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Risk Assessment for a Chemical Spill into a River

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Abstract

A chemical spill into a river presents a significant threat to human health and the aquatic environment. A mathematical model is presented for predicting the chemical concentrations in a river resulting from a chemical spill. A screening risk assessment approach is presented to characterize the risk to humans and aquatic life resulting from a single spill. Human exposure is evaluated using two approaches; exposure from drinking contaminated water and aggregate exposure. The potential for adverse effect to aquatic organisms is evaluated by comparing the predicted environmental concentrations to the lethal effect concentration for the most sensitive species as well as to the no observed effect concentration. The model and the approach are used to evaluate a small hypothetical spill of methanol. The example provides guidance for evaluating other chemical spill scenarios.

Keywords: River dilution model, aggregate exposure, aquatic exposure, methanol.

1. Introduction

The capability to determine the human and aquatic exposure from a chemical spill into a river is necessary for industry to evaluate the risk from an actual spill. This capability is also useful for emergency response planners to evaluate hypothetical spill scenarios. The first step of a chemical spill analysis may use a mathematical model to predict the chemical concentrations in a river. Models are particularly useful when measurements cannot be taken, for example when predicting the effects of a chemical not actually spilled or perhaps not even manufactured yet. A short literature review [1] of models for predicting the chemical concentration in a river after a spill has been previously reported. Models can be classified as simple or refined; the model complexity can range from a single equation based on complete mixing to a refined model for evaluating the chemical distribution in an entire river system. A simple model can be applied when chemical concentrations are reduced primarily by dilution. One of the simplest models is the volumetric dilution equation [2] to estimate the chemical concentration after complete mixing in a river. The river dilution model (RDM) [1] provides more information about the spill than the volumetric dilution equation while it requires less input data and training than a refined model. A refined model needs more input data so it is typically applied to

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a well defined river. Another way to classify the models is by the release type, either a continuous release or an instantaneous release; each release type uses a different model formulation.

The second step of a spill analysis is to characterize the risk using the model predicted chemical concentrations. This step provides guidance on whether the potential exposure to humans and aquatic life is acceptable or unacceptable. Human exposure is sometimes evaluated using the assumption that the contaminated water is the primary drinking water source. This is a conservative assumption but it may not be realistic since most people do not drink untreated river water. This study presents a second approach for assessing human exposure based on aggregate (oral, dermal, and inhalation) exposure.

2. Spill Requirements and Legislation

A chemical spill may result from a tank rupture, equipment failure, overfilling, vandalism, transportation accident, or improper operation. At a stationary facility, a secondary containment structure is required around a storage tank so any spilled liquid can be recovered. However, spilled or leaked liquids without secondary containment may flow into surface water or infiltrate into the ground. A transportation accident on land may result in a spill which flows into surface water if secondary containment is not immediately installed. Industry has a financial incentive to prevent spills because they have to pay to remove contaminated soil and also have to replace the spilled material. Industry also wants to prevent spills for regulatory reasons since they may have to cease operations during an inspection and they may be fined if the spill was preventable. Thus, there is a strong interest to prevent chemical spills and contain a spill if it occurs.

There are many Federal regulations [3] in the U. S. A. concerning chemical spill reporting. Section 311 of the Clean Water Act requires notifying the National Response Center (NRC) for any release that violates applicable water quality standards, causes a discoloration of the water, or deposits sludge. Section 103 of the Comprehensive Emergency Response, Compensation, and Liability Act requires notifying the NRC for release of any listed hazardous substance with a reportable quantity. Any person in charge of a facility (or a vessel) must immediately notify the NRC as soon as there is knowledge of a release greater than the reportable quantity. Section 304 of the Emergency Planning and Community Right-To-Know Act requires notification to each Local Emergency Planning Committee for a spill over the reportable quantity. Section 1808 of the Hazardous Material Transportation Act of 1974 requires notification to NRC for a release of a DOT hazardous material that occurs during transport. The Oil Pollution Prevention regulation applies to a spill containing oil which flows into a surface water; reporting such a spill to the National Response Center is required. The U.S. Coast Guard (USCG) has jurisdiction concerning spills on navigable waters. Most state regulatory agencies also regulate chemical spills but the specific regulations are too numerous to describe here.

This study used the model and the approach for risk characterization to evaluate a hypothetical spill of methanol and its subsequent environmental fate. Methanol (methyl alcohol), CAS 67-56-1, was selected to evaluate because it is commonly used, its chemical properties are well known [4], and its toxicity is well characterized. Methanol is used as feed stock for manufacturing organic chemicals; it is an ingredient in antifreeze products, solvents, gasoline, and hydraulic fracturing fluids. The U.S. production is about 2.25 billion gallons of methanol per year.[4] It is transported as 99-100% (w/w) methanol by barge, railcar, tank truck, totes, drums, and smaller containers. For the purposes of demonstrating the utility of the proposed model we have selected the example of a small instantaneous spill with a mass well below the reportable quantity of 2,272 kg; it is not intended to reflect a worst case release. This study is not intended to provide a rigorous evaluation of all possible methanol spill scenarios.

The objective of this paper is to present a screening model to predict concentrations from a chemical spill in a non-tidal river and how to use the predicted concentrations to characterize the potential human and aquatic risks using appropriate toxicity benchmarks. It presents an example screening level evaluation which can be applied to other chemical spill scenarios. This study is a significant contribution because little information has been published on how to use model predicted concentrations to evaluate the risk from an instantaneous chemical spill into a river.

3. Methods

The following are discussed below: exposure scenario, model description, model input data, model calibration, and risk characterization.

3.1. *Exposure Scenario*

This study evaluated a 150 kilogram spill of pure methanol which is equivalent to an entire 190 liter (50 gal) drum. This study assumed that the entire volume flowed instantaneously into the river. While there is low probability that the entire spill mass would flow instantaneously into the water, a screening model has not been identified for a quasi-instantaneous release [1]. The instantaneous release model provides a conservative prediction of the peak concentration for a quasi-instantaneous release. Although it may be more common for methanol to be spilled onto the ground, such an evaluation is beyond the scope of this study.

3.2. *Model Description*

The mixing zone is the area where a chemical spill is initially mixed and diluted as it is transported downstream; this study assumes the chemical is not instantaneously mixed across the river width. The potential exposure is high in the mixing zone because the concentrations are high. A descriptive analysis of an instantaneous chemical release into a river can be obtained using a model. RDM2D, an improved version of RDM, is used in this analysis. The model equations have been previously derived and described, see Refs. 5-7 for details. The peak concentration, C_1, in the mixing zone is predicted as a function of the time after release using Eq. (1):

$$C_1 = \frac{M}{4\pi dt(D_x D_y)^{0.5}} \exp\left(-\frac{x^2}{4D_x t} - \frac{y^2}{4D_y t}\right) \qquad (1)$$

where C_1 is the peak concentration (mg/l), M is the chemical mass (mg) spilled into river, d is river depth (m), D_x is the longitudinal mixing coefficient (m^2/s), D_y is the lateral mixing coefficient (m^2/s), x is the longitudinal distance (m) downstream of the release point, y is the lateral distance (m), and t is the time (s) after the chemical spill enters the river. Eq. (1) shows the peak concentration is directly proportional to the mass spilled. The chemical dilution is due to the water turbulence and it is quantified using lateral and longitudinal mixing coefficients whose values depend primarily on the river velocity which is estimated by the model. The vertical mixing is assumed to be fast compared to the longitudinal mixing and the vertical mixing (D_z) is ignored in the two-dimensional dilution calculations.

A second equation is used to predict the peak concentration, C_2, for distances beyond the mixing zone where the chemical is uniformly mixed across the river width, as shown in Eq. (2):

$$C_2 = \frac{M}{A(4\pi D_x)^{0.5}} \qquad (2)$$

If one wants to predict the chemical concentration, C_3, versus time at a fixed distance downstream of the release point after uniform mixing, then Eq. (3) is used:

$$C_3 = \frac{M}{A(4\pi D_x)^{0.5}} \exp\left(-\frac{x^2 - ut}{4D_x t}\right) \qquad (3)$$

where u is the river velocity (*m*/s). The three equations listed above are easy to solve in an Excel spreadsheet. RDM2D has options for a release from the river bank and a release at the center of river. Although the model assumes the river flow, width, and depth are uniform in a reach, it can evaluate sequential reaches with different property values. It can estimate the travel time for a spill to reach a specified distance downstream from the release point, such as a drinking water intake. The dilution model applies only to soluble chemicals; it does not apply to slightly soluble chemicals such as heavy oils which may sink or to light oils which may float on the water surface. RDM2D conservatively assumes there is no chemical loss due to hydrolysis, evaporation, reaction, or sorption. This assumption is acceptable for a screening analysis which predicts concentrations near the release point where concentrations are reduced primarily by dilution.

3.3. *Model Input Data*

One needs values for several parameters to execute the model: the total mass of chemical released, chemical properties, river flow rate, river width, and river depth. The Material Safety Data Sheet (MSDS) is the first place to search for information and it can typically provide the physical and chemical properties. The MSDS should be reviewed closely to determine if the model is applicable. The MSDS may also have human

and aquatic toxicity information for the chemical of interest. The USEPA has excellent websites, such as IRIS (Integrated Risk Information System) [8] for human toxicity information and ECOTOX (ECOTOXicology) [9] database, for aquatic toxicity information. The mass of chemical released can be estimated from the container volume and the chemical density. The mass of each component of a mixture is modeled separately.

The USGS [10] website has river flow rate and other data measured at over 8000 sites. If one is modeling an actual event then the river conditions at the time of the event should be used. If one is modeling a hypothetical event, then a range of river conditions [1, 11] could be evaluated such as small, medium, and large rivers.

This study evaluates a hypothetical spill into two surface waters; Granny Creek which discharges into the Elk River, a small river located in central West Virginia, USA. This study illustrates a common occurrence where a spill initially flows into a creek with a small flow rate which discharges into a river with a larger flow. This study also illustrates how the river flow conditions can vary significantly. Table 1 presents USGS [10] measured values for six flow conditions. The flow, width, and depth vary with the flow conditions. The minimum flow rate represents the worst case since there is the least amount of water available for chemical dilution and it would result in the highest chemical concentration while the maximum flow rate represents the best dilution case.

Table 1. Flow conditions for the Elk River and Granny Creek.

River	Flow cond.	Flow (m^3/s)	Width (m)	Depth (m)
Elk River	Min.	0.01	32.9	0.4
	10^{th} pct.	12	63.7	1.8
	50^{th} pct.	40	70.7	2.3
	Mean	59	73.2	2.5
	90^{th} pct.	142	79.3	3.0
	Max.	1646	98.8	4.9
Granny Creek	Min.	0.001	1.8	0.001
	10^{th} pct.	0.05	3.3	0.02
	50^{th} pct.	0.2	4.0	0.06
	Mean	0.3	4.1	0.09
	90^{th} pct.	0.6	4.6	0.15
	Max.	8.0	.6	1.04

3.4. *Model Calibration*

The RDM2D performance is evaluated by comparing its predictions to measured concentration values reported in Ref. 12 for releases of radioactive tracers into Copper Creek near Gate City, VA, USA. The Copper Creek data set measured concentrations as close as 0.2 km to the release point for flow rates in the same range as those for Granny Creek. RDM2D was executed to match the reported experimental conditions as closely as possible for each of the four sets of experimental data. The model has been previously calibrated with other chemicals in other rivers. Environment Canada [13] developed the EnviroTIPS manual for use by specialists to assess spill effects on the environment. The RDM2D predictions were compared to the EnviroTIPS example for a 20 tonne spill of acetic acid in a river. RDM2D predicted concentrations were compared to the measured and predicted concentrations reported in Ref. 6 for an actual 791,000 kg spill of ethylene dichloride into a river after a train derailment.

3.5. *Risk Characterization*

The USEPA[2, 14] guidance documents provide detailed discussions of the risk characterization for exposure to contaminated water. Although this paper provides a simple discussion of risk characterization and the selection of a toxicity benchmark, this complex topic has been ignored in most papers on modeling exposure to an instantaneous chemical spill. To quantitatively characterize the risk to humans and aquatic life for a chemical spill, the predicted chemical concentration should be compared to an appropriate toxicity benchmark, exposure duration, and health effect. Because a spill typically has a short release duration and it occurs infrequently, a spill is difficult to evaluate because the concentration and duration of exposure vary with distance from the release point and the time after the release. This section is intended to provide guidance to emergency response planners on how to better characterize the health risk. Although it is common to use a national primary drinking water regulation (*e.g.*, a drinking water standard) or perhaps use a discharge limit from a wastewater treatment plant to characterize the exposure, these apply to a continuous release and they may provide an overly conservative risk characterization for an instantaneous spill.

The most commonly evaluated human exposure scenario for a chemical spill into a river is drinking contaminated water, perhaps because a large population could potentially be exposed via a contaminated potable water distribution system. One should compare the oral exposure to the appropriate oral toxicity benchmark to

evaluate this scenario. Dermal exposure may also occur via a contaminated potable water system and the dermal exposure should be compared to an appropriate dermal toxicity benchmark. If the chemical causes skin irritation, then the predicted chemical concentration may be compared directly to a concentration based on a skin irritation benchmark. Inhalation exposure may occur via a contaminated drinking water system due to the chemical evaporation in a shower or bathtub, and the inhalation exposure should be compared to an appropriate inhalation toxicity benchmark. The ingestion of contaminated fish is not typically considered a significant source of exposure for a single chemical spill into a flowing river because the fish would likely have negligible uptake within the limited time frame.

The human risk can be simply characterized using the hazard quotient (HQ) described in Eq. (4):

$$HQ = \frac{EXP}{TOX} \tag{4}$$

where EXP is the calculated exposure (mg/kg body weight/d) and TOX is the toxicity benchmark (mg/kg body weight/d). A HQ value less than one is typically acceptable provided the toxicity benchmark includes appropriate uncertainty factors (UF) for the extrapolation of the test animal response to humans. The individual chemicals in a mixture are evaluated separately because the human health impact is based on the effect for the individual chemical. The total exposure may be characterized by summing the HQ value for each of the chemicals. There is potential for risk if an individual HQ is greater than one or the sum of all HQs (called the Hazard Index or HI) is greater than one. If the HQ or HI is unacceptable then the exposure analysis may be refined.

One would prefer to compare the predicted exposure to a toxicity benchmark derived from an acute dose which had no adverse health effect to the tested species or perhaps a temporary health effect, such as irritation. Although the LC_{50} is a commonly available acute toxicity concentration, this is not an appropriate effect for human exposure since it is based on death of 50% of the test animals. If appropriate acute human toxicity data are not available, then one may have to use a toxicity benchmark based on repeated dose (*i.e.*, chronic) animal exposure, have a study performed to determine the toxicity, or use a surrogate with similar chemical properties.

The USEPA[15] has established an enforceable standard, the maximum contaminant level (MCL), in drinking water for about 80 chemicals. The MCL has a low value because it applies to long term, repeated oral exposure. The chemical concentration to which one may be exposed should ideally be lower than the MCL value. However, it is conservative to compare a chemical concentration from a single spill in a river with short exposure duration to the MCL which is based on long term exposure and this point is missed in some risk assessments.

As an alternative to the MCL, the USEPA [16] established Health Advisories (HA) as an estimate of the acceptable drinking water level which can be used for evaluating a chemical spill. Although the HA provides guidance on acceptable exposure, it is not a legally enforceable Federal standard. The one-day, ten-day, and lifetime HA values are considered protective of adverse noncancer health effects in a child who may receive a greater dose (*e.g.*, on mg/kg basis) than an adult. A short duration toxicological study may be used to derive a one-day HA although a long duration toxicological study may be substituted. The one-day HA is derived using Eq. (5):

$$HA = \frac{NL \times BW}{UF \times DWI} \tag{5}$$

where the NL is the no observed adverse effect level, NOAEL, (mg/kg/d) from a study of an appropriate duration, BW is the body weight (kg), UF (unitless) is the total uncertainty factor, and DWI is the default daily water intake for a child (1 l/day). The default body weight of 10 kg correlates to a one year old child. The entire chemical dose is assumed to be from drinking water contaminated by the chemical spill. Only the lifetime HA has an adjustment for possible carcinogenicity. The USEPA [12] provided guidance on selecting the uncertainty factors; their values depend on the quality of the available toxicity studies, the extent of the chemical toxicity database, and scientific judgment. The Integrated Risk Information System (IRIS)[8] may be helpful for deriving a HA value since it has a compilation of human health effects including the oral NOAEL for approximately 540 chemicals.

Human exposure to a chemical spill via a contaminated potable water system may have a low probability of occurrence, so this study also evaluated

the aggregate exposure (oral, dermal, and inhalation) for a fisherman. It is assumed the fisherman incidentally ingested contaminated water while wading in the creek and the oral dose is estimated using Eq. (6):

$$Dose_{oral} = \frac{C_w \times I_{dw}}{BW} \quad (6)$$

where $Dose_{oral}$ is the oral dose (mg/kg/d), C_w is the water concentration (mg/l), I_{dw} is the drinking water intake rate (l/d), and BW is the adult body weight. The dermal dose is estimated using Eq. (7):

$$Dose_{dermal} = \frac{C_w \times SA_{skin} \times T_{film} \times DA \times E}{BW \times 1000 cm^3 l^{-1}} \quad (7)$$

where $Dose_{dermal}$ is the dermal dose (mg/kg/d), C_w is the water concentration (mg/l), SA_{skin} is surface area of the skin (cm^2), T_{film} is the water film thickness on the skin (cm), DA is the relative dermal absorption of the chemical (%), and E is the number of events per day. The inhalation dose is estimated using Eq. (8):

$$Dose_{inhalation} = \frac{C_{air} \times I_{air} \times D}{BW} \quad (8)$$

where $Dose_{inhalation}$ is the inhalation dose (mg/kg/d), C_{air} is the air concentration (mg/m^3), I_{air} is the default inhalation rate (m^3/h), and D is the exposure duration (h/day). The methanol evaporation rate is estimated using an evaporation model [17]. The methanol concentration in the air over the spill is estimated using the evaporation rate in a simple air dispersion model [18]. The USEPA[19] characterizes the acute exposure to fish or invertebrate species using the risk quotient (RQ) approach described in Eq. (9):

$$RQ = \frac{EXP}{TOX} \quad (9)$$

The RQ is a single point estimate of acute risk based on EXP, the peak chemical concentration (mg/l) in the river and TOX, the single point estimate of the toxicity (mg/l), either the LC_{50} or the EC_{50}. The LC_{50} is a lethal effect and the lowest value (most sensitive) of all tested freshwater species is typically used. The USEPA[19] interprets a RQ less than 0.1 as acceptable in most cases. However, the USEPA requires a RQ less than 0.1 for an endangered species and it may be appropriate to use a lower RQ for commercially or recreationally important species. The risk characterization is more complicated because there are many aquatic species and test data are reported for different test conditions, effects, and units. One should select a species which could be present in the river of interest.

4. Results

RDM2D is applied in a case study to illustrate the approach to evaluate human and aquatic exposure for a hypothetical spill. The results are discussed below.

4.1. *Model Performance*

RDM2D conservatively over predicts the measured concentrations reported in Ref. 12 by up to a factor of 2.8 at distances greater than 0.7 km downstream of the release point in the model calibration, as shown in Fig. 1. RDM2D under predicts the measured concentrations by a factor of 0.4 to 0.7 at 0.2 km from the release point.

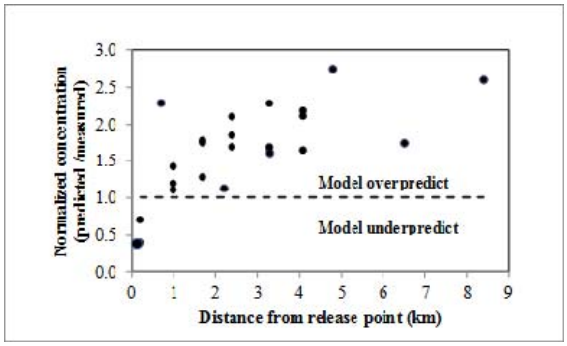

Fig.1. RDM2D Normalized (predicted/measured) concentrations versus distance from the release point.

Another measure of model performance is how well it predicts the time for the arrival of the peak concentrations. RDM2D under predicts the measured time for the arrival of the peak concentrations; it under predicts as much as a factor of two at distances beyond 5 km.

4.2. *Toxicity Benchmarks*

Methanol does not have a MCL or a HA so a one-day HA is developed. The reported RfD [8] is 0.5 mg/kg/d based on the NOEL of 500 mg/kg/d from a subchronic oral study in rats using a total UF of 1,000. The current analysis used the NOEL and a UF of 10 to account for

interspecies extrapolation (from animals to humans) and a UF of 10 to account for intraspecies extrapolation (potentially sensitive individuals). This analysis did not include the USEPA [8] proposed UF of 10 to account for extrapolation from subchronic to chronic exposure since this analysis is determining an acceptable exposure for one-day of exposure rather than chronic exposure. The one-day HA is calculated as 50 mg/l using Eq. (5).

The aggregate exposure calculation requires an inhalation dose and a toxicity benchmark. The USEPA has not established an inhalation toxicity benchmark for methanol. A chronic reference exposure level (REL) [20] of 4 mg/m^3 was established after observation of developmental malformations in mice. This study converted the REL to an allowable daily dose of 1 mg/kg/d for an adult with a mean inhalation rate [21] of 20 m^3/d and a mean body weight [21] of 80 kg.

The ECOTOX [9] database reports over 400 values for methanol. The MSDS [22] reports methanol toxicity results for several freshwater aquatic species. *Daphnia pulex*, a common species of the water flea, has a LC_{50} of 19,500 mg/l for the 18 h test duration. *Daphnia obtuse*, another common species of the water flea, has an EC_{50} of 23,500 mg/l for the 24 h test duration. *Pimephales promelas* (fathead minnow) has a LC_{50} of 29,700 mg/l for the 24 h test duration. Daphnia has a no observed effect level (NOEL) of 10,000 mg/l for the 48 h test duration. The no-observed-effect concentration (NOEC) to a freshwater aquatic ecosystem is reported in Ref. 23 as 23.75 mg/l based on sublethal effects of methanol in a mesocosm study for a 90 day period. The LC_{50} of 19,500 mg/l for *Daphnia pulex* was selected to calculate the RQ for lethal effects and the NOEC of 23.75 mg/l was selected as the no effect concentration.

4.3. *Model Predictions*

RDM2D is used to predict concentrations versus distance downstream from the release point for the hypothetical methanol spill scenario because a specific location in a river could not be identified where a person might be exposed (*e.g.*, a drinking water intake). Figure 2 presents the predicted methanol concentrations versus distance for a spill into Granny Creek.

Table 2 summarizes the predicted distances to methanol toxicity benchmarks for the different flow conditions. The spill would be diluted below the LC50 concentration of 19,500 mg/l within about 130 m of the release point for the 10th percentile flow, within 28 m for the mean flow rate, and within 17 m for the 90th percentile flow rate in Granny Creek.

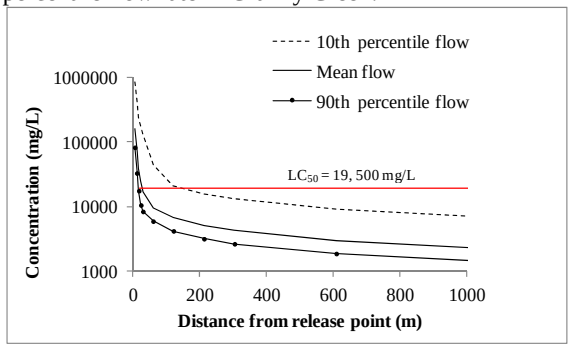

Fig.2. RDM2D predicted methanol concentrations versus distance in Granny Creek.

The spill would be diluted below a concentration of 1,950 mg/l (which is equal to an RQ of 0.1) within about 13,700 m for the 10th percentile flow, within 1,430 m for the mean flow, and within 560 m for the 90th percentile flow. The predicted distances to concentrations below the NOEC of 23.75 mg/l far exceed the actual length of the creek. The distance to the HA value of 50 mg/l is not predicted because Granny Creek is not a drinking water source.

Table 2. Summary of model predicted distances to the toxicity benchmarks for various flow conditions.

River	Flow cond.	Toxicity benchmark	Value (mg/l)	Distance to (m)
Granny Creek	10th pct.	LC_{50}	19,500	130
	Mean	LC_{50}	19,500	28
	90th pct.	LC_{50}	19,500	17
	10th pct.	RQ=0.1	1,950	13,700
	Mean	RQ=0.1	1,950	1,430
	90th pct.	RQ=0.1	1,950	560
	10th pct.	NOEC	23.75	>10^6
	Mean	NOEC	23.75	>10^6
	90th pct.	NOEC	23.75	>10^6
Elk River	10th pct.	LC_{50}	19,500	<1
	Mean	LC_{50}	19,500	<1
	90th pct.	LC_{50}	19,500	<1
	10th pct.	RQ=0.1	1,950	7
	Mean	RQ=0.1	1,950	4
	90th pct.	RQ=0.1	1,950	3
	10th pct.	1-d HA	50	70
	Mean	1-d HA	50	40
	90th pct	1-d HA	50	30
	10th pct.	NOEC	23.75	120
	Mean	NOEC	23.75	80
	90th pct.	NOEC	23.75	70

Figure 3 shows the predicted concentrations are much lower for the same spill into the Elk River. The spill would be diluted below the LC_{50} of 19,500 mg/l at a distance of about one m from the release point for all flow rates. The spill would be diluted below 1,950 mg/l (equivalent to an RQ of 0.1) for the 10th percentile flow rate within about 7 m from the release point, within 4 m for the mean flow rate, and within 3 m for the 90th percentile flow rate. The spill would be diluted below the HA of 50 mg/l for the 10th percentile flow rate within about 70 m from the release point, within 40 m for the mean flow rate, and within 30 m for the 90th percentile flow rate. The spill would be diluted below the NOEC of 23.75 mg/l for the 10th percentile flow rate within about 120 m from the release point, within 80 m for the mean flow rate, and within 70 m for the 90th percentile flow rate.

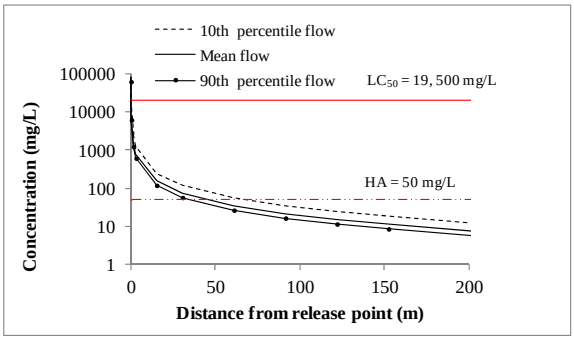

Fig.3. RDM2D predicted methanol concentrations versus distance in Elk River.

Figure 4 presents some details on travel time and methanol concentrations versus time for the spill into Granny Creek during the 10th percentile flow rate. The spill length is stretched and the peak concentration decreases as the spill flows downstream. This type of analysis might be performed at a drinking water intake.

- At 300 m downstream, the leading edge of the spill arrives after 60 s, the peak arrives at 220 s, and the trailing edge passes at 760 s, the potential exposure duration is about 700 s, and the time weighted average (TWA) concentration is estimated as 4,075 mg/l using Eq. (3).
- At 600 m downstream, the leading edge of the spill arrives after 200 s, the peak arrives at 470 s, and the trailing edge passes at 1,000 s; the potential exposure duration is about 800 s and the TWA methanol concentration is 3,150 mg/l.

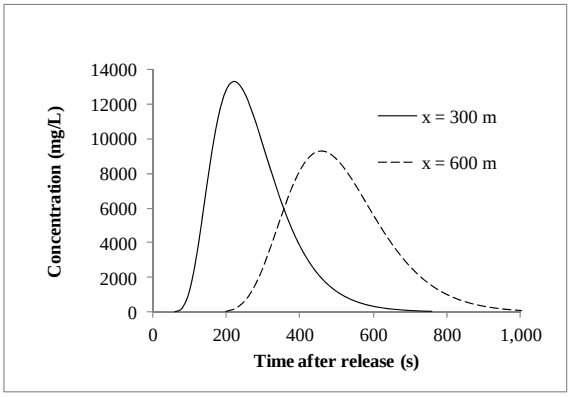

Fig.4. RDM2D predicted methanol concentrations versus time after release into Granny Creek.

4.4. *Aggregate Human Exposure*

The aggregate exposure is evaluated for an adult fisherman wading in Granny Creek using the worst case scenario with the highest predicted concentrations for the spill during the 10th percentile flow rate. It evaluated the TWA concentration at 300 m downstream of the spill. Granny Creek is only 0.02 m deep and 3.3 m wide during the 10th percentile flow rate.

It is assumed that the fisherman immersed his feet and the dermal dose is calculated using the following assumptions: C_w is the TWA methanol concentration of 4,075 mg/l, SA_{skin} is mean surface area of the adult male feet [21] of 1,370 cm^2, T_{film} is the water film thickness on the skin [21] of 0.005 cm, E is one event per day, DA is the default relative dermal absorption of 100 %, and BW is the default mean adult body weight [21] of 80 kg. The predicted dermal dose is calculated as 0.35 mg/kg/d using Eq. (7) and the HQ_{dermal} is calculated as 0.13 using Eq. (4).

The inhalation dose calculation assumed the fisherman inhaled methanol evaporating from the spill. The methanol evaporation rate is estimated as 0.025 g/s at 298K for a 1 m/s wind speed using the evaporation model. The methanol concentration in the breathing zone over the spill, C_{air}, is estimated as 2.9 mg/m^3 using the air dispersion model. The default inhalation rate [21], I_{air}, is 0.013 m^3/min and D is the exposure duration of 11.7 min. The predicted inhalation dose is calculated as 0.006 mg/kg/d using Eq. (8) and the $HQ_{inhalation}$ is calculated as 0.01 using Eq. (4).

The USEPA [21] reported an incidental water ingestion of 0.053 l/event (maximum value) for an adult during swimming or diving activities and this value is extrapolated to 0.053 l/d for a fisherman wading in Granny Creek. The worst case oral dose is calculated for incidental ingestion of methanol contaminated water using the following assumptions: the water concentration, C_w, is 4,075 mg/l, and the incidental water ingestion, I_{drw}, is 0.053 l/d. The predicted oral dose is calculated as 2.7 mg/kg/d using Eq. (6) and the HQ_{oral} is calculated as 0.54 using Eq. (4). The aggregate HQ (or HI) of 0.62 is the sum of HQ_{dermal} of 0.07, the $HQ_{inhalation}$ of 0.01, and the HQ_{oral} of 0.54; the HI value is acceptable since it is less than one.

5. Discussion

The RDM2D model allows for a quick screening analysis of a chemical spill by providing details about its dilution and travel time. The model shows the highest concentrations occur within the mixing zone and decrease with distance from the release point. RDM2D calculates the peak concentration on the release centerline at the river surface as a function of downstream distance in the mixing zone. This provides a conservative screening estimate since the maximum predicted concentration is on the release centerline. The release centerline location is influenced by river flow irregularities and one cannot simply predict its exact location. The RDM2D model under predicted measured concentrations at 0.2 km from the release and it over predicted as much as a factor of three at distances greater than 0.7 km from the release. Ref 5. states if the model predicted concentration value is within a factor of four of the observed value then this is considered a reasonably good agreement. The rationale is that dilution varies in a river due to irregularities (bends, sandbars, dead zones, riffles, structures, etc.) which alter the dilution but cannot be precisely defined so the mixing coefficients cannot be accurately defined nor can their variability be considered in a simple model. The RDM2D predictions compared well to predictions from the two other screening models[6, 13]. The model performance may be improved by tuning it to the river of interest using a better representation of the channel shape and cross-sectional area.

RDM2D conservatively assumes there is no chemical loss due to hydrolysis, evaporation, reaction, or sorption. Although this assumption may cause it to over predict concentrations for long travel times, it is a reasonable assumption because the travel time is shorter (highest travel time is three h in Granny Creek) than the chemical decay half-life in the river (lowest value is about one d) as discussed below in environmental fate.

This study identified several key parameters for dilution of a chemical spill and exposure. The river flow rate is a critical parameter; the highest concentration occurs for the lowest flow condition. Table 1 shows a wide range in flow conditions, for example the 90th percentile flow rate is about 12 times greater than the 10th percentile flow rate for both Granny Creek and the Elk River. Granny Creek provided much less dilution especially at low flow conditions. The spill travel time is important because the slowest travel time and the highest potential exposure duration occurs for the low flow conditions. The predicted spill travel time is also important for emergency response immediately after a spill; the fastest travel time gives less time to respond and it occurs for high flow conditions. The spill mass is a key exposure parameter because the predicted chemical concentration is directly proportional to the mass.

For the small methanol spill example, the human impact based on the one-day HA value of 50 mg/would be limited to a distance less than 70 m from the release point in Elk River. The Elk River has a greater capacity to dilute a spill since its 10th percentile flow rate is 240 times greater than that for Granny Creek. For a methanol spill into Granny Creek, the concentrations would be quickly diluted as the stream flows into the Elk River; the spill dilution below 50 mg/l is estimated to occur within 70 m from the above results.

If the USEPA has not developed a HA value for the chemical of interest then the risk characterization for a chemical spill can be complex. One can see why it is common to simply use a drinking water standard, such as a MCL, to characterize the exposure to a spill even though it applies to a continuous exposure. However, the HA provides a higher allowable exposure for a spill than the MCL. For example, the one-day HA for toluene is 20 times higher than its MCL.[16] The one-day HA derived in this study provides a conservative toxicity benchmark since it is based on a NOAEL from a repeat dose study rather than a short duration study.

The aggregate exposure approach provides another way to characterize the potential human exposure to a spill that is more realistic if exposure via contaminated

drinking water has a low probability of occurrence. The aggregate exposure calculation, which evaluated an adult fisherman wading in the creek, is more relevant to Granny Creek since it is not used as a drinking water source. Oral exposure has the highest hazard quotient (HQ_{oral} of 0.54). However, the HI of 0.08 for inhalation and dermal exposure would better characterize the potential exposure if there is no incidental ingestion of the contaminated creek water.

Figure 4 shows the exposure duration is about 0.2 h for the spill into Granny Creek at the 10th percentile flow rate. Because the LC_{50} value is based on an 18 h test duration, it provides a very conservative risk characterization; the calculated exposure duration of only 0.2 h is 90 times lower than that for the LC_{50} test. Others [24] have reported the inconsistency of using LC_{50} results based on 48 or 96 h tests to characterize the aquatic risk for a spill with a short exposure duration. However from a practical standpoint, one must either use the available LC_{50} test results or perform additional toxicity testing. It is assumed that the remaining aquatic population will recover, but the recovery could take a long time during which the rest of the aquatic community and food chain are disturbed. The spill concentration would never be diluted below the no effect concentration, the NOEC, in Granny Creek for the 10th percentile flow rate but it would be diluted within about 120 m after it flows into the Elk River.

Ref. 4 reports the fate of methanol spilled into surface water. Methanol is completely miscible in water and it will dissolve quickly. Methanol will biodegrade after its concentration is diluted below the toxic level. Its biodegradation half-life (the time required for 50% mass reduction) is 1 to 7 days in surface water. Methanol is not expected to adsorb to suspended solids and sediment. Its bioconcentration potential in aquatic organisms is low. [22] Methanol evaporates slowly from an aqueous solution because the methanol molecules form a strong bond to the water molecules. The USEPA [25] EPI Suite™ v4.1 program predicted the volatilization half-life as three days using its river model with the default conditions.

6. Conclusions

The RDM2D model is suitable for a practical, screening level analysis of an instantaneous chemical spill into a non-tidal river. The model predicted concentrations provided reasonably good agreement in the calibration to the measured values reported in the literature. Guidance is provided on quantifying river parameters, evaluating chemical properties, and characterizing the human and aquatic risks. If one is modeling an actual spill event then the river conditions at the time of the spill should be used. The flow conditions in a river can vary widely and this needs to be accounted for in modeling a hypothetical spill scenario. The low flow rate represents the worst case since it results in the highest chemical concentrations while the high flow rate predicts the fastest travel time giving less time for emergency response immediately after a spill.

The methanol spill example provides guidance which can be used to evaluate other chemical spill scenarios. Two approaches are presented to characterize the potential human risk from a hypothetical spill; exposure via drinking water and aggregate exposure. RDM2D predicted the small methanol spill in the Elk River would be diluted below the one-day HA value for human exposure within 30 to 70 m of the release point. The aggregate exposure (oral, dermal, and inhalation) for a fisherman wading in Granny Creek during the worst case flow conditions had a HI of 0.62 which is acceptable. The aquatic risk, based on 0.1 of the LC_{50} concentration (corresponding to an RQ of 0.1), could extend the entire length of Granny Creek while the spill into the Elk River would be diluted below this value within about 7 m. The spill would never be diluted below the no effect concentration in Granny Creek before it flowed into the Elk River, but the same spill into the Elk River would be diluted below the no effect concentration within about 120 m.

The human toxicity benchmark selection and the risk characterization can be a complex process. Characterization of the aquatic risk is complicated by the wide range of species, toxicity values, test durations, and effects. The approach described in this paper provides a better risk characterization for a spill. The human and aquatic toxicity benchmarks suitable for a continuous chemical release may be used when they are readily available but they may provide an overly conservative characterization of a spill and this point is missed in some risk assessments.

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