

ESTIMATING EXPOSURE FROM A CHEMICAL SPILLED INTO A RIVER

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Summary

There is always the possibility of an accidental discharge of a chemical into a flowing river system. When it happens, knowledge is needed of the concentrations that can be expected downstream of the discharge. By taking advantage of an actual derailment in British Columbia it was possible to validate a set of dispersion equations for making such predictions. The model has been programmed to operate on a small microprocessor which makes the results immediately accessible to the decision makers.

Introduction

When an accidental discharge of a chemical occurs in a river there is an immediate need to know the risks associated with the exposure. For example, if municipalities downstream are using the river as a source of drinking water then it becomes necessary to make a decision regarding closing the water intakes. These and other types of questions can be answered more intelligently if information is quickly available on both effects and exposure. The purpose of the present report is to update our previous work on the exposure side of this question [1-3]. The effects will be the subject of a future article.

The basis for the model used in predicting concentrations will be presented along with a report on an actual accident. The results from the theoretical analysis will then be compared to the measured values.

Model description

The mathematical description of how a material disperses in a river has been investigated by many authors [4, 5]. For a detailed derivation of the equations either of these two references should be examined. The present discussion will be limited to a general overview.

Once a material has been added to a flowing water system it begins to spread in all three directions where the dispersion is controlled by the coefficients D_x , D_y and D_z . In the case of a river the vertical mixing in the z direction is relatively fast compared to the lateral (y) and longitudinal (x) mixing, and to a first approximation may be ignored. Accordingly, the concentrations at any point downstream from the spill is given by eqn. (1)

$$C(x,y,t) = C_1(x,t) C_2(y,t) \quad (1)$$

where $C(x,y,t)$ is a product of two one-dimensional equations,

$$C_1(x,t) = \frac{M}{(4 \pi D_x t)^{0.5}} \exp \left(-\frac{x^2}{4 D_x t} \right) \quad (2)$$

where M = amount spilled, and D_x = diffusion coefficient, and a similar equation for $C_2(y,t)$ [4].

Multiplying C_1 by C_2 yields eqn. (3):

$$C(x,y,t) = \frac{M}{4 \pi t(D_x D_y)^{0.5}} \exp \left(-\frac{x^2}{4 D_x t} - \frac{y^2}{4 D_y t} \right) \quad (3)$$

By including advection in the direction of stream flow the final diffusion equation in two dimensions is derived:

$$C(x,y,t) = \frac{M}{4 \pi t(D_x D_y)^{0.5}} \exp \left(-\frac{(x-vt)^2}{4 D_x t} - \frac{y^2}{4 D_y t} \right) \quad (4)$$

where v = velocity of stream flow.

Since only maximum concentrations are of concern the exponential terms in eqn. (4) will be equal to 1. Thus the maximum concentration at any point downstream along the center line of the spill ($y = 0$) is given by eqn. (5):

$$C(x,t) = \frac{M}{4 \pi t(D_x D_y)^{0.5}} \quad (5)$$

If the discharge of material occurs near the bank of the river, the estimated concentration in eqn. (5) needs to be multiplied by 2. The factor 2 is derived from the observation that material added in the middle of the river may disperse towards each bank. This should be compared to the situation for a spill from the side where the lateral dispersion occurs in only one direction.

As soon as the material becomes uniformly distributed across the width of the river the concentration is given by eqn. (6):

$$C(x,t) = M/[A (4 \pi D_x t)^{0.5}] \quad (6)$$

where A = cross-sectional area of the river.

The distance required for uniform mixing is a function of the width, shear velocity and dispersion coefficient in the lateral direction [4, 6]. If the chemical is discharged in the middle of the river the mixing length is determined by eqn. (7).

$$L = (0.1 U^* W^2)/D_y \quad (7)$$

where U^* = shear velocity, and L = length in meters from the spill site.

On the other hand, if a material is spilled from the shore, as in a derailment, the length required is four times the distance indicated in eqn. (3) [6]. Both of these estimations apply to a straight channel. If there are many bends in the river, consideration should be given to modifying this length. The above discussion has assumed that the chemical is conservative, i.e., there are no dissipating reactions operating. It is generally accepted that loss mechanisms operate via a first-order process; consequently, each of the concentration equations should be multiplied by expression (8)

$$\exp(\Sigma kt) \quad (8)$$

where Σk represents the sum of all the rate constants responsible for removing the chemical from the water system.

Estimating the hydrodynamic constants

From eqns. (5) and (6) it is apparent that the key properties required for an analysis are M , the amount of chemical added to the water column, the shear velocity, and the two dispersion coefficients, D_x and D_y . If available, these values should be based on the actual conditions of the spill site. In the absence of field data the following procedures will generate the three hydrodynamic coefficients.

a. *Shear velocity.* To a first approximation the shear velocity is about 0.1 times the mean velocity of the river [4].

b. *Longitudinal dispersion coefficient.* This becomes a very critical coefficient since the extent of spreading in the direction of flow is directly related to the magnitude of this number. There have been many studies on how to estimate D_x using readily available river data. After examining the many correlations the one that has the most acceptance is the analysis by Liu [7, 8], summarized in eqn. (9):

$$D_x = 0.5 U^* W^2/d \quad (9)$$

where W = width, U^* = shear velocity, and d = depth.

c. *Lateral dispersion coefficient.* Fisher et al. [4] have reviewed the present state of knowledge for estimating D_y . This is illustrated with eqn. (10), where the value of A varies with the type of stream.

$$D_y = A d U^* \quad (10)$$

For straight channels A is in the range of 0.1 to 0.2. Irregularities cause

the coefficient to increase. For most streams, including the present analysis, A is given a value of 0.6.

The accident

At 15.27 hours (3:27 pm) Pacific time on March 3, 1982, a train operated by the Canadian National Railway was derailed 8 miles south of Blue River, British Columbia. The accident allowed 1.74 million pounds of ethylene dichloride (EDC) to enter the Thompson River. An emergency response team from Dow Canada located at Fort Saskatchewan, Alberta was alerted and immediately flown to the scene. Through their efforts a great deal of monitoring data was obtained which will form the basis for validating the proposed model. The field data are shown in Tables 1 and 2. Table 1 also includes several relevant observations that were made regarding the topography of the spill site.

Table 3 contains the available hydrological information on the Thompson River as well as the climatic conditions at the time of the accident. Table 4 summarizes the key properties of ethylene dichloride.

TABLE 1

Field data from the site of the accident

Distance (miles)	Time post derailment (hours)				Site conditions
	44	68	92	20 ^a	
0.1				no	opposite from spill
0.1	8 ^b	6	10	yes	same side
4	4				
5				yes	both sides of the river
5				yes	
7				yes	mile 1 to 10 rapids
8	5	7	4		
10				yes	
12	14				mile 16 to 32 is flat and ice covered
16	45			no	
20	80				
21				no	
28	220	12	15		
32	180				mile 32 to 48 rapids
40	N.D.		10		
52	N.D.	33	18		
60		40			mile 62 to 100 generally flat and wide
64			13		
68		19			
72			8		
80		12	14		

^aThis column refers to the detection of odor.

^bConcentrations are in mg/L.

TABLE 2

Concentration of ethylene dichloride in the Thompson River

Days ^a after accident	From the site concentration (mg/L)		
	0.01 km	38 km	51 km
6		3.9	3
7	22		
8	7	3	2
9	3.6	2	1.7
14	3.2	N.D.	N.D.

^aDerailment occurred on March 3, 1982.

Results

Several simulations will illustrate how estimations can be improved by including more site-specific data. Improvement will be judged by how close the predictions are to the measured concentrations as shown in Table 1. The results are reported in Table 5 as concentrations of EDC, 28 and 50 miles downstream of the accident. The simulations will progress from a minimum data base to the situation where all the available information is used.

a. Simulation 1. Incorporating the hydrological data in Table 3 into the model equations, a spill of 1.74 million pounds (7.88×10^5 kg) of EDC was simulated. For this first case EDC was treated as a conservative chemical. This is a worst case situation which will yield the maximum predicted concentrations. As can be seen from Table 5 this is exactly what occurred. With the inclusion of more site-specific data the results should begin to approach the measured values.

TABLE 3

Hydrological and climatic conditions at the time of the accident

Flow	25.2 m ³ /s
Depth	1.5 m
Velocity	0.3 m/s
Water temperature	4°C
Air temperature	10°C
Wind speed	4 m/s
Surface of water	50% covered with ice

b. Simulation 2. There are two possible mechanisms for dissipation of EDC from the river. These are adsorption to sediments and volatility. With the low value for the partition coefficient (Table 4) it would be predicted that binding of EDC to sediments would be small. This is partially sub-

stantiated by the work of Dilling et al. [10]. While these authors did not investigate EDC, they did study chloroform, a halocarbon with very similar properties. In their report [10] the conclusion was reached that little or no binding of CHCl_3 to sediments occurred. Accordingly, adsorption will be ignored as a possible mechanism for lowering the water concentration of EDC.

TABLE 4

Chemical and physical properties of ethylene dichloride

<i>Properties</i>	
Molecular weight	98.9
Melting point	-35°C
Boiling point	83.3°C
Water solubility (20°C)	8800 mg/L
Vapor pressure (25°C)	0.11 atm
Flash point	18°C
Specific gravity	1.2457
Octanol water partition coefficient	250
<i>Estimated properties</i>	
Vapor pressure (4°C)	0.03 atm
Rate constant for volatility at 4°C and wind speed of 4 m/s	1.16×10^{-2} m/h

In order to evaluate the rate constant for volatility it is necessary to have a vapor pressure at the temperature of interest (4°C). The procedure described by Grain [11] was used for this estimation. By applying the model of Liss and Slater [12] as modified by Wolff and van der Heijde [13], the loss by volatility under the influence of a 4 m/s wind speed was calculated (Table 4). Since the river was 50% covered with ice, the rate constant had to be reduced by one-half before using it in eqn. (4). The results of including volatility are shown in Table 5.

c. *Simulation 3.* The concentration numbers in Table 5 from the previous simulation are still too large, which would suggest that either the initial input was too great or some other loss mechanism must be operating. Since the major route of dissipation was considered in simulation 2, the present simulation will focus on the actual amount of chemical that entered the river.

Ethylene dichloride is slightly soluble and heavier than water; consequently, the bulk of the material will fall to the bottom of the water column as a cohesive mass. Once on the bottom the material can form pools. Some of these pools may be protected from the turbulent action of the river and will form a reservoir which will be slowly solubilized. The problem of estimating how much of the discharge is solubilized has been studied by Thibodeaux [14] and was discussed by Neely et al. [1].

TABLE 5

Results of simulation studies compared to measured values

	Concentration of EDC (mg/L) at	
	28 miles	60 miles
Measured values	220 (44) ^a	40 (68)
Simulations		
1. Conservative	1211 (42)	827 (89)
2. Volatility	1030 (42)	584 (89)
3. Reduced input	207 (42)	117 (89)
4. Velocity = 0.39 $D_x = 334 \text{ m}^2/\text{s}$		58 (68)
5. Summer conditions, water temperature 20°C	171 (42)	78 (89)

^aNumber in parenthesis indicates time in hours after the accident where the concentration was either measured or predicted.

At this time only a crude calculation of the initial amount in solution will be made, based on the study of the chloroform accident [1]. From that analysis it was estimated that about 15–20% of the original mass went into solution. The remainder was on the bottom and contributed to the residual tail that was observed long after the initial wave front had passed [1]. By accepting the hypothesis that miscible materials go into solution quickly as compared with 20% for chemicals like chloroform, Table 6 was formulated. Recognizing that the fractions assigned are arbitrary, it appears to be a reasonable first approximation of what will occur during a spill. Obvious, this is an area that needs further study.

TABLE 6

Solubility vs. fraction of material that goes into solution

Class	Solubility (mg/L)	Fraction solubilized
Insoluble	<1,000	0.05
Slightly soluble	1,000–50,000	0.20
Moderately soluble	50,000–500,000	0.5
Very soluble	500,000–1,000,000	0.8
Miscible	>1,000,000	

Since the solubility of chloroform (10,000 mg/L) [9] is similar to EDC (Table 4), it will be assumed that 20% of the 1.74 million pounds ($1.57 \times 10^5 \text{ kg}$) of EDC is immediately solubilized. The remainder goes into solution over a period of several days, giving rise to the low background level of EDC reported in Table 2. The results of this simulation are shown in Table 5.

In most cases the simulation would stop at this point since it is most unlikely that additional information would be available. The next step would be to make predictions of concentrations with distance and match these values with the toxicological information.

d. Simulation 4. From Table 5 it is seen that the data at mile 28 are close to the measured values. The major discrepancy is at mile 60 where the concentration is too high and the time of arrival is too long. From Fisher et al. [4], the length of river necessary to contain 95% of the mass is given by eqn. (7):

$$L = 4(2 D_x t)^{0.5} \quad (7)$$

From eqns. (4) and (5), D_x is estimated to be 31.6 m²/s. Using eqn. (7), L at 68 hours becomes 16 km. However, the actual data in Table 1 indicate that 32 miles or 51 km is a more appropriate value. Substituting this new value for L into eqn. (7), D_x is calculated to be 334 m²/s at 68 hours. By noting the time of arrival of the peak at mile 60, a velocity of 0.38 m/s was estimated. Using these two numbers simulation 4 was carried out with the results indicated in Table 5. As can be seen, the new predictions at mile 60 are in close agreement with the measured numbers. The revised estimates of the dispersion coefficient and velocity are a direct consequence of the rapids between mile 32 and 48 (Table 1). This is a further illustration of how site-specific information can improve the predictions.

e. Simulation 5. This simulation was performed to demonstrate the influence of climatic conditions. Everything was similar to simulation 3, except that the water temperature was increased to 20°C. In effect, this will approach summer conditions. From the results in Table 5 it is obvious that the change in temperature causes a more rapid loss of EDC (half-life of 41 hours under summer conditions, compared to the 57 hours for simulation 3).

Conclusion

Given the hydrological data on a river it is apparent that reasonable estimations of the concentrations downstream from a spill site can be derived. Furthermore, the more site-specific information that is available, the closer the predictions will be to the measured numbers. In the final analysis, if the analyst had all the data, there would be a theoretical one-to-one correspondence between prediction and observation. Recognizing that the ideal is never reached, it is still necessary to approach the goal as closely as possible. From an emergency response point of view the initial predictions are ideal in that they are conservative. Thus, with minimum data the concentration numbers are high, and the risk assessment will be on the safe side. It is only by including more site-specific information that the predictions can be lowered.

The equations and data have been programmed to run on the IBM Personal Computer. Such a system makes for rapid analysis, which is exactly what is needed during an emergency. Consequently, as new information is made available, the predictions can be quickly updated for the benefit of the decision makers at the scene of the accident.

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