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A simplified approach to evaluate human and aquatic exposure to a chemical spilled in a river

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ABSTRACT

This study presents an approach and a model to evaluate the potential exposure from an episodic chemical spill into a river. The River Dilution Model (RDM) was developed to predict chemical concentrations in a river as a function of the downstream distance and the time after an instantaneous release. RDM is one-dimensional dilution model in an Excel spreadsheet which allows for a quick screening appraisal. RDM predictions showed reasonably good agreement with measured values of peak concentration and arrival time at distances of 3.1–7.7 km downstream of the dye release point. RDM significantly over predicted peak concentrations at greater distances because it did not consider chemical removal processes occurring in the long travel time. This paper describes how to use the predicted chemical concentrations to assess the potential human and aquatic hazards. Several sources of information were identified to define model input and toxicity information. RDM and the approach were applied in a case study to demonstrate how to evaluate the potential hazard for a spill of hydraulic fluid. The approach will enable facilities to assess potential impacts with readily available tools, and then decide which engineering or administrative controls are needed to prevent or manage a chemical spill.

1. Introduction

Evaluating the potential exposure to an episodic chemical spill into a river is a critical interest for the chemical industry and hazardous materials professionals. In evaluating a chemical spill, the potential human and aquatic exposures must be quantified to determine the hazard or risk. For either a hypothetical release or an actual release, the first step is to determine the chemical concentrations in the river. This paper presents an approach which describes how to use the predicted concentrations to assess the potential exposures and determine the hazard. It is a significant contribution because little information has been published on how to use the model predicted concentrations.

Mathematical models are frequently used to estimate the distribution of a chemical in surface water after a hypothetical or an actual spill. Leeuween et al. [1] describe the models as ranging from a simple equation to a sophisticated model for evaluating for an entire river system. The sophisticated models may consider removal processes, such as volatilization, adsorption, and degradation as well as the hydrodynamics for a river, lake, or estuary. Although most of the simple river models ignore the removal processes, a simple model may be applied when concentrations are reduced primarily by dilution and the elapsed time after the spill is too short for the removal processes to reduce the concentration. Perhaps, the simplest model is the USEPA [2] initial dilution equation. Several one-dimensional river dilution models have been reported on [3–7]. Fischer et al. [8] provided the theoretical basis for many of these models. Martin et al. [9] suggest a simple one-dimensional model may suffice in some cases and the simple model will require less input data and training than a sophisticated model.

Some of the sophisticated models include advanced modeling technology combined with a geographical information system (GIS) to better support planning and real-time response to spills. GIS is valuable in that some data are more easily conveyed in a geographical context than in a tabular form. Camp et al. [10] describe the Spill Management Information System (SMIS 2.0) and its simulation of hypothetical oil and a chemical spills within the Tennessee River to pre-plan the boom placement locations, the containment strategy, and resource needs. Samuels et al. [11] describes another GIS based system, RiverSpill, for chemical spill response, planning, and training which has been applied to numerous river systems. Wang et al. [12] describe the GIS-ROUT model for determining the concentration of a chemical discharged from wastewater treatment plant using a with a one-dimensional river flow model in a sophisticated GIS system. The National Oceanic and Atmospheric Administration [13] developed GNOME (General NOAA Operational Modeling

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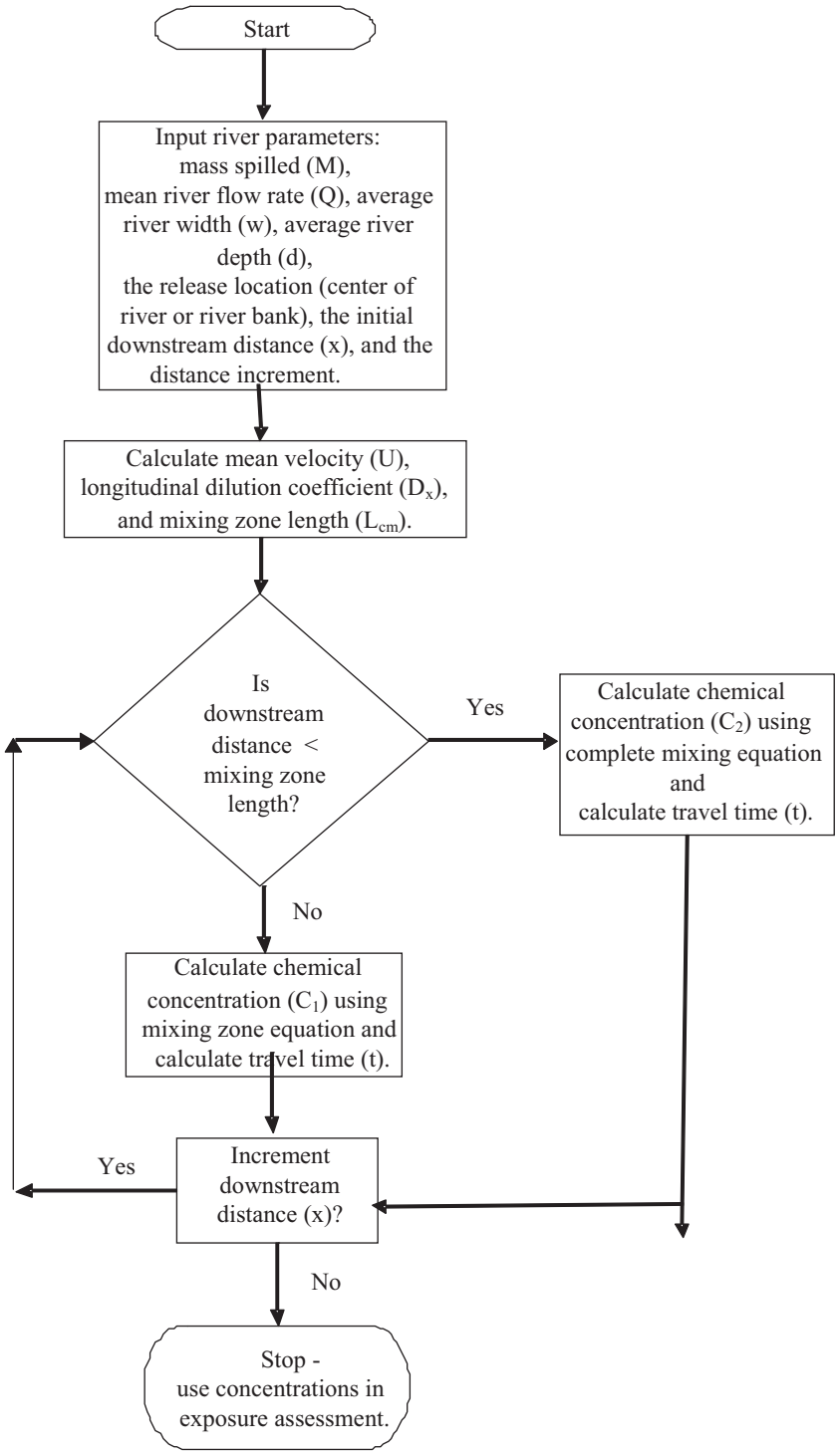

Fig. 1. Flowchart for calculation of peak concentration versus distance from release point.

Environment) which is commonly used to evaluate the trajectory of an oil spill, although it does not appear to apply to soluble chemicals. The Center for Exposure Assessment Modeling (CEAM) website lists several surface water models developed by the USEPA [14] and a few of these public-domain models may be used to evaluate chemicals released into a river. Some of the sophisticated models link to the human and aquatic toxicity data from the Chemical Hazards Response Information System (CHRIS) developed by the U.S. Coast Guard or other sources toxicity information [9].

This paper presents a model, RDM, which can be used to simply, quickly, and inexpensively perform a screening evaluation for either a generic chemical spill or a specific spill situation.

RDM was developed using several simplifying assumptions to minimize the input data requirements. Many catastrophic events release liquids quickly enough to be modeled as an instantaneous spill (i.e. a slug dose), for example, ruptures of a storage tank, tank truck, or hydraulic line. The screening model can predict concentrations in a river for an instantaneous chemical release; a continuous release is not discussed.

This paper also presents an approach to use the predicted concentrations to assess the potential exposure. There has been little published on how to use model predicted concentrations to evaluate the exposure and hazard, probably because it involves two different scientific fields; mammalian toxicology and aquatic toxicology. Some response planning models simply compare the predicted chemical concentration to a level of concern extracted from a toxicity database. Unfortunately, the toxicity database may not have information for the chemical of interest or the toxicity data may not be for the appropriate exposure duration and health effect to evaluate acute human exposure to a chemical spill, as discussed in Section 3.

The objective of this paper is to present a simplified approach to predict concentrations from a chemical spill in a river and how to use the predicted concentrations to characterize the potential human and aquatic hazards using appropriate toxicity benchmarks.

2. Approach

The development of the dilution model for an instantaneous release, model performance, selecting model input data, calculating exposure, and hazard characterization are discussed below.

2.1. Model description

RDM predicts the peak concentration on the flow centerline as a function of the downstream distance from the release point and the time after an instantaneous chemical spill on a river surface. The Excel spreadsheet presents the predictions in tabular and graphical formats and the model is provided in supplemental information. RDM assumes a point release with negligible momentum or buoyancy; the release location may be either the river bank or the center of river. Chemical dilution is due to the water turbulence and it is quantified using lateral and longitudinal mixing (i.e. dispersion) coefficients whose values depend primarily on the water velocity. Because concentrations in the lateral (e.g., y) direction are not calculated, the lateral mixing term is ignored in the RDM dilution calculations. Vertical mixing of the chemical is assumed to be fast compared to the longitudinal mixing and mixing in the vertical (e.g., z direction) is also ignored in the dilution calculations. Chemical dilution within the mixing zone uses a Gaussian dilution equation with a river bank reflection term, as shown in Eq. (1):

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

where C_1 is the peak concentration (mg L^{-1}) on the plume centerline in the mixing zone; M is the chemical mass spilled into river (g); t is the time after chemical spill enters the river (s); D_x is the longitudinal dispersion coefficient (m^2 s^{-1}), and x is the longitudinal distance downstream of the release point (m).

Chemical dilution beyond the mixing zone after the plume is uniformly mixed across the river width uses Eq. (2):

$$C_2 = \frac{M}{4\pi(AD_x t)^{0.5}} \quad (2)$$

where C_2 is the peak concentration after uniform mixing (mg L^{-1}); and A is the cross sectional area (m^2). Three additional key parameters, not shown, are the longitudinal mixing coefficient, the length of the mixing zone, and the lateral mixing coefficient required in the mixing zone equation. All the equations are described in detail in Neely and Lutz [5] and Fischer et al. [8]. Fig. 1 presents a flowchart with the key steps in calculating the peak concentration versus distance from the release point.

RDM assumes the river flow, width, and depth are uniform for the entire reach. Fischer et al. [8] suggest this approach is acceptable for many practical problems because the actual cross section shape is not known and will probably vary for a natural river. Fischer et al. [8] also state a high accuracy in estimating mixing coefficients is not necessary because all the irregularities in the river, which cause mixing, are not known and can not be considered in a simple model. RDM initially calculates the peak concentration on the centerline ($y = 0$) at the river surface ($z = 0$) as a function of downstream distance (x) as shown in Fig. 2. Since the release centerline location is influenced by river flow irregularities, one cannot predict its exact location, and it is conservative to use the maximum concentration on the release centerline for a screening evaluation. RDM was developed using common units of feet, miles, and pounds because many of the data sources report common units and common units are more convenient for non-technical users.

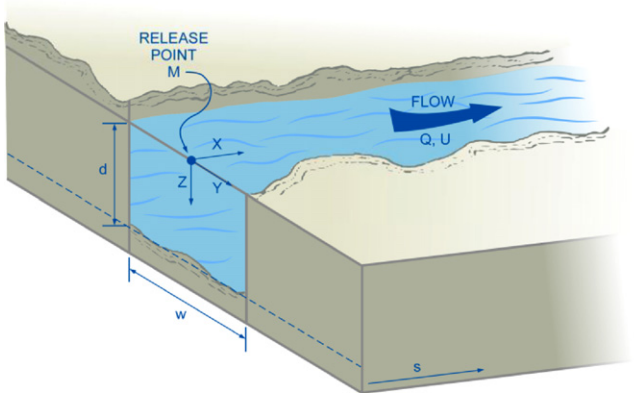

Fig. 2. An illustration of the RDM idealized river cross-section, the important parameters, and the cartesian coordinate system.

Because an instantaneous release will be dispersed and stretched as it is transported down river, the following additional calculations were included to better interpret the model results: the length of the release at a specific distance and the travel times for both the leading and trailing edge of the release. Fischer et al. [8] described the equations and the logic behind including these parameters where a length of four standard deviations (σ) contains 95% of the mass of the release. Fig. 3 illustrates the predicted chemical concentration versus distance for a release moving down the river; the peak concentration is 450 mg L^{-1} at 1 km from the release point while the leading edge is at about 1.5 km and the trailing edge is about 0.5 km as defined by 95% of the mass of the release. RDM can be used to estimate the travel time for a spill to reach a specified distance downstream from the release point, such as a drinking water intake. However, if there is a spill, it is advisable to issue a warning to close water intake to prevent human exposure via a drinking water intake.

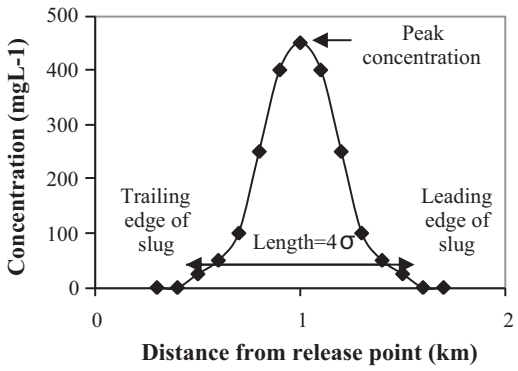

Fig. 3. Chemical concentration versus distance from the release point.

Table 1
Soldier Creek parameters.

Measurement site #	Distance from dye release point (km)	Width (m)	Depth (m)	Flow ($m^3 s^{-1}$)	Velocity ($m s^{-1}$)
1	0.32	6	0.3	0.5	0.3
2	3.1	3.7	0.9	0.5	0.1
3	5.8	8.2	0.5	0.5	0.1
4	7.7	2.9	1.5	0.5	0.1
5	16.1	4.3	0.3	0.5	0.3
Average conditions		5.2	0.8	0.5	0.2

Table 2
RDM predicted peak concentrations compared to measured values for a dye release.

Site #	Distance from dye release point (km)	Prediction for site 1 conditions ($mg L^{-1}$)	Prediction for average conditions ($mg L^{-1}$)	Measured value ($mg L^{-1}$)
1	0.32	3.4	2.6	8.0, 25.3[a]
2	3.1	1.1	0.9	0.53
3	5.8	0.8	0.6	0.32
4	7.7	0.7	0.5	0.22
5	16.1	0.5	0.4	0.05

[a]Bath et al. [15] show a maximum measured value of 8.0 $mg L^{-1}$ with the actual value off the scale; Neely [3] reported 25.3 $mg L^{-1}$.

2.2. Model performance

RDM performance was evaluated by comparing its predictions to measured concentration values from a water soluble uranine dye test in Soldier Creek near Grove, Kansas as reported by Bath et al. [15]. This data set was selected over other studies because it measured concentrations as close as 0.32 km to the release point and as far downstream as 16.1 km. Table 1 presents the creek parameters used for RDM input for each measurement site and the average value for the five sites. Although the creek flow was the same at all the measurement sites, the creek width and depth changed downstream from site 1 so the velocity decreased. Because RDM applies to a single set of input parameters (e.g., a single reach), it was executed for two conditions; the creek parameters for site 1 (labeled as site 1 conditions) and the average creek parameters for sites 1–5 (labeled as average conditions) over the 16 km reach. Table 2 shows the RDM predicted concentrations compared to the measured concentrations. There is some experimental uncertainty at site 1, the measurement point closest to the dye release, RDM under predicted the reported concentration of 25.3 $mg L^{-1}$ by a factor of seven for site 1 conditions and it under predicted by a factor of ten for average conditions. However, RDM under predicted by only a factor of three for the reported concentration of 8.0 mg/L^{-1} at site 1. RDM over predicted the measured concentrations up to a factor of three for the sites 2, 3, 4 located 3.1–7.7 km downstream. RDM over predicted the measured concentrations by a factor of eight to ten at site 5 located 16.1 km downstream. Fig. 4 shows the RDM predicted concentrations versus downstream distance; RDM predicted slightly closer to measured values at sites 2, 3, 4, and 5 using the average conditions than using the site 1 conditions. RDM may be under predicting the concentrations at distances less than about 2 km based on Fig. 4.

Another measure of RDM performance is the predicted time for the arrival of the peak concentrations versus the measured values in the dye release. Table 3 shows the average conditions resulted in a closer prediction of the time of arrival of the peak concentration for all sites but site 1. Using the average conditions for the 16 km reach, RDM over predicted the time of arrival of the peak concentration at site 1 by a factor of two, it matched at site 2, it under predicted the time of arrival at sites 3 and 4 by up to 19% and it under predicted at site 5 by about a factor of two.

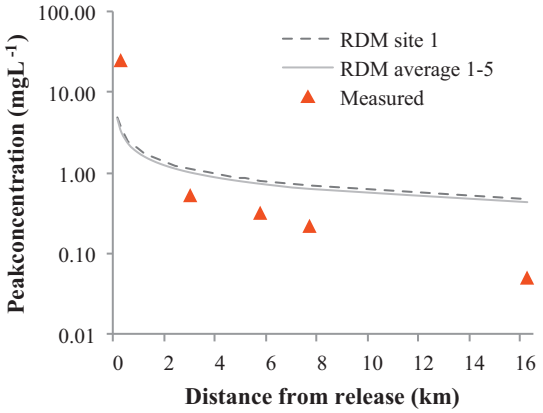

Fig. 4. RDM predicted chemical concentration versus distance from the release point compared to measured values.

2.3. Model accuracy

An agreement of the predicted concentration value within a factor of four of the observed value is reasonably good [8]. The rationale is dilution varies in natural rivers due to irregularities, such as bends, sandbars, dead zones, riffles, manmade structures, etc. These irregularities alter the dilution but they cannot be precisely defined

Table 3
RDM predicted time for arrival of peak concentration compared to measured values for a dye release.

Site #	Distance from dye release point (km)	Predicted for site 1 conditions (h)	Predicted for average conditions (h)	Measured value (h)
1	0.32	0.3	0.7	0.3
2	3.1	3.1	6.7	6.5
3	5.8	6	13	15
4	7.7	7.8	17	21
5	16.1	16	36	66

so the mixing coefficients cannot be accurately defined nor can their variability be considered in a simple model. Ahsan [16] evaluated several theoretical and empirical correlations for the longitudinal mixing coefficient, found considerable variation in the correlation predictions, and also reported its value may vary along the river reach as the parameters (depth, width, and velocity) change. Liu [17] reported his simple equation predicted the longitudinal mixing coefficient within a factor of six. It is difficult to accurately predict the concentrations in the mixing zone near the release and the model should not be applied closer than about 100 m from the release point. RDM conservatively assumes there is no chemical loss due to hydrolysis, evaporation, reaction, or sorption and this assumption may cause it to over predict concentrations for long times after the release.

2.4. Model caveats

RDM provides an approximate solution to a practical river mixing problem and shows the dependence of the most important parameters. The caveats for RDM application are it applies to non-tidal rivers with a defined water flow; it does not apply to high momentum releases, tidal rivers, lakes, estuaries, or the open sea. Some dilution problems will require a more sophisticated model and an expert user. RDM applies to soluble chemicals; it does not apply to slightly soluble chemicals such as heavy oils which may agglomerate and sink or to light oils which may float on the water surface. Assuming the river flow, width, and depth were uniform for the entire reach simplified the model development but this assumption should only be applied for downstream distances where there is no significant change in the river flow. RDM produces a discontinuity in the concentration predictions when it transitions from the mixing zone equation to the complete mixing equation.

2.5. Model input data

The first step in running RDM is to collect input values for the river flow rate, width, and depth. The U.S. Geological Survey (USGS) provides river flow rate data for the entire nation on the internet [18]. Real-time data are collected at over 8000 sites using automated equipment and these data are available online for 31 days. Daily values for the mean, median, maximum, and minimum flow rate are summarized for over 24,000 sites. Other websites associated with reservoirs or rivers may provide information, the Sabine River Authority [19] is an example.

The USGS [20] provides free topographical maps for download; the width of a large river can be estimated using one of these maps. Google is another internet source which provides free satellite maps. Maps can also be useful to evaluate a reach to identify tributaries where the river flow may increase. These maps typically do not have enough resolution to estimate the width for small streams. A Global Positioning System (GPS) can be used to estimate the width of large rivers since the resolution for a GPS is about 20–30 m.

The river depth typically varies with the flow rate. The depth can be estimated using a simple calculation in RDM based on Manning's formula provided the river flow rate, width, slope, and channel characteristics are known. A USGS topographical map with contour lines may be used estimate to estimate the slope of the river bed. If parameters for a specific river are not available, then one might use values for a similar river. For a generic spill screening study, one may simply evaluate a small, medium, or large river using the default values presented below.

The mass of chemical released is a key input parameter. If the mass is not known then it may be estimated from the storage capacity of the vessel. For a generic spill screening study, one may simply evaluate a small, medium, or large spill using the default values presented below.

The Material Safety Data Sheet (MSDS) should provide the physical and chemical properties for the spilled chemical; these should be reviewed to make sure the model applies. If the chemical is soluble in water it will tend to mix into the river but if it is partially soluble or insoluble it may not mix. If the chemical is denser than water it will tend to sink until it is diluted to the density of water and if the chemical is less dense than water it may float on the water surface. If the chemical is volatile, it may evaporate quickly. The temperature of both the spilled chemical and the environment are important since chemical properties typically vary with temperature. Ice cover on a river may decrease the dilution by decreasing the surface turbulence due to wind.

3. Hazard characterization

Although this paper provides only a simple discussion of hazard characterization and the selection of an appropriate toxicity benchmark, this complex topic has been ignored in most papers on modeling of chemical spills. One should review the USEPA [2,21] guidance document for a more detailed discussion of the health considerations for exposure to contaminated water. To characterize the human hazard associated with a chemical spill, the predicted chemical concentration should be compared to an appropriate toxicity benchmark, exposure duration, and health effect. Drinking water contaminated by a chemical spill is probably the most common exposure pathway and one should compare the oral exposure to the appropriate oral toxicity benchmark. Dermal exposure from swimming or bathing in contaminated water is another potential pathway and it should be compared to an appropriate dermal toxicity benchmark although the oral toxicity may be extrapolated if there is no dermal toxicity benchmark. If the chemical causes skin irritation, then the predicted chemical concentration may be compared directly to a concentration based skin irritation benchmark. The potential exposure to inhaled vapors from the evaporation of a volatile chemical is beyond the scope of this paper because it requires a sophisticated model. Ingestion of contaminated fish is not considered a significant source of exposure for a single chemical spill in a flowing river.

The predicted exposure should be lower than the human toxicity benchmark but how much lower depends on how the toxicity benchmark was developed since the benchmark may already include large uncertainty factors for extrapolation of the test animal response to humans. A chemical spill may be quickly diluted so the exposure duration may be short, i.e. an acute exposure. 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 LD_{50} is a commonly available acute toxicity benchmark, it is based on death of 50% of the test animals, and this is not appropriate effect for human exposure. If appropriate acute human toxicity data are not available, then one may have to use a toxicity benchmark based on chronic (repeated dose) animal exposure, as discussed below, or have a study performed to determine the chemical toxicity.

There are several sources of information on human response to chemical exposure. The MSDS is the first place to search for toxicological information for the chemical of interest. The USEPA [22] has established the maximum contaminant level (MCL) in drinking water, an enforceable standard, for about 80 chemicals. The MCL has a low value because it applies to long term oral exposure. For example, xylene has a MCL of 10 mg L^{-1} which includes an uncertainty factor of 1000 for extrapolation of the test animal response to humans. Some states have also established MCLs, for example

California [23] has set the xylene MCL at 1.75 mg L^{-1}. The chemical concentration to which one may be orally exposed from a spill should ideally be lower than the MCL. However, it is conservative to compare a chemical concentration from a single episodic spill to the MCL based on long term exposure and this point is missed in some hazard assessments. Use of an alternative to the MCL in evaluating a chemical spill is discussed below.

The USEPA [24] established Health Advisories (HA) for several chemicals as an estimate of the acceptable drinking water level for evaluating chemical spills, although the HA 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 10 kg child consuming 1 L d^{-1} of water. The concern is a child may receive a greater dose than an adult on a mg kg^{-1} basis and children's exposure may not be considered in some toxicity databases or in levels of concern in some response planning tools. The USEPA [24] provides details on derivation of the one-day HA; it uses a short duration toxicological study although a long duration toxicological study may be substituted if short duration data are unavailable. The one-day HA can serve as a guideline for each day for up to 5 consecutive days of exposure and it would be appropriate for evaluating a chemical spill. For example, xylene has a one-day HA value of 40 mg L^{-1} which is 4 times higher than the MCL. The USEPA [24] derived the one-day HA using Eq. (3):

$$\mathrm{HA} = \frac{\mathrm{NOAEL} \times \mathrm{BW}}{\mathrm{UF} \times \mathrm{DWI}} \quad (3)$$

where the NOAEL is the no observed adverse effect level (mg kg^{-1} bw/day) from a study of an appropriate duration, BW is the body weight of a child (10 kg), UF is the uncertainty factor in accordance with EPA guidelines, and DWI is the assumed daily water intake for a child (1 L/day). This equation assumes all the chemical dose is from the drinking water contaminated by the chemical spill. Only the lifetime HA includes an adjustment for possible carcinogenicity [24]. The USEPA [21] provided guidance on selecting the uncertainty factors; their values depend on the quality of the available toxicity studies, the extent of the toxicity database for the chemical, and scientific judgment. The USEPA Integrated Risk Information System (IRIS) [25] has a compilation of human health effects including the oral NOAEL for approximately 540 chemicals. The individual chemicals in a spilled mixture are typically evaluated separately because the human health impacts are based on individual chemicals.

The MSDS is usually a good source for an acute aquatic toxicity benchmark. The USEPA Aquatic Life Benchmarks website [26] is another source. The USEPA [27] reported one can use a hazard quotient (HQ) approach to quantitatively characterize acute exposure to aquatic species. The HQ is the diluted chemical concentration divided by the toxicological endpoint concentration (LC_{50} or EC_{50}) for the most sensitive species. The EC_{50} is defined the "effective concentration" of a single chemical dose in water which caused a biological effect on 50% of a group of test animals exposed up to 48 h and the effect may be death. A HQ less than one is considered protective of marine life, thus, a river concentration less than the EC_{50} is acceptable. It is assumed the remaining aquatic population will recover because an episodic spill is a transient event. There is potential for risk to the species if the HQ is greater than one.

4. Application

To illustrate the approach to evaluate human and aquatic exposure, RDM was applied in a case study for a hypothetical spill of hydraulic fluid. It was assumed the hydraulic fluid spill was not contained and it flowed directly into a river or entered the river through a storm drainage system at the river bank. UCON™ Trident™ 68 AW Hydraulic Fluid, simply designated as Trident 68, was evaluated. The MSDS for Trident 68 reported the composition as a trade secret but its properties are: liquid at 293 K, low vapor pressure (<1.3 Pa at 293 K), boiling point > 473 K at atmospheric pressure, 100% soluble in water, and a specific gravity of about 1.03 at 293 K [28]. Trident 68 is readily biodegradable according to the OECD 301F test guideline and it does not form an oil film on a water surface [28].

RDM was used to evaluate a generic spill situation for planning purposes. A matrix hypothetical of spill volumes and river sizes was evaluated, as shown in Table 4. The Mississippi River was selected as the large river because hydraulic equipment is commonly used near this river. The Kanawha River was selected to assess a spill into a medium river and Soldier Creek was selected as a small river. The selected spill volumes (converted from gallons) were: 26,498 L for a catastrophic loss of an entire storage tank volume, 379 L for the loss two entire drums, and 76 L for the loss of all the hydraulic fluid in a machine. The temperature of the spilled chemical and the environment were assumed to be 293 K.

4.1. Toxicity benchmarks

A short duration spill can be modeled as an instantaneous event. Although Trident 68 hydraulic fluid has LD_{50} values for acute animal toxicity, no data were found for acute exposure without adverse human health effects. There is no MCL or HA for Trident 68 hydraulic fluid. However, the major component of the hydraulic fluid has an oral NOAEL of 500 mg kg^{-1} d^{-1} based on a two year rat study [29] and a second two year dog study reported an oral NOAEL of 600 mg kg^{-1} d^{-1} [30]. After a review of the Trident 68 toxicology, the total uncertainty factor of 30 was based on a factor of 10 for interspecies uncertainty and a factor of 3 for intraspecies variability. The one-day HA was calculated below using Eq. (3):

$$= \frac{500 \ \ \mathrm{mg} \ \ \mathrm{kg}^{-1} \ \ \mathrm{d}^{-1} \times 10 \ \ \mathrm{kg}}{\text{total uncertainty factor of } 30 \times 1 \ \ \mathrm{L} \ \ \mathrm{d}^{-1}} = 167 \ \ \mathrm{mg} \ \ \mathrm{L}^{-1}$$

$$(\text{rounded to } 170 \ \ \mathrm{mg} \ \ \mathrm{L}^{-1})$$

A child could consume 1 L d^{-1} of river water with 170 mg L^{-1} of Trident 68 hydraulic fluid without an adverse health effect. Therefore, 170 mg L^{-1} was used as the target concentration for human oral toxicity in this case study. Following USEPA [24] guidance, an adult with a 70 kg body weight consuming 2 L d^{-1} of water would have an allowable chemical concentration of 583 mg L^{-1} or 3.5 times higher than that for a child.

The MSDS [28] listed the EC_{50} value as 170 mg L^{-1} based 48 h exposure to the hydraulic fluid for the most sensitive aquatic species, the water flea. The EC_{50} would be higher for other aquatic species. The EC_{50} was used as the target concentration for aquatic

Table 4
Input data matrix for hypothetical Trident 68 hydraulic fluid spills.

Scenario description	Location	Flow (m^3 s^{-1})	Width (m)	Depth (m)	Spill volume (L)	Spill mass (kg)
Large river, large spill	Mississippi River at Tarbert Landing, MS	14,209	1128	8.2	26,498	27,270
Medium river, medium spill	Kanawha River at South Charleston, WV	419	192	2.5	379	390
Small river, small spill	Soldier Creek near Grove, KS	0.5	6	0.3	76	78

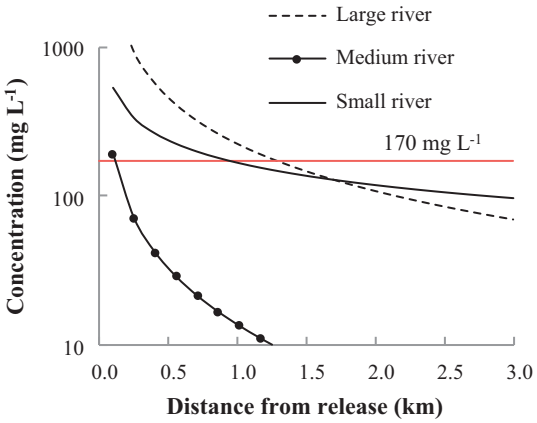

Fig. 5. Predicted Trident 68 concentrations versus distance from the release point.

toxicity in this case study. For comparison, m-xylene has an EC_{50} value as 4.7 mg L^{-1} for the water flea based 24 h exposure [31].

4.2. Model results

For this generic spill scenario a specific location in a river (e.g. a drinking water intake) could not be identified where a person might be exposed. Therefore, RDM was used to predict the distance downstream from the release point where the spill would be diluted to a concentration of 170 mg L^{-1} which is the one-day HA for a human and EC_{50} concentration for the water flea. It was assumed the river contained the water flea, the most sensitive aquatic species. The predicted Trident 68 concentrations versus distance are shown in Fig. 5. The distances and travel times are summarized below and in Table 5:

- For the small river, the 170 mg L^{-1} concentration extended 0.97 km downstream and the spill leading edge arrived there at 0.66 h after the spill, the peak arrived at 0.96 h, and the time trailing edge passed at 1.26 h.
- For the medium river, the target concentration extended 0.11 km downstream and the spill leading edge and peak arrived there quickly at 0.03 h after the spill and the time trailing edge passed at 0.04 h.
- For the large river, the target concentration extended 1.3 km downstream and the spill leading edge, the peak, and the time trailing edge passed at about the same time at 0.24 h because it was well diluted.

5. Discussion

In the performance evaluation, RDM was executed as a generic river spill model without tuning. RDM predictions showed reasonably good agreement with measured values of peak concentration and arrival time at distances of 3.1–7.7 km downstream of the dye release point for the average river conditions. Fig. 4 shows the model over prediction increased with distance and in the 66 h travel time to the 16.1 km site, removal processes (volatilization, adsorption, and degradation) reduced the measured concentrations. An accurate concentration prediction is preferred; however, if the concentration is over predicted then the hazard assessment will be conservative. Table 4 shows there is a small little difference in RDM predictions for the two modeled creek conditions. The creek conditions are considered in the $(A\ D_x)^{0.5}$ term in Eq. (2) and it takes large changes in their values to significantly change the predicted concentration. The parameters did not vary significantly for Soldier Creek.

RDM did not agree as well with the measurement at 0.32 km, closest measurement site to the dye release; RDM under predicted the measured concentrations by a factor of three to ten depending on which of the two the reported values is used. Therefore, the model and data for the 0.32 km site was more closely evaluated. It was determined that RDM performed as designed using a model to model comparison. RDM compared well to predictions from the SPILL model as close as 0.1 km to the release point [32]. Bath et al. [15] reported 85–125% of the dye mass was recovered in their experiments so there is some uncertainty associated with the measured concentrations but not enough to account for the large under prediction by RDM. RDM predicted the mixing zone extended about 20 m downstream from the dye release point so the complete mixing equation was used for predicting all the concentrations. Samuels et al. [11] reported the difference between the model predicted and the measured concentrations was typically due to the uncertainty in the initial dilution of the dye. RDM may have under predicted the concentration at 0.32 km because the dye was not well mixed in the creek.

RDM performance may be improved by tuning it to the specific river of interest but this would require measurements. Velocity is a key model parameter which is used to calculate the longitudinal and lateral dispersion coefficients as well as the time of arrival of the peak concentration. The velocity was calculated from the river flow, width, and depth. The RiverSpill model performance was improved by tuning its velocity [11]. Others suggested a dye study should be performed to better determine the river specific velocity and longitudinal dispersion coefficient [6]. The Duflow model was tuned by adjusting the friction factor for the river bottom [7].

This study provided an assessment of the hazard zone for human and aquatic exposure to a spill of Trident 68. The 170 mg L^{-1} represents a conservative target as the one-day HA concentration was based on the NOAEL from a two year animal study and the EC_{50} for aquatic toxicity was based on 48 h exposure. RDM may be under predicting concentrations at distances less than about 2 km while the predicted hazard zone distances in Table 5 range from 0.11 km to 1.3 km. The Trident 68 hazard zone as defined by the 170 mg L^{-1} concentration was predicted to pass in less than an hour. Should one decide to include a safety factor, then the hazard zones could be extended to 2 km for the small and large rivers where the predicted concentrations were 116 and 104 mg L^{-1}, respectively. The hazard zone could be extended to 0.2 km for the medium river where the predicted concentration is 57 mg L^{-1} or three times lower than the target concentration.

The duration to define and evaluate a spill varies considerably because the data collection step can be prolonged. RDM requires a value for the chemical mass released and values for three river specific parameters. RDM might be run several times for a sensitivity analysis but this can be done quickly. The default river values

Table 5
Predicted distances to the 170 mg L^{-1} Trident 68 concentration and arrival times.

Scenario description	Spill volume (L)	Distance (km)	Arrival time after spill (h)
Large river	26,498	1.30	0.24
Medium river	379	0.11	0.03
Small river	76	0.97	0.66

provided here for the generic spill approach can be used for quick range finding. For performing the hazard assessment, chemical specific toxicological data, such as the EC_{50}, can usually be obtained from the MSDS. However, if toxicity information is not readily available, it can take hours to derive a one-day HA value.

6. Conclusions

RDM can be used by a non-technical person for a quick prediction of concentrations after a chemical spill into a river. The model has several advantages; it requires minimal input data and it is easy to use. RDM predictions showed reasonably good agreement with measured values of peak concentration and arrival time at distances of about 3–8 km downstream of the dye release point. RDM over predicted peak concentrations by a factor of ten at a distance of 16 km because it did not consider chemical removal processes. RDM performance might be improved for a specific river by tuning the model. It is recommended that additional testing of RDM predictions near the release point be performed using another measured data set.

Guidance was provided on quantifying river parameters, evaluating chemical properties, and characterizing the human and aquatic hazards. Although the approach provided guidance on assessing the human and aquatic hazards, this task requires some technical skill to derive a one-day HA value.

RDM and the hazard assessment approach can provide a practical evaluation for a chemical spill. The case study demonstrated a spill of hydraulic fluid would be diluted quickly below the hazardous concentration and the hazard zone would extend less than 2 km from the release point.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.07.052.

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