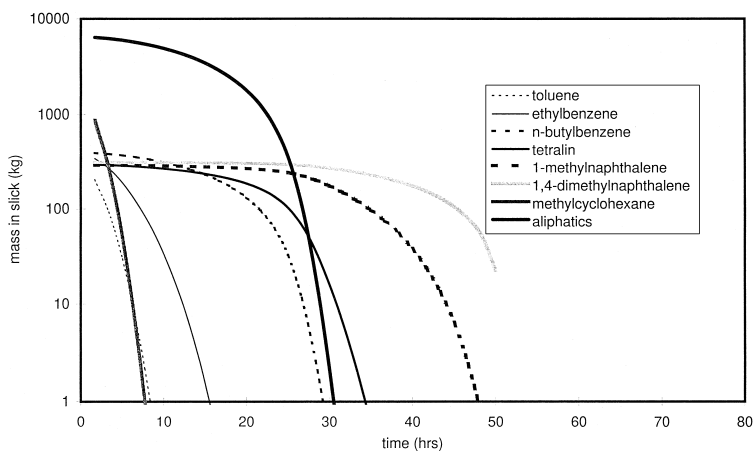


Fig. 4. Results of jet fuel spill simulation: Mass of compounds in slick.



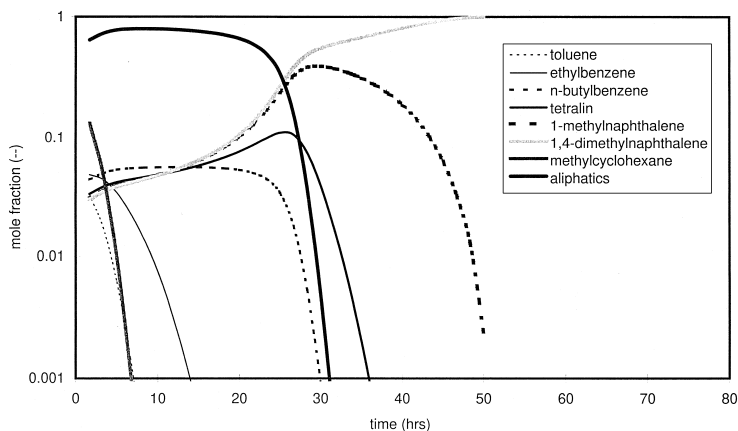


Fig. 5. Results of jet fuel spill simulation: Mole fraction of compounds in slick.

parameters, but also by slick composition. Since the slick composition is constantly changing over time, the concentration of compounds in the slick must be modeled in conjunction with the aqueous concentrations.

As shown in Fig. 5, the composition of the slick, and therefore the nature of the slick, can change drastically over the duration of the spill as the more volatile, more soluble and lower molecular weight compounds evaporate and dissolve from the slick. Most notably, the specific gravity of the slick increases over time. At 30 h, the specific gravity of the slick reaches 1.0 and the slick should break-up into globules dispersed in the water column or sink to the bottom. However, even if the slick breaks up, the aqueous concentration of the compounds remaining in the oil phase will continue to rise, though perhaps not precisely as shown in Fig. 3. If the slick degrades to small globules suspended in the water column, the aqueous concentrations of the compounds in the oil phase will increase more rapidly than predicted in Fig. 3 due to the increased surface area of the globules compared to the surface slick. If the globules sink, they will not be drifting downstream suspended in the water column, and therefore the peak concentrations will likely be lower than those predicted by Fig. 3 which assumes that the slick is drifting at roughly the same velocity as the river. The viscosity of the slick also increases over time, leading to an increase in resistance to transfer in the oil phase. Additionally, the surface tension and the activity coefficients of the compounds in the slick will change over time, altering the spreading rate and the slick-water and slick-air equilibrium partitioning of the compounds. Thus, the slick composition can affect the physical characteristics of the slick and consequently the aqueous concentrations resulting from the spill. However, actual effect on the aqueous concentrations is difficult to estimate at this time.

#### 4. Spatial variations in slick composition

The preceding application was modeled using only one slick, and thus it was assumed that the concentration of compounds within the slick were uniform over the entire length

of the slick. However, for slicks that are several kilometers in length or slicks that are being fed slowly by a point source such as a leaky pipe, the concentration of compounds within the slick may in fact vary with distance downstream. Since the aqueous concentration is controlled largely by the concentration within the overlying slick, the assumption of a uniform concentration over the entire length of the surface slick may introduce significant errors in the prediction of the aqueous concentration.

Assuming that the evaporation rate coefficient,  $k_{\text{evap}}$ , is constant over the entire length of the slick, a streamwise variation in the concentrations of compounds within the slick can be caused in only two ways. First, a variation in slick composition could be caused by spilling a mixture of compounds into one end of a slick while compounds rapidly and selectively evaporate and dissolve from the slick. In such a case, the composition of the slick near the spilling point would resemble the composition of the spilled product, while the portions of the slick far downstream from the spilling point could contain less of the more volatile compounds. Second, a variation in slick composition may be caused by variations in the aqueous concentration of a compound beneath the slick. If the aqueous concentration beneath the slick varies significantly from one end of the slick to the other, the dissolution rate, which is driven by the difference between the actual water concentration and the equilibrium concentration in the water, would also vary from one end of the slick to the other. Over time the variation in dissolution rate could create a variation in slick composition.

To investigate the conditions under which the slick composition could vary from one end to the other due to rapid evaporation, consider the following analysis of a binary spill. Let compound 1 be volatile and semi-soluble, and let compound 2 be perfectly nonvolatile and insoluble. The mass balance for compound 1 in the furthest downstream end of the slick can be simplified from Eqs. (4) and (5) by assuming that the evaporative flux is much greater than the dissolution flux, and by setting  $M_1 = M_2$ :

$$\frac{dm_1}{dt} = -k_{\text{evap}} \frac{m_1}{m_1 + m_2} \frac{P_1^\circ M_1}{RT} \quad (9)$$

where  $t$  is the time since the product was spilled onto the water surface. Integrating Eq. (9) from  $t = 0$  to  $t$  and from  $m_1 = m_1^\circ$  to  $m_1$ , the time to achieve a specified reduction in the initial, or the spilled, concentration of compound 1 in the slick can be estimated as:

$$t = \frac{RT}{P_1^\circ M_1 k_{\text{evap}}} \left[ (m_1^\circ - m_1) - m_2 \ln \frac{m_1}{m_1^\circ} \right] \quad (10)$$

Thus, larger variations in the concentration of a compound within a slick (as indicated by  $m_1/m_1^\circ$ ) will occur when the duration of the spilling period is long (i.e.  $t$  is large), when one of the compounds evaporates quickly (i.e.  $P_1^\circ \times k_G$  is large), or when the slick is thin (i.e.  $m_1$  and  $m_2$  are small). Inserting values of  $m_1^\circ = 100 \text{ g/m}^2$  and  $m_2 = 900 \text{ g/m}^2$  (i.e. slick thickness approx. = 1 mm),  $k_{\text{evap}} = 5 \times 10^{-4} \text{ m/s}$ ,  $P_1^\circ = 10^{-1} \text{ atm}$ , and  $M_1 = 100 \text{ g/mol}$  into Eq. (10), the time to achieve a 10% reduction in the concentration of compound 1 in the downstream end of the slick is on the order of  $t = 10 \text{ min}$ .

The second possible cause of streamwise variations in concentrations of compounds in the slick could be the variation in dissolution rates due to streamwise gradients in the aqueous concentration beneath the slick. Consider again the simplified spill of a binary mixture, where compound 1 is volatile and semi-soluble and compound 2 is perfectly nonvolatile and insoluble. The aqueous concentration of compound 1 under the center of the slick is assumed to be at saturation, such that there is no dissolution flux and the aqueous concentration under the leading edge of the slick is assumed to be zero, such that there is a maximum dissolution flux. The mass balance for compound 1 at the leading edge of the slick can be simplified from Eqs. (4) and (5) by letting  $M_1 = M_2$ :

$$\frac{dm_1}{dt} = \frac{m_1}{m_1 + m_2} \left[ -k_{\text{dis}} C_{\text{w}1}^{\text{sat}} - k_{\text{evap}} \frac{P_1^\circ M_1}{RT} \right] \quad (11)$$

Integrating Eq. (11) from  $t = 0$  to  $t$  and from  $m_1 = m_1^\circ$  to  $m_1$ :

$$\frac{m_1}{m_1^\circ} - 1 + \frac{m_2}{m_1^\circ} \ln \frac{m_1}{m_1^\circ} = \left[ -k_{\text{dis}} C_{\text{w}1}^{\text{sat}} - k_{\text{evap}} \frac{P_1^\circ M_1}{RT} \right] \frac{t}{m_1^\circ} \quad (12)$$

Since we are interested in the conditions under which the difference between  $m_1$  and  $m_1^\circ$  is large, let  $m_1/m_1^\circ \rightarrow$  small and Eq. (12) becomes:

$$\left( \frac{m_1}{m_1^\circ} \right)_{\text{edge}} = \exp \left[ \frac{m_1^\circ}{m_2} - \left( k_{\text{dis}} C_{\text{w}1}^{\text{sat}} + k_{\text{evap}} \frac{P_1^\circ M_1}{RT} \right) \frac{t}{m_1^\circ} \right] \quad (13)$$

A similar expression, minus the dissolution term, can be obtained for compound 1 at the center of the slick:

$$\left( \frac{m_1}{m_1^\circ} \right)_{\text{center}} = \exp \left[ \frac{m_1^\circ}{m_2} - \left( k_{\text{evap}} \frac{P_1^\circ M_1}{RT} \right) \frac{t}{m_1^\circ} \right] \quad (14)$$

From Eqs. (13) and (14), the conditions necessary to produce a significant streamwise gradient in the concentration of compound 1 in the slick due to variations in the aqueous concentration under the slick can then be estimated from the following expression:

$$k_{\text{dis}} C_{\text{w}1}^{\text{sat}} \frac{t}{m_2} = \ln \alpha \quad (15)$$

where:

$$\alpha = m_{1\text{edge}}/m_{1\text{center}} \quad (16)$$

Inserting values of  $m_2 = 70 \text{ g/m}^2$  and  $k_{\text{dis}} = 2 \times 10^{-6} \text{ m/s}$  into Eq. (15), it would take an extremely soluble compound with a  $C_{\text{w}1}^{\text{sat}} > 10^{-0.50} \text{ mol/l}$  to obtain even a small gradient of  $\alpha = 0.95$  within the slick over a 10-h period. Thus, significant streamwise concentration gradients within the slick are not likely to be caused by concentration driven variations in dissolution fluxes.

#### 4.1. Short-duration spill simulation

The results of a series of simulations of the jet fuel spill using the multiple slicks are consistent with the above analysis. The concentrations of the more volatile compounds in the downstream end of the slick decrease only slightly during the 10 min that the jet

fuel is being spilled onto the water. Fig. 6 shows the maximum aqueous concentration of four compounds resulting from a 10-min spill plotted as a function of the number of slicks used in the model. As more slicks are used in the model, larger concentration gradients develop in the slick, and the maximum aqueous concentration decreases.

The variations in the slick concentration that occur while the slick is being formed not only affect the maximum highest aqueous concentrations resulting from the spill, but also the location and the time at which the maximum aqueous concentration occur after a spill. Fig. 7 shows the model simulation results for a spill of 10 000 kg spill of jet fuel over a period of 10 min. The peak aqueous concentrations of ethylbenzene and 1-methylnaphthalene are plotted against time for simulations using the single slick model and a 10-slick model. Similar to what was shown in Fig. 6, the peak concentration of both compounds are roughly 25% lower when 10 slicks were used than when only 1 slick was used in the simulation. Also, the highest aqueous concentration occurs roughly 25% earlier when 10 slicks are used in the simulation than when only 1 slick is used. The decrease in the maximum aqueous concentration and the shift in the time of occurrence of the maximum aqueous concentration can be attributed to the selective evaporation of the more volatile compounds over the length of the slick during the period that the fuel is being spilled onto the water surface. We were surprised that the results of the single-slick model and the multi-slick model would differ for a spill of such short duration. We thus investigated the mechanisms in some detail.

Using the 10-slick model for this 10-min spill, each individual slick has fuel added to it for 60 s. The slick then drifts downstream while the more volatile compounds rapidly evaporate, creating a concentration gradient in the overall slick. The effective length of the overall slick for dissolution of the volatile compounds becomes shorter as the more volatile compounds evaporate from the downstream end of the slick. At roughly 6 h, the effective length of the slick has become so small that the dispersion in the river dilutes any further dissolution from the slick, and the peak aqueous concentration of ethylbenzene begins to decline. In the single slick model, the concentration of ethylbenzene is

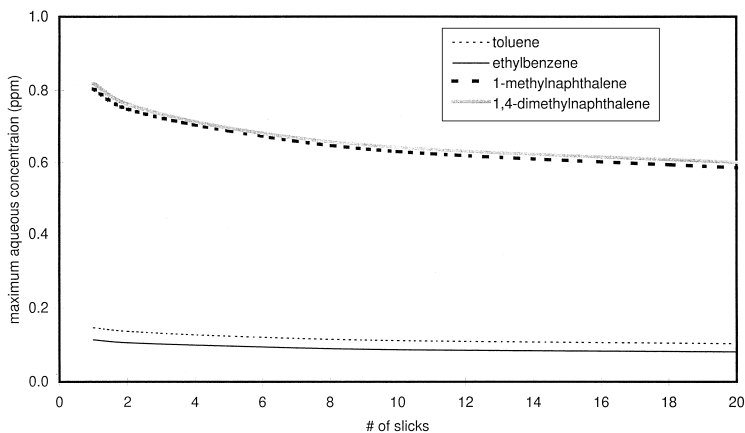


Fig. 6. Multiple slick model: Effect of the number of slicks on the maximum aqueous concentration for a release of 10 000 kg of jet fuel over 10 min.

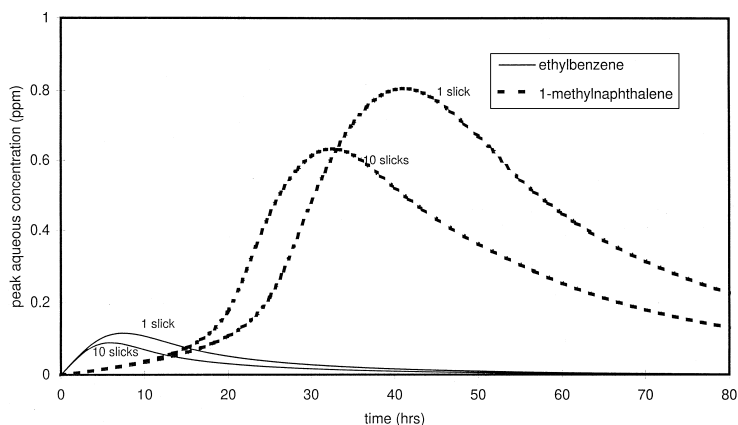


Fig. 7. Multiple slick model: Peak aqueous concentrations resulting from a release of 10000 kg of jet fuel over 10 min.

uniform throughout the slick, thus it has a long effective length for dissolution. The peak aqueous concentration is able to increase until roughly 8 h, after which the dispersion in the river overpowers the declining dissolution flux.

While the effective length of the slick for the volatile compounds is decreasing, the effective length for dissolution of the nonvolatile compounds is increasing. The peak aqueous concentration of 1-methylnaphthalene in the 10-slick model in Fig. 7 rises slightly faster than the peak aqueous concentration of the single-slick model. The 1-methylnaphthalene dissolves and volatilizes faster from the effectively longer 10-slick model than from the single slick model, thus the 1-methylnaphthalene is completely gone from the slick faster in the 10-slick model than in the single slick model, resulting in a lower maximum aqueous concentration.

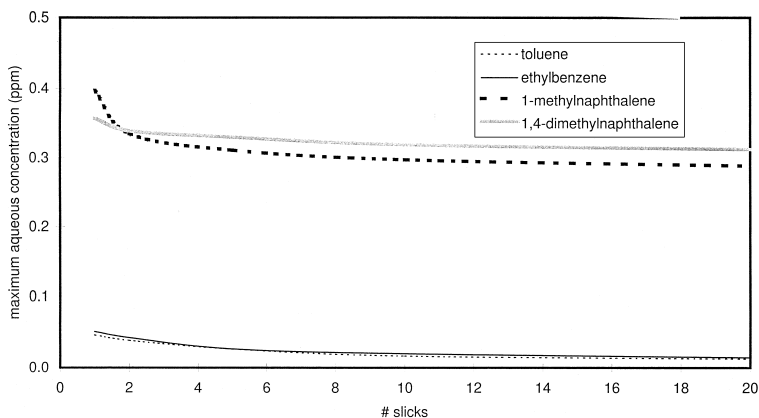


Fig. 8. Multiple slick model: Effect of the number of slicks on the maximum aqueous concentration for a release of 10000 kg of jet fuel over 10 h.

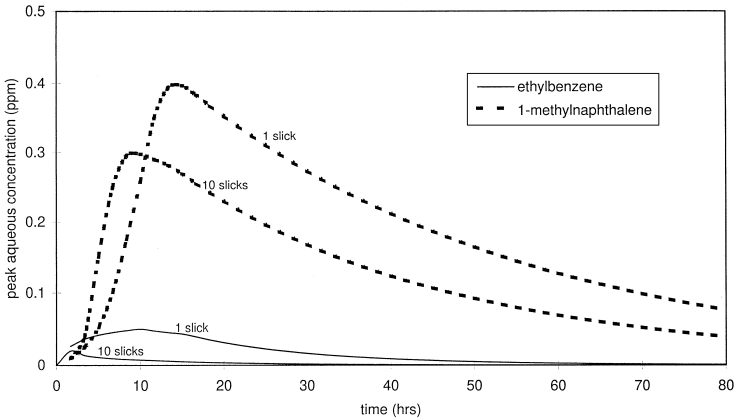


Fig. 9. Multiple slick model: Peak aqueous concentrations resulting from a release of 10000 kg of jet fuel over 10 h.

4.2. Long-duration spill simulation

The same selective evaporation phenomena illustrated in Figs. 6 and 7 can be seen in a similar plot of peak aqueous concentrations resulting from a 10-h release of 10 000 kg of jet fuel, shown in Figs. 8 and 9. Fig. 8 shows the maximum aqueous concentration of four compounds plotted as a function of the number of slicks used in the model. As in the 10-min spill simulation, the highest aqueous concentration of all compounds decrease as the number of slicks in the model increase.

Fig. 9 shows peak aqueous concentrations of ethylbenzene and 1-methylnaphthalene plotted against time for simulations using the single slick model and a 10-slick model. In the 10 min release shown in Fig. 7, each slick in the 10-slick model was filled with jet fuel for 1 min before being released. In the 10-h spill simulation shown in Fig. 9, each slick is filled with jet fuel for 1 h before being released. During that 1-h time period, a significant portion of the more volatile compounds evaporate from the slick. By the time the slick is released to drift downstream, most of the volatile compounds have already evaporated from the slick. Any remaining dissolution of the more volatile compounds is diluted by dispersion. Consequently, the maximum aqueous concentration of ethylbenzene occurs very early after the spill. With the single slick model, new jet fuel is uniformly distributed over the entire slick during the 10-h spilling period. Consequently, the peak aqueous concentration of ethylbenzene continues to rise until 10 h, after which the peak concentration is diluted by dispersion in the river.

The maximum aqueous concentrations shown in Figs. 6 and 8 appear to decrease logarithmically as a function of the number of slicks used in the model, suggesting that there is a diminishing rate of return on the quality of the model prediction with increasing number of slicks used in the model. The decrease of the maximum aqueous concentration for each compound can be described by the empirical equation:

$$\frac{dC_{max}}{dn} = \beta(C_{max} - C_{\infty}) \tag{17}$$

Table 2

Extrapolation of  $C_{\max}$  to an infinite number of slicks.  $C_{\max}$  is determined from spill simulations.  $C_{\infty}$  and  $\beta$  are determined from a curve fit of  $C_{\max}$  vs. the number of slicks using Eq. (22)

	$C_{\infty}$ (ppm)	$\beta$	$C_{\max}$ as a percentage of $C_{\infty}$ (i.e. $C_{\max} / C_{\infty} \times 100$ )				
			1 slick	2 slicks	5 slicks	10 slicks	20 slicks
<i>10-min release</i>							
Toluene	0.103	-0.193	142	133	120	108	101
Ethylbenzene	0.081	-0.195	140	130	119	107	101
1-Methylnaphthalene	0.585	-0.194	138	128	118	108	100
1,4-Dimethylnaphthalene	0.603	-0.213	136	127	116	107	100
<i>10-h release</i>							
Toluene	0.012	-0.214	386	325	224	141	105
Ethylbenzene	0.015	-0.253	337	283	181	135	96
1-Methylnaphthalene	0.297	-0.889	134	113	105	100	97
1,4-Dimethylnaphthalene	0.314	-0.312	114	108	105	101	99

where  $C_{\max}$  is the maximum aqueous for a given number of slicks,  $n$  is the number of slicks used in the simulation,  $\beta$  is a fitted constant, and  $C_{\infty}$  is a fitted constant that representing the maximum aqueous concentration for an infinite number of slicks. Table 2 shows values of  $\beta$  and  $C_{\infty}$  for four compounds determined from regressions of Eq. (17) against the data shown in Figs. 6 and 8. Table 2 also shows the maximum aqueous concentrations plotted in Figs. 6 and 8 as a percentage of  $C_{\infty}$ . For the 10-min release simulation, the concentrations of all four compounds were within 50% of  $C_{\infty}$  using only one slick, within 10% of  $C_{\infty}$  using 10 slicks, and within 1% of  $C_{\infty}$  when using 20 slicks. For the 10-h release simulation, the maximum aqueous concentrations of the volatile compounds varied from nearly four times the value of  $C_{\infty}$  using only one slick to within 5% using 20 slicks, while the range of variation of the maximum aqueous concentrations of the nonvolatile compounds was similar to that of the 10-min release simulation. Thus, number of slicks used in the simulation can have a significant impact on the predicted aqueous concentrations, especially in models of slow, continuous spills of highly volatile compounds.

## 5. Conclusions

Streamwise concentration gradients caused by the rapid evaporation of the more volatile compounds can have a significant impact on the resulting aqueous concentrations during non-instantaneous riverine spills. A multiple-slick spill model can account for these streamwise gradients with the slick. The use of the single-slick spill model in place of the multi-slick model results in the overprediction of the maximum aqueous concentration and a delayed prediction of the maximum aqueous concentration, especially in the prediction of aqueous concentrations of volatile compounds resulting during long duration spills. For short duration spills, differences in the predicted aqueous concentrations using the single-slick model and the multiple-slick model are small. For

instantaneous spills, the aqueous concentrations predicted using the multiple-slick model and the single-slick model are nearly identical.

The application of the model to a hypothetical spill of 10,000 kg of jet fuel into a tributary to a navigable river indicates that the more soluble and more volatile compounds reach the highest aqueous concentrations within 10 h of the spill. After that time, the slick is composed primarily of less soluble and less volatile compounds. The aqueous concentrations of the low volatility compounds continues to rise until the slick evaporates, dissolves, or breaks into globules. Regardless, the potential for high aqueous concentrations of low solubility, low volatility compounds is recognized and should be considered in the investigation of future riverine spills.

## 6. Nomenclature

$A$	Cross-sectional area of river
$C_{\max}$	Maximum aqueous concentration during a spill simulation
$C_w$	Aqueous concentration
$C_w^{\text{sat}}$	Aqueous saturation concentration
$D_L$	Longitudinal dispersion coefficient
$D_{L\text{-add}}$	User specified value of the longitudinal dispersion coefficient
$D_{L\text{-num}}$	Numerical dispersion
$k_{\text{dis}}$	Dissolution rate coefficient
$k_{\text{evap}}$	Evaporation rate coefficient
$k_{\text{vol}}$	Volatilization rate coefficient
$m$	Mass in slick
$m^\circ$	Initial mass in slick
$M$	Molecular weight
$n$	Number of slicks
$P^\circ$	Vapor pressure
$Q$	Discharge in river
$r$	Release rate
$R$	Universal gas constant
$T$	Temperature
$t$	Time
$U$	Mean river velocity
$U_{\text{slick}}$	Streamwise velocity of centroid of slick
$U_{\text{leading}}$	Streamwise velocity of leading edge of slick
$U_{\text{trailing}}$	Streamwise velocity of trailing edge of slick
$U_{\text{wind}}$	Streamwise component of the wind speed vector
$W$	Width of slick and width of river
$x$	Distance downstream
$X_o$	Mole fraction of compound in the slick
$\Delta x$	Length of river cell
$\alpha$	Ratio of mass of compound 1 in the edge of the slick to mass of compound 1 at the center of the slick



$\alpha_{\text{drift}}$	Velocity profile correction factor
$\alpha_{\text{vel}}$	Wind drift correction factor
$\beta$	Regression constant
$\phi$	Phase marker indicating the presence of a slick

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