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Spill hazard evaluation for chemicals shipped in bulk using modeling

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Abstract

A wide variety of chemicals are shipped in bulk world-wide, raising concerns regarding the ecological and human health risks of spills of hazardous materials. A screening analysis was performed, using the chemical spill model CHEMMAP to estimate the expected fate and concentrations of chemical in water resulting from a spill into a large estuary and the potential ecological hazards to aquatic biota. A representative sample of chemical products, including floating, sinking, soluble and insoluble chemicals, was evaluated. The model uses physical-chemical properties to simulate fate processes, including: (1) slick spreading, transport, and entrainment of floating materials, (2) transport of dissolved and particulate materials in three dimensions, (3) evaporation and volatilization, (4) dissolution and adsorption, (5) sedimentation and resuspension, and (6) degradation. The model estimates the distribution of chemical (as mass and concentrations) on the water surface, on shorelines, in the water column, in the sediments, and in the lower atmosphere (in the zone where there would be exposure to humans and wildlife) over time. Chemicals typically shipped in bulk were classified into groups based on physical-chemical characteristics. Hypothetical spills representative of each class were simulated to estimate maximum exposure concentrations around the spill site at any time after the spill. Since currents are the most critical environmental input data to these results, current data from a calibrated and validated hydrodynamic model were used as spill model inputs. The spill modeling was performed in stochastic mode, i.e. multiple model runs are simulated by randomly selecting dates and times for the release, sampling the range of possible tidal current and wind conditions. Maximum predicted environmental concentrations (PECs) were mapped in terms of hazard quotients (HQ), analogous to PEC divided by Predicted No Effects Concentration (PEC/PNEC). The area where the HQ > 1 was calculated for each model run. The mean and standard deviation for the set of stochastic runs within a scenario describes the expected hazard and its variability caused by varying wind and current conditions at the time of the spill.
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Keywords: Hazardous materials; Chemical spills; Ecological risk; Modeling

Software availability

The CHEMMAP system is a commercial product of Applied Science Associates, Inc. (70 Dean Knauss Drive, Narragansett, RI 20882 USA, Tel. +1-401-7896224,

Fax +1-401-7891932), which may be run on any personal computer operating with a Microsoft Windows 95 or newer system. The software requires a VGA color monitor, a Microsoft-compatible mouse and an IBM-compatible 486 or better PC; with 64 MB RAM, 100 MB free disk space on the hard drive. Several different models are available in CHEMMAP: trajectory and fate model, biological effects model, and a stochastic model. The models are programmed in Fortran, and the graphical user interface is in Visual Basic. While the

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model system has been under development since 1984, the commercial product CHEMMAP first became available in 1999. Additional information is available on http://www.chemmap.com. [Contacts: Deborah French McCay dfrench@appsci.com; Nicole Whittier nwhittier@appsci.com]

1. Introduction

While many tonnes of chemicals are shipped in bulk worldwide on a routine basis, the potential ecological hazards of spills related to this shipping have not been examined. In October 2000, a tanker, the *Ievoli Sun*, sank in the English Channel containing about 4000 MT of styrene, 500 MT of methyl ethyl ketone (MEK), and 1000 MT of isopropanol. This incident raised awareness of the potential ecological risks of chemical spills.

The U.S. Coast Guard has proposed regulations mandated under the 1990 Oil Pollution Act that require response plans for marine transportation-related facilities (US CFR Vol.65, No. 63, March 31, 2000) and tank vessels (US CFR Vol.64, No. 54, March 22, 1999) carrying hazardous substances (U.S. Coast Guard, 1999). The list of hazardous substances included are those (1) containing at least 10% by weight of a chemical covered by the U.S. Clean Water Act and (2) transferred to/from or shipped in a vessel in bulk quantities. The response plans are to include an impact analysis for a worst case discharge, which will pre-identify the area in which adverse impact to human health and the environment could occur.

International treaties, including the MARPOL and the International Bulk Chemical Code, address hazardous spill response requirements. In 1999, the International Maritime Organization's (IMO) approved a new regulation 16 to Annex II of MARPOL that will require all ships of greater than 150 gross tonnes, which are certified under MARPOL Annex II to carry noxious liquid substances (NLS), to have an approved Emergency Response Plan based on guidelines developed by the Marine Environment Protection Committee (MEPC). The Protocol on Preparedness, Response and Co-operation to Pollution Incidents by Hazardous and Noxious Substances 2000 (OPRC-HNS Protocol) was adopted by the IMO in March 2000. The draft guidelines are similar to that provided for response to oil spills. In 1996, IMO adopted the International Convention on Liability and Compensation for Damage in Connection with the Carriage of Hazardous and Noxious Substances (HNS) by sea, which provides for a compensation and liability regime for incidents involving these substances.

In this study, we address the potential ecological hazards of chemical spills, performing a screening analysis using a hypothetical spill site in Narragansett Bay (Rhode Island, USA) as a representative large estuary. ASA's chemical spill model, CHEMMAP, was used to predict the fate of a representative sample of chemicals and spill scenarios to identify the degree to which adverse impacts to marine biota could occur.

Chemicals were classified into groups based on their physical-chemical characteristics. Hypothetical spills representative of each class are simulated to estimate maximum concentrations in water over time. The expected fate and concentrations of equal sized spills of chemicals with similar physical-chemical properties would be approximately the same. Thus, the results of the representative chemical are used to estimate concentrations for spills of other chemicals in that class.

Concentrations are compared to ecological effects endpoints to determine areas of potential ecological impact. [An endpoint is a threshold defining a hazardous condition, such as an exposure level (e.g., dose) or pollutant concentration.] Maximum predicted environmental concentration (PEC) was mapped as a hazard quotient (HQ), which is the PEC divided by an endpoint such as the Predicted No Effects Concentration (PEC/PNEC). The PNEC divisor was derived from acute toxicity bioassay data compiled by the U.S. Environmental Protection Agency (USEPA). The area where the HQ > 1 was calculated for each model run evaluated.

The probable consequences of a spill were estimated using CHEMMAP applied in stochastic mode, where a large number of model simulations were run for a given spill scenario (chemical and spill amount), randomly varying the spill date and time, and thus the wind and current conditions, for each run. A three-month period of tidal current data generated by a hydrodynamic model (Ward et al., 2002) was sampled, running 20 simulations. Hourly wind speed and direction data for the period were used. As tidal currents are the dominant transport mechanism, 20 randomized start times were considered sufficient to characterize the variation in dispersion.

The mean and standard deviation of the area where HQ > 1 were calculated for the set of stochastic runs within a scenario. These statistics describe the expected hazard and its variability caused by varying wind and current conditions at the time of the spill.

2. CHEMMAP model description

The chemical spill model CHEMMAP has been developed over two decades for assessment of physical fate, biological impacts, natural resource damages and ecological risks. Originally it was designed to simulate specific spill incidents for evaluating impacts and damages (French et al., 1996). More recently, the model has been set up in a probabilistic stochastic configuration, allowing evaluation of risks of consequences and

statistical computations (French McCay and Isaji, 2004). While a few chemical spill models exist that can simulate transport and physical fate of single events (Lunel, 1991; Shen et al., 1995; Rusin et al., 1996), CHEMMAP is unique in being able to evaluate biological impacts, in its stochastic implementation, and in its interconnection with hydrodynamic models, geographical information systems, and its graphical user interface. This makes the system flexible and applicable to marine and freshwater systems anywhere in the world. The algorithms and assumptions of the chemical spill model have been described previously (French et al., 1996; French McCay and Isaji, 2004). The fates model processes and database are briefly summarized below.

The chemical fates model estimates the distribution of chemical (as mass and concentrations) on the water surface, on shorelines, in the water column and in the sediments. The model is three-dimensional, separately tracking surface floating chemical, entrained droplets or suspended particles of pure chemical, chemical adsorbed to suspended particulates, and dissolved chemical. Processes that are simulated are spreading (floating liquids), transport, dispersion, evaporation–volatilization, entrainment (liquids), dissolution, partitioning, sedimentation, and degradation.

The model uses physical-chemical properties to predict the fate of a chemical spill, including density, vapor pressure, water solubility, environmental degradation rates, adsorbed/dissolved partitioning coefficients (K_{ow}, K_{ow}), viscosity, and surface tension. The spilled mass is initialized at the location and depth of the release, in a state dependant upon the physical-chemical properties of the material. In the first hours to days after a spill, when acute effects to water column organisms would occur, the most important properties determining fate are density, vapor pressure, and water solubility. The adsorbed/dissolved partitioning coefficient (K_{oc}), which is used in the model to compute the fraction dissolved versus adsorbed to suspended sediments, is functionally related and highly correlated with solubility. The value of K_{oc} was calculated from K_{ow} (which was obtained from literature compilations) using the regression equation from DiToro et al., 1991):

$$\log(K_{oc}) = 0.983 \log(K_{ow}) + 0.00028 \qquad (1)$$

Chemical mass is transported in three-dimensional space and time, by surface wind drift, other currents, and vertical movement in accordance with buoyancy and dispersion. The other currents are those provided by the hydrodynamic simulation (Ward et al., 2002). Wind-driven current (drift) in the surface water layer (down to 5 m) is calculated within the fates model, based on hourly wind speed and direction data (Youssef and Spaulding, 1993). Stokes' Law is used to compute the vertical velocity of pure chemical particles or suspended sediment with adsorbed chemical. If rise or settling velocity overcomes turbulent mixing, the particles are assumed to float or settle to the bottom. Settled particles may later resuspend (assumed to occur above 20 cm/s current speed). Turbulent dispersion is modeled using a random walk scheme (Bear and Verruijt, 1987), with the magnitudes scaled by horizontal and vertical diffusion coefficients (Okubo, 1971). The vertical diffusion coefficient is computed as a function of wind speed in the wave-mixed layer, approximated as 1.5 times wave height, based on Thorpe (1984). Wave height is calculated using the algorithm in CERC (1984).

The spilled chemical is modeled using the Lagrangian approach, where multiple sublots, called spillets, of the entire mass (or volume) spilled are tracked as they move in three-dimensional space over time (by addition of the transport vectors due to wind, currents, and buoyancy). For surface floating liquids, the model estimates surface spreading of mass in each spillet (using the approach of Mackay et al., 1980) to a viscosity-dependent terminal thickness (based on data in McAuliffe, 1987), spreading of spillets by the random walk algorithm representing turbulent dispersion, and entrainment into the water column (modeled as for oil as described in French et al., 1996, using data in Delvigne and Sweeney, 1988). At each time step, phase transfer rates (evaporation, dissolution, volatilization, and entrainment) are calculated and a proportionate percentage of the spillets are transferred to the new phase.

Dissolution is modeled using algorithms previously developed (French et al., 1996) based on Mackay and Leinonen (1977). The slick (spillet) is treated as a flat plate, with a mass flux (Hines and Maddox, 1985) related to solubility and temperature, and assuming a well-mixed layer with most of the resistance to mass transfer lying in a hypothetical stagnant region close to the slick. For subsurface droplets or particles, dissolution is treated as a mass flux across the surface area of a sphere in a calculation analogous to the Mackay and Leinonen (1977) algorithm.

Dissolved chemical in the water column is assumed to adsorb to natural particulate matter based on linear equilibrium partitioning theory, where concentrations of dissolved (C_d) and adsorbed (C_a) chemical are constant proportions and dependent on suspended particulate concentration (C_{ss}):

$$C_a/C_d = K_{oc} C_{ss} \qquad (2)$$

The adsorbed fraction of the total mass, $C_a/(C_a + C_d)$, settles through the water at a rate based on Stokes' Law and subject to turbulent mixing. The chemical is assumed to adsorb to silt particles, of diameter 50 μm and density 1.0512 g/cm³. Using Stokes' Law, these

settle at about 3 m/day in seawater (density = 1.024 g/cm^3) and calm waters.

Evaporation from slicks of floating chemicals is modeled following the approach in Mackay and Matsugu (1973) where the rate of mass flux to the atmosphere increases with vapor pressure, temperature, wind speed and surface area. Conceptually, this model assumes that the transfer of mass from liquid to the air is limited by molecular diffusion across a stagnant boundary layer in the air just above the chemical's surface. Diffusivity is scaled using molecular weight from that of a reference chemical cumene (from Mackay and Matsugu, 1973, for MW > 100 g/mol) or pentane (from Kawamura and Mackay, 1987, for MW < 100 g/mol) based on the relationship described in Thibodeaux (1979).

Volatilization from the water column is calculated from the chemical's vapor pressure (a strong function of temperature) and solubility. The procedure in the model is as outlined by Lyman et al. (1982), based on Henry's Law and mass flux being controlled by diffusion in both the water and the air near the interface (Hines and Maddox, 1985). The volatilization depth for dissolved substances in the water column is limited to the maximum of one half the wave height. Wave height is computed from the wind speed (CERC, 1984).

Chemical reactions are not specifically addressed in the model, i.e. the spilled mass is tracked through phase changes and transport, with all reaction products assumed to move together. Loss of chemical by reaction to some other form no longer of concern is included as degradation. Degradation is estimated assuming a constant rate of 'decay' specific to the environment where the mass exists (i.e., atmosphere, water column or sediment). It may include biological, chemical or photochemical processes.

3. Testing and validation of model algorithms

The accuracy of the transport algorithms depend on the accuracy of the current data used and the specification of the random turbulent diffusion coefficients. The current data used in this study were produced by a hydrodynamic model (Muin and Spaulding, 1997a,b; Spaulding et al., 1999a,b; Sankaranarayanan and Spaulding, 2003) calibrated and validated to data from Narragansett Bay (Rhode Island, USA, Ward et al., 2002). This interconnected hydrodynamic and chemical fate model system has been used in other studies (e.g., Boehm et al., 2001; French McCay and Isaji, 2004). The turbulent diffusion algorithms in CHEMMAP have been scaled and validated by dye studies (Okubo and Ozmidov, 1970; French et al., 1997) and observations of dispersion of (purposefully) spilled emulsions (the

Venezuelan product Orimulsion) in the Caribbean Sea (French et al., 1997).

The results of the evaporation algorithm for surface floating slicks were tested against experimental data from Kawamura and Mackay (1985, 1987), who conducted seven experiments using toluene, cyclohexane, hexane and dichloromethane, measuring evaporation rates of chemical volatilizing from a galvanized sheet-metal pan. To keep temperature constant and avoid any heat conduction from the ground, the pans were placed on Styrofoam boards. Temperature and wind conditions were recorded for the time of the particular experiment. Two experiments were conducted for each chemical, with the exception of hexane. CHEMMAP simulations were performed using the conditions of the experiments, i.e. volume of chemical, temperature (3–38 °C), and wind speed (various outdoor). The normal spreading algorithms in CHEMMAP were disabled and the chemical thickness held constant at that used in the pan experiments. Table 1 contains the results and Fig. 1 shows a comparison of the experimental evaporation to the CHEMMAP-predicted evaporation. The agreement is good (Pearson $r^2 = 0.421$) and the linear regression through the data falls close to a 1:1 relationship (slope = 0.906, with standard error 8.16).

The entrainment and dissolution algorithms, which are also used in the companion oil spill model SIMAP, have been validated for spills where subsurface concentration data are available. In the oil model SIMAP, dissolution and volatilization of mono- and polynuclear aromatic hydrocarbons (PAHs) are estimated and predicted PAH concentrations agreed with measured values from field samples (French McCay, 2002). We have not identified similar data for a pure chemical spill with which to perform a validation exercise.

Test runs with CHEMMAP and three commonly transported petrochemicals, benzene, toluene and styrene demonstrate model behavior. The conditions run were a constant wind speed of 3 m/s or 8 m/s and no background current, such that all the dispersion and transport would be wind-driven. Environmental

Table 1
Measured and predicted percentage evaporated by 1 h for chemicals held in a pan at the indicted thickness

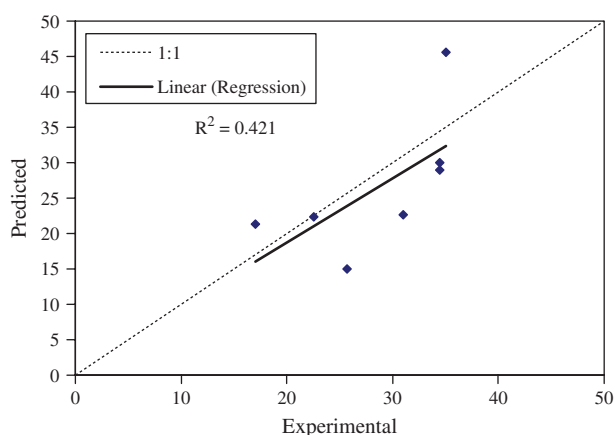| Experiment	Chemical name	Thickness of chemical in pan (mm)	Evaporation (%) in 1 h	
			Experimental	Model predicted
1	Toluene	23	22.5	22.3
2	Toluene	23	17.0	21.3
3	Cyclohexane	22	34.4	30.0
4	Cyclohexane	22	34.4	28.9
5	Hexane	24	35.1	38.4
6	Dichloromethane	23	31.0	22.6
7	Dichloromethane	22	25.7	15.0

Fig. 1. Comparison of measured and model-predicted percentage evaporated by 1 hour for four chemicals in seven experimental tests.

conditions were: salinity, 30 ppt; water temperature 10 °C; and suspended sediment concentration 10 mg/L. Instantaneous releases at the water surface and at 5 m were simulated. The mass balances over time for these tests are in Figs. 2–4. Fig. 2 shows the typical behavior of a floating volatile chemical, benzene. If released at the water surface, some benzene dissolves, but most of the mass floats and immediately evaporates. When released at 5 m (subsurface, Fig. 2), more benzene dissolves in the water as the buoyant liquid (as droplets) rises through the water column. However, more than 85% of the spilled mass reaches the surface and rapidly evaporates off. The behavior of toluene and styrene are similar, but with progressively smaller percentages dissolved as solubility decreases (solubility of benzene > toluene > styrene). Figs. 3 and 4 show the percentage in the atmosphere (having evaporated from the surface slicks or volatilized from the water) for all three chemicals and the two wind speeds. With the same chemical, higher wind speed increases the rate of volatilization, as expected as the increased turbulence increase flux across the air-sea boundary.

4. Classification of chemicals and scenarios examined

Table 2 lists chemicals carried in bulk, along with their Chemical Abstract System (CAS) registry number, the typical state when shipped. The list of representative chemicals was based on the U.S. Coast Guard list and reported incidents (such as the *Ievoli Sun*). The chemicals in Table 2 were classified into groups based
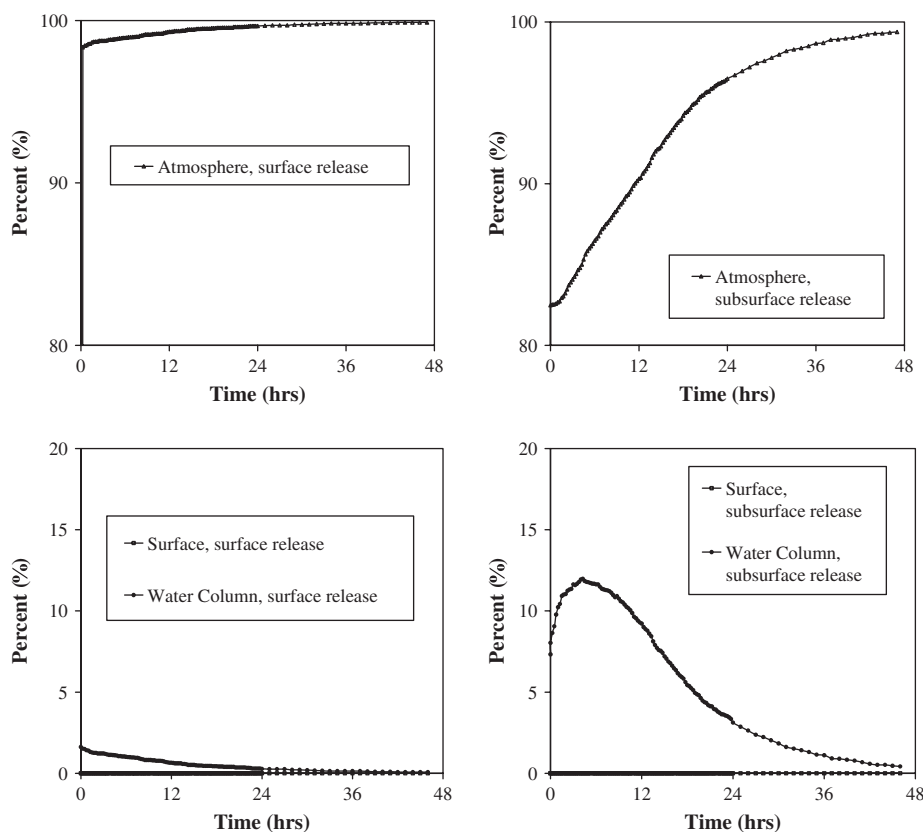

Fig. 2. Mass balance over time for a 1000 MT release of benzene (wind speed 3 m/s) at either the water surface or at 5 m depth (subsurface).
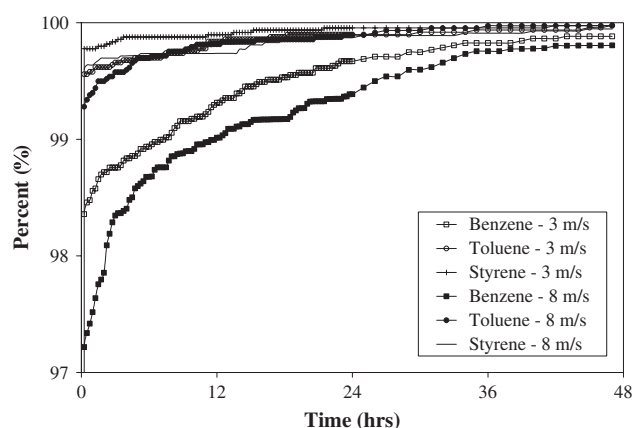
Fig. 3. Percentage of the spilled mass volatilized to the atmosphere over time after an instantaneous release of 1000 MT at the water surface. (Wind speed indicated in the legend).

on their major physical-chemical characteristics that determine fate: density, water solubility, and vapor pressure. The chemical quickly disperses in a dissolved state if water solubility is high, or floats or sinks (depending on density) if solubility is low. Adsorption to suspended particulate matter is proportional to degree of insolubility. Volatilization rate is a function of vapor pressure. The classification of chemicals was based on the property ranges in Table 3. Table 4 lists the physical behavior classes of chemicals evaluated in this study. This classification scheme is similar in concept to the standard classification system used in Europe under the Bonn Agreement (http://www.bonnagreement.org/), although the threshold in that system for an 'evaporator' is 300 Pa, as compared to 100 Pa used here.

Hypothetical spills representative of each physical behavior class were simulated (Table 5) to estimate maximum concentrations in water over time. The initial
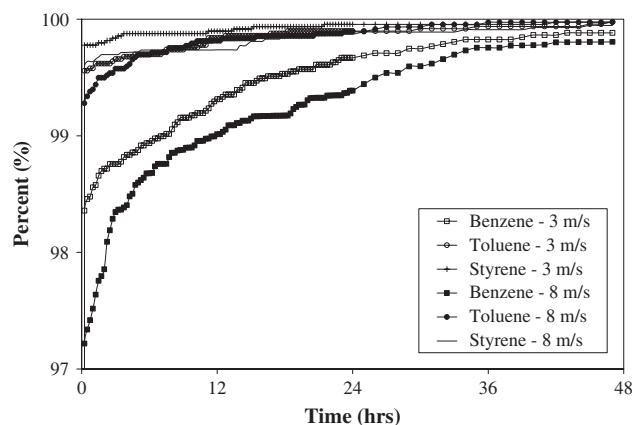

Fig. 4. Percentage of the spilled mass volatilized to the atmosphere over time after an instantaneous release of 1000 MT at 5 m depth. (Wind speed indicated in the legend).

state assumed was a likely shipping state for the chemical. Three spill sizes were run, using chemicals with more likelihood (than others in their class) to be spilled at that hypothetical spill amount. Spill release times were assumed to be 4 h for large 1000 MT spills, and 1 h for medium (10 MT) and small (0.5 MT) spills. The length of the simulation was selected based on preliminary runs and comparison of concentrations to estimated toxicity thresholds values (described below). Table 6 contains additional chemical properties assumed in the simulations.

5. Environmental and other input data for model simulations

A geographical database defines water depth, shoreline type, sediment type, and habitat type in the model. A grid covering Narragansett Bay was prepared using Arc View (ESRI) software and habitat maps from French et al. (1991). The cell size in the habitat grid was 0.00045 degrees latitude by 0.00045 degrees longitude (50 × 37 m). A depth data grid of the same dimensions as the habitat grid contained bathymetry from the NOS soundings database (National Ocean Service, Hydrographic Survey Data, Version 3.2), averaging soundings within each cell.

Tidal currents for Narragansett Bay and surrounding waters were simulated for the period September–November 2000 and verified against observational data (Ward et al., 2002). This data set provides a realistic current transport pattern for the spill simulations, representing a large estuary dominated by tides. The length of the simulation includes several spring and neap cycles, as well as other variability in tidal component amplitude and phasing.

The horizontal dispersion coefficient for randomized mixing of spillet centers was computed from the current data. The coefficients (D_{xx}, D_{yy}) are calculated according the following equations (Ippen, 1966):

$$D_{xx} = 14.2 * (2*g)^{1/2} * U * H/C_h \qquad (3)$$

$$D_{yy} = 14.2 * (2*g)^{1/2} * V * H/C_h \qquad (4)$$

where g is the gravity, H is local depth (m), U and V are velocity in the easterly and northerly directions, and C_h is the Chezy coefficient, $(8*g/f)^{1/2}$, where f is the friction coefficient. D_{xx} and D_{yy}, therefore, reflect local depth and current speed each time step. The effect of the bottom friction is not significant; most of the variation is due to current speed.

The model uses an hourly wind time series specific to the time and location of the spill. This data is more influential to the fate of insoluble floating chemicals

Table 2
Chemicals carried in bulk (physical behavior classes are defined in Tables 3 and 4)

Chemical name	CAS Number	State	Density of pure chemical (g/cm^3)	Solubility (in pure water, mg/L)	Vapor pressure (kPa, at 25 °C)	Physical behavior class #
Acetaldehyde	75-07-0	Liquid	0.4528[d]	1000000[d]	121.286[d]	1
Ammonia	7664-41-7	Gas or Liquid	0.6800[g]	346000[f]	1013.250[e]	1
Benzene	71-43-2	Liquid	0.8770[e]	1780[a]	12.696[a]	1
Carbon tetrachloride	56-23-5	Liquid	1.5940[e]	800[c]	15.249[c]	5
Chlorobenzene	108-90-7	Liquid	1.1070[e]	484[a]	1.580[a]	5
Chloroform	67-66-3	Liquid	1.4830[e]	8200[c]	26.243[c]	3
Cyclohexane	110-82-7	Liquid	0.7780[e]	55[c]	12.696[c]	2
Ethylbenzene	100-41-4	Liquid	0.8650[f]	152[a]	1.270[a]	2
Ethylene glycol	107-21-1	Liquid	1.1400[f]	1000000[d]	0.012[d]	4
Ethylenediamine	107-15-3	Liquid	0.9000[e]	1000000[e]	1.429[e]	1
Furfural	98-01-1	Liquid	1.1600[e]	79400[d]	0.310[d]	3
Formaldehyde	50-00-0	Liquid	0.6520[d]	1000000[d]	6.080[f]	1
Hydrochloric acid	7647-01-0	Liquid	1.1600[f]	1000000[e]	3.2424[f]	3
Isopropanol	67-63-0	Liquid	0.7850[e]	1000000[d]	5.700[d]	1
Methanol	67-56-1	Gas or Liquid	0.7910[e]	1000000[d]	16.212[d]	1
Methyl ethyl ketone	78-93-3	Liquid	0.8050[e]	240000[d]	12.098[d]	1
Naphthalene	91-20-3	Solid	1.1620[e]	31[b]	0.010[b]	7
Phenol	108-95-2	Solid	1.1320[f]	88360[d]	0.047[d]	4
Sodium hydroxide	1310-73-2	Liquid	2.1300[e]	521500[f]	0.000[h]	8
Styrene	100-42-5	Liquid	0.9060[f]	300[c]	0.880[c]	2
Tetraethyl lead	78-00-2	Liquid	1.6590[e]	2[f]	0.036[f]	7
Toluene	108-88-3	Liquid	0.8669[f]	515[a]	3.800[a]	2
Trichloroethylene	79-01-6	Liquid	1.4650[e]	1100[c]	9.900[c]	3
Triethylamine	121-44-8	Liquid	0.7290[e]	12300[e]	7.643[e]	1
Xylene (mixed isomers)	1330-20-7	Liquid	0.8697[a]	198[a]	1.337[a]	2

[a] Mackay et al. (1992a).
[b] Mackay et al. (1992b).
[c] Mackay et al. (1992c).
[d] Mackay et al. (1992d).
[e] French et al. (1996).
[f] EnvironTIPS, Environment Canada, 1984.
[g] Environment Canada, 1984.
[h] CambridgeSoft Corporation, 2000.

than contaminants in the water column. However, wind speed, duration and fetch are used to estimate wave height (CERC, 1984) and vertical dispersion in the surface mixed layer. Wind data were obtained from the NOAA Ports Website (http://www.co-ops.nos.noaa.gov) for the Prudence Island station (for September–November 2000). The data is collected by the National Ocean Service data collection platforms and stored in the Center for Operational Oceanographic Products and Services databases. Other environmental data inputs were assumed as follows, which are mean values for Narragansett Bay

(French et al., 1996): salinity, 30 ppt; water temperature 10 °C; suspended sediment concentration 10 mg/L.

The spill was assumed to be a grounding on a rock just west of the shipping channel running the length of Narragansett Bay to the major port of Providence (Fig. 5). Table 7 lists the spill site latitude and longitude, along with other inputs defining the scenario, environmental conditions, and simulation parameters. For within spillet concentration distributions, minimum horizontal and vertical diffusion coefficients over the potential range of values were assumed to provide

Table 3
Classification of physical behavior

Buoyancy relative to water	Solubility behavior	Volatility
Floater: density <1.0 g/cm^3	Highly soluble: solubility > 1000 mg/L	Highly volatile: vapor pressure > 0.1 kPa
Neutral: density 1.01–1.03 g/cm^3	Soluble: solubility 100–1000 mg/L	Semi-volatile: vapor pressure 10^{-5}–0.1 kPa
Sinker: density >1.03 g/cm^3	Semi-soluble: solubility 1–100 mg/L	Non-volatile: vapor pressure <10^{-5} kPa
	Insoluble: solubility <1 mg/L	

Table 4
Classification of chemicals by physical behavior

Chemical name	Buoyancy relative to water	Solubility behavior	Volatility	Physical behavior class #
Acetaldehyde	Floater	Highly	Highly	1
Ammonia	Floater	Highly	Highly	1
Benzene	Floater	Highly	Highly	1
Ethylenediamine	Floater	Highly	Highly	1
Formaldehyde	Floater	Highly	Highly	1
Isopropanol	Floater	Highly	Highly	1
Methanol	Floater	Highly	Highly	1
Methyl ethyl ketone	Floater	Highly	Highly	1
Triethylamine	Floater	Highly	Highly	1
Cyclohexane	Floater	Semi-soluble	Highly	2
Ethylbenzene	Floater	Soluble	Highly	2
Styrene	Floater	Soluble	Highly	2
Toluene	Floater	Soluble	Highly	2
Xylene (mixed isomers)	Floater	Soluble	Highly	2
Chloroform	Sinker	Highly	Highly	3
Furfural	Sinker	Highly	Highly	3
Hydrochloric acid	Sinker	Highly	Highly	3
Trichloroethylene	Sinker	Highly	Highly	3
Ethylene glycol	Sinker	Highly	Semi-volatile	4
Phenol	Sinker	Highly	Semi-volatile	4
Carbon tetrachloride	Sinker	Soluble	Highly	5
Chlorobenzene	Sinker	Soluble	Highly	5
Naphthalene	Sinker	Semi-soluble	Semi-volatile	7
Tetraethyl lead	Sinker	Semi-soluble	Semi-volatile	7
Sodium hydroxide	Sinker	Highly	Non-volatile	8

conservatively high estimates of potential concentrations resulting from spills. Fig. 5 also shows concentrations resulting from one of the spills simulated (one of the 0.5 MT phenol runs).

6. Estimation of thresholds of concern

The thresholds of concern (PNEC) were estimated using acute toxicity bioassay data compiled by the USEPA, 2002. The endpoints used for this estimation were the LC_{50} (lethal concentration to 50% of exposed organisms), EC_{50} (effects concentration for a 50% reduction in a measured rate of growth or other function, and LOEC (lowest observable effects concentration). The PNEC value was assumed equivalent to the minimum of (1) 10% of the minimum LC_{50} for any species test, (2) the minimum EC_{50} for any species test, or (3) the minimum LOEC reported in the USEPA database. Bioassay results for fish and invertebrates in either freshwater or saltwater were included. The use of 10% of the LC_{50} is based on the estimated ratio of sublethal to lethal thresholds from Geisy and Graney (1989). Table 8 lists the PNEC values estimated for the chemicals analyzed below.

These estimated PNEC values are actually the lowest concentrations where a sublethal effect has been observed in at least one bioassay test. The durations of exposure for those tests are listed in Table 8. In the spill model simulations, the duration of exposure is typically less than in these bioassay tests. As toxicity increases (threshold concentration for effects decreases) as duration of exposure increases (French McCay, 2002), particularly at the time scale of a few hours (which is often the exposure time for a chemical spill), and the concentration for the most sensitive species is assumed, the estimated PNECs are conservative thresholds indicating *potential* for impact on some, but not necessarily all species.

Table 5
Hypothetical spill scenarios simulated using CHEMMAP

Chemical name	Physical behavior class #	State modeled	Spill quantity	Amount spilled (MT)	Duration of release (h)	Length of simulation (days)
Ammonia	1	Liquid	Small	0.5	1	2
Benzene	1	Liquid	Large	1000	4	4
Carbon tetrachloride	5	Liquid	Small	0.5	1	2
Carbon tetrachloride	5	Liquid	Medium	10	1	2
Ethylene glycol	4	Liquid	Medium	10	1	4
Hydrochloric acid 10% solution	3	Dissolved in an aqueous solution	Medium	10	1	2
Methyl ethyl ketone	1	Liquid	Medium	10	1	4
Naphthalene	7	Solid, pellets	Small	0.5	1	2
Naphthalene	7	Solid, pellets	Medium	10	1	7
Phenol	4	Solid, pellets	Small	0.5	1	2
Sodium hydroxide 25% solution	8	Dissolved in an aqueous solution	Small	0.5	1	1
Sodium hydroxide 25% solution	8	Dissolved in an aqueous solution	Medium	10	1	2
Styrene	2	Liquid	Small	0.5	1	2
Styrene	2	Liquid	Medium	10	1	3
Styrene	2	Liquid	Large	1000	4	5
Trichloroethylene	3	Liquid	Small	0.5	1	2

Table 6
Modeled chemicals and additional physical properties used in simulations (n/a, not applicable)

Chemical name	Molecular weight (g/mol)	Viscosity (at 25 °C, cp)	Octanol/water partition coefficient as $\log(K_{ow})$	Sorption coefficient for organic carbon as $\log(K_{oc})$	Degradation rate in surface waters (instantaneous, per day)
Ammonia	17.03[g]	0.300[f]	0.23[h]	0.22637[i]	0.1586[e]
Benzene	78.11[a]	0.602[e]	2.13[a]	2.09407[i]	0.097835[a]
Carbon tetrachloride	153.82[c]	NA	2.65[c]	2.60523[i]	0.0097835[c]
Ethylene glycol	62.07[d]	NA	−1.36[d]	−1.3366[i]	0.3024[d]
Hydrochloric acid 10% solution	36.46[e]	NA	0.311[i]	0.30557[e]	0.01899[e]
Methyl ethyl ketone	72.11[d]	0.477[f]	0.29[d]	0.28535[i]	0.3024[d]
Naphthalene	128.19[b]	NA	3.37[b]	3.31229[i]	0.097835[b]
Phenol	94.10[d]	NA	1.46[d]	1.43546[i]	0.3024[d]
Sodium hydroxide 25% solution	40.0[e]	NA	0.502[i]	0.4936[e]	0.01899[e]
Styrene	104.14[c]	0.703[e]	3.05[c]	2.99843[i]	0.097835[c]
Trichloroethylene	131.39[c]	NA	2.53[c]	2.48727[i]	0.03024[c]

[a] Mackay et al. (1992a).
[b] Mackay et al. (1992b).
[c] Mackay et al. (1992c).
[d] Mackay et al. (1992d).
[e] French et al. (1996).
[f] Lyman et al. (1982).
[g] U.S. Secretary of Commerce (2000) — NIST.
[h] Syracuse Research Center (2000).
[i] Calculated using regression of $\log(K_{oc})$ on $\log(K_{ow})$ from DiToro et al. (1991).

7. Results

The model results indicate that the chemicals would disperse throughout the water column within a few hours after the spill release ends. The areas of water where the vertical average concentration exceeded the PNEC at any time after the spill were calculated for each model run. The mean and standard deviation of the area where HQ>1 were calculated for the set of stochastic runs within a scenario. These statistics describe the
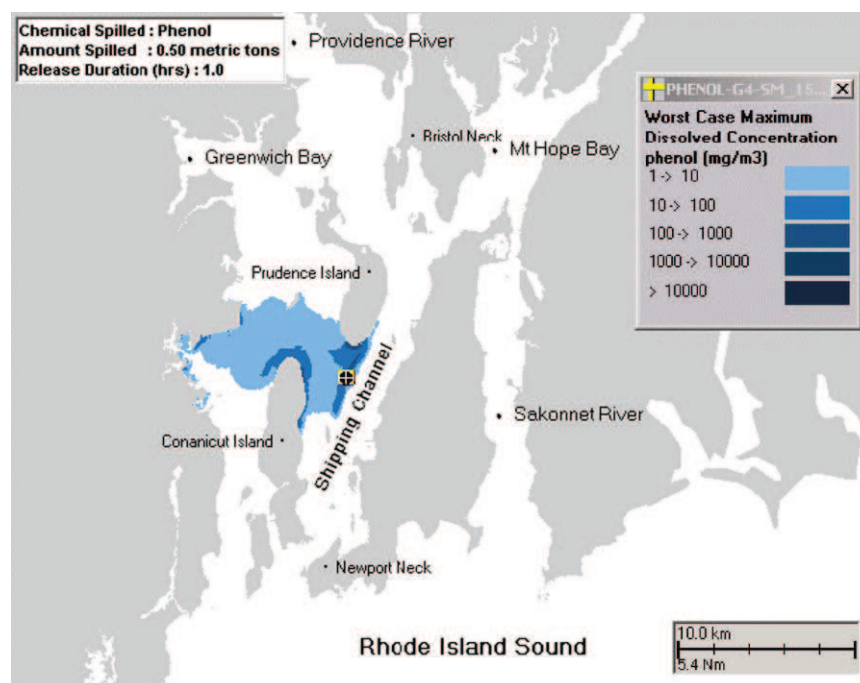

Fig. 5. Location of spill site in study area, and maximum concentrations resulting from a 0.5 MT spill of phenol for a sample spill date and time.

Table 7
Assumed model input parameters for all modeled chemicals

Name	Description	Value(s)
Spill latitude	Latitude of the spill site	41° 33.818′ N
Spill longitude	Longitude of the spill site	71° 19.924′ W
Depth of release	Depth below the water surface of the release or 0 for surface release	5 m
Model time step	Time step used for model calculations	0.25 h
Number of runs	Number of random start times to run in stochastic mode	20
Number of Lagrangian particles	Number of Lagrangian elements used to simulate spilled mass	5000
Salinity	Surface water salinity	30 ppt
Temperature	Water temperature	10 °C
Suspended sediment concentration	Average suspended sediment concentration during spill period	10 mg/l
Horizontal turbulent diffusion coefficient	Randomized turbulent mixing parameter in x and y, for concentration distribution within a spillet	0.1 m^2/s
Vertical turbulent diffusion coefficient	Randomized turbulent mixing parameter in z, below the wave mixed layer	0.001 m^2/s

expected hazard and its variability caused by varying wind and current conditions at the time of the spill. Tables 9–11 contain results for large, medium and small spills. (Note that the units for area are km^2 in Tables 9–10, but m^2 in Table 11).

The expected fate and concentrations of equal sized spills of chemicals with similar physical-chemical properties would be approximately the same. Thus, the results of the representative chemical were used to estimate concentrations for spills of other chemicals in that physical behavior class. The spill scenarios where areas > HQ were estimated from maximum concentration results for another chemical in the same class are indicted in Tables 9–11. The physical behavior class number in Tables 9–11 indicates the spill scenario (from Table 5) used to make the calculations. Note that for

Table 8
Estimated PNEC values assumed to be the minimum endpoint for any aquatic animal species of: (1) 10% of the minimum LC_{50}, (2) the minimum EC_{50}, or (3) the minimum LOEC

Chemical name	PNEC (mg/m^3)	Endpoint	Species (Latin name) or Reference	Species: English name	Duration of Exposure (h)
Acetaldehyde	210	(1)	Lepomis macrochirus	Bluegill	96
Ammonia	72	(2)	Strongylocentrotus purpuratus	Purple sea urchin	48–120
Benzene	351	(1)	French McCay (2002)		
Carbon tetrachloride	20	(1)	Dugesia japonica	Flatworm	7
Chlorobenzene	2	(1)	Leuciscus idus melanotus	Carp	48
Chloroform	52	(2)	Daphnia magna	Water flea	48
Cyclohexane	240	(1)	Crangon franciscorum	Bay shrimp	96
Ethylbenzene	39	(1)	French McCay (2002)		
Ethylene glycol	10000	(1)	Crangon crangon	Common shrimp, sand shrimp	48
Ethylenediamine	1400	(1)	Artemia salina	Brine shrimp	96
Furfural	1057	(1)	Americamysis bahia	Opossum shrimp	96
Formaldehyde	4	(1)	Ictalurus punctatus	Channel catfish	96
Hydrochloric acid 10% solution	510	(2)	Osteichthyes	Bony fish superclass	560
Isopropanol	2128	(1)	Spirostomum ambiguum	Protozoa	24
Methanol	3702	(1)	Anodonta imbecillis	Mussel	96
Methyl ethyl ketone	40000	(1)	Cyprinodon variegatus	Sheepshead minnow	24–96
Naphthalene	26	(1)	French McCay (2002)		
Phenol	1	(2)	Daphnia magna	Water flea	24
Sodium hydroxide 25% solution	40380	(2)	Ceriodaphnia dubia	Water flea	48
Styrene	47	(1)	French McCay (2002)		
Tetraethyl lead	2	(1)	Crangon crangon	Common shrimp, sand shrimp	96
Toluene	102	(1)	French McCay (2002)		
Trichloroethylene	170	(1)	Dugesia japonica	Flatworm	7
Triethylamine	3200	(3)	Oncorhynchus mykiss	Rainbow trout, Donaldson trout	60
Xylene (mixed isomers)	34.7	(1)	French McCay (2002)		

Table 9
Estimated areas where water concentrations exceed the PNEC for large spills, under the minimum turbulent mixing assumptions

Chemical name	Physical behavior class #	Calculated from results of another chemical in class	Mass spilled (MT)	Estimated PNEC (mg/m^3)	Mean area exceeding PNEC (km^2)	Standard deviation of area exceeding PNEC (km^2)
Acetaldehyde	1	×	1000	210	9.14	4.35
Ammonia[c]	1	×	1000	72	81.19	25.64
Benzene	1		1000	351	64.69	24.14
Carbon tetrachloride	5		1000	20	*	*
Chlorobenzene	5		1000	2	*	*
Chloroform[d]	3		100	52	*	*
Cyclohexane	2	×	1000	240	68.35	23.83
Ethylbenzene	2	×	1000	39	89.52	24.27
Ethylene glycol[a]	4		1000	10000	*	*
Ethylenediamine	1	×	1000	1400	46.17	19.27
Furfural[d]	3		100	1057	*	*
Formaldehyde	1	×	1000	4	91.54	26.52
Hydrochloric acid 10% solution	3		1000	510	*	*
Isopropanol	1	×	1000	2128	39.94	16.76
Methanol[c]	1	×	1000	3702	31.86	13.32
Methyl ethyl ketone	1	×	1000	40000	4.21	1.41
Naphthalene	7		1000	26	*	*
Phenol[b]	4		1000	1	*	*
Sodium hydroxide 25% solution	8		1000	40380	*	*
Styrene	2		1000	47	87.83	24.37
Tetraethyl lead[a]	7		1000	2		
Toluene	2	×	1000	102	79.22	24.58
Trichloroethylene[d]	3		100	170	*	*
Triethylamine	1	×	1000	3200	34.10	14.35
Xylene (mixed isomers)	2	×	1000	34.7	90.50	24.24

* No model scenario for physical behavior class.
[a] Modeled as solid, but commonly shipped as a liquid.
[b] Modeled as liquid, but commonly shipped as a solid.
[c] Modeled as liquid, commonly shipped as gas or liquid.
[d] Simulated chemical was in solution, accounting for lower mass spilled.

model runs of solutions (10% hydrogen chloride and 25% sodium hydroxide), the amount of chemical released is the indicated percentage (by weight) of the total mass of solution spilled. This spilled mass of chemical is applicable to other chemicals in the physical behavior class where areas > HQ are estimated.

Also note that the areas in Tables 9–11 are those where there is the *potential* for sublethal or lethal impact on some, but not necessarily all species. The areas are not where there would be a total or even significant loss of water column organisms. Species are highly variable in their sensitivity to chemical toxins, and the threshold for concern for individual species would vary over orders of magnitude (USEPA, 2002; French McCay, 2002). The estimated PNEC values used here are simply indicators of concern. Additional analysis of exposure dose and resulting effects is needed to estimate a potential impact for a spill of that chemical.

Of the 25 chemicals and spill scenarios evaluated, the chemicals presenting the highest hazard to aquatic biota per unit mass are phenol and formaldehyde. Ammonia, chlorobenzene, tetraethyl lead, acetaldehyde, xylene,

ethylbenzene, styrene and carbon tetrachloride are in the next tier with respect to ecological hazard. Note that the 10 MT spills of phenol, formaldehyde, and tetraethyl lead potentially impact areas as large as 1000 MT spills of benzene, cyclohexane and toluene. The least hazardous to water column communities of the chemicals studied are ethylene glycol, hydrochloric acid solution, sodium hydroxide solution (caustic soda), methanol, and MEK. Acids and bases, in particular, would quickly dissipate in seawater, due to its high buffering capacity.

The concerns with such chemicals as MEK and benzene are more with human health hazards in air, as these chemicals are highly volatile and toxic via the inhalation pathway. MEK presents one of the lowest hazards to aquatic biota of those spills examined here. Ammonia, and the solvents chlorobenzene and carbon tetrachloride, are very hazardous to both aquatic biota and human health.

The potential spill sizes examined range from relatively small 0.5 MT to loss of a significant tanker cargo, 1000 MT. The large spill of 1000 MT would only be a possibility for chemicals carried in these large

Table 10
Estimated areas where water concentrations exceed the PNEC for medium spills, under the minimum turbulent mixing assumptions

Chemical name	Physical behavior class #	Estimated from results of another chemical in class	Mass spilled (MT)	Estimated PNEC (mg/m^3)	Mean area exceeding PNEC (km^2)	Standard deviation of area exceeding PNEC (km^2)
Acetaldehyde	1	×	10	210	13.3	3.9
Ammonia[c]	1	×	10	72	28.3	10.3
Benzene	1	×	10	351	8.90	2.09
Carbon tetrachloride	5		10	20	12.7	2.3
Chlorobenzene	5	×	10	2	39.3	9.6
Chloroform[d]	3	×	1	52	4.05	0.98
Cyclohexane	2	×	10	240	1.98	0.60
Ethylbenzene	2	×	10	39	11.16	6.11
Ethylene glycol[a]	4		10	10000	0.235	0.103
Ethylenediamine	1	×	10	1400	2.14	0.58
Furfural[d]	3	×	1	1057	0.164	0.103
Formaldehyde	1	×	10	4	67.4	18.1
Hydrochloric acid 10% solution	3		10	510	0.406	0.220
Isopropanol	1	×	10	2128	1.33	0.40
Methanol[c]	1	×	10	3702	0.69	0.25
Methyl ethyl ketone	1		10	40000	0.023	0.022
Naphthalene	7		10	26	6.74	2.17
Phenol[b]	4	×	10	1	64.86	21.87
Sodium hydroxide 25% solution	8		10	40380	0.0007	0.0016
Styrene	2		10	47	9.40	4.94
Tetraethyl lead[a]	7	×	10	2	60.0	17.7
Toluene	2	×	10	102	4.22	1.70
Trichloroethylene[d]	3	×	1	170	1.38	0.44
Triethylamine	1	×	10	3200	0.83	0.29
Xylene (mixed isomers)	2	×	10	34.7	12.37	6.92

[a] Modeled as solid, but commonly shipped as a liquid.
[b] Modeled as liquid, but commonly shipped as a solid.
[c] Modeled as liquid, commonly shipped as gas or liquid.
[d] Simulated chemical was in solution, accounting for lower mass spilled.

quantities, such as styrene, benzene, MEK, and the alcohols. Phenol and formaldehyde are not transported in such quantities. Thus, the risk of a large spill of these chemicals is essentially zero. We have not attempted to evaluate the risk of these size spills occurring. An ecological risk assessment for spills of these chemicals should include such a risk assessment of spill probability.

8. Conclusions

The chemicals that would have the highest ecological consequences after a spill are those that disperse readily (are soluble), are not highly volatile, and are most toxic to aquatic biota. Of the spill scenarios evaluated, the chemicals presenting the highest hazard to aquatic biota per unit mass are phenol and formaldehyde, followed by ammonia, chlorobenzene, tetraethyl lead, acetaldehyde, xylene, ethylbenzene, styrene and carbon tetrachloride. The least hazardous to water column communities of the chemicals studied are ethylene glycol, hydrochloric acid solution, sodium hydroxide solution, methanol, and MEK.

The distance from the spill site where the HQ = 1, and the area potentially impacted, increases with increasing amount spilled relative to the toxicity endpoint of concern. Potential spill volumes should be considered with respect to their spill probability in a larger risk assessment, in order to put the results for different spill sizes into context. In applying the model to other spill sites and ambient current conditions, the distance from the spill site where the HQ = 1 would decrease with increasing dispersive forces related to wind and current.

This paper provides a screening analysis of chemicals that would be most ecologically detrimental if spilled and demonstrates an approach for evaluating potential ecological consequences of spills. The stochastic modeling approach provides an objective, quantitative method for comparing the consequences of chemical releases, avoiding the bias of subjectively choosing individual model runs to examine a priori, and providing a distribution of results that may be statistically described. This type of approach is an important advancement in performing ecological risk assessments for spills.

Table 11
Estimated areas where water concentrations exceed the PNEC for small spills, under the minimum turbulent mixing assumptions

Chemical name	Physical behavior class #	Estimated from results of another chemical in class	Mass spilled (MT)	Estimated PNEC (mg/m^3)	Mean area exceeding PNEC (m^2)	Standard deviation of area exceeding PNEC (m^2)
Acetaldehyde	1	×	0.5	210	400000	211000
Ammonia[c]	1		0.5	72	1372000	542000
Benzene	1	×	0.5	351	200000	117000
Carbon tetrachloride	5		0.5	20	36000	41000
Chlorobenzene	5	×	0.5	2	983000	316000
Chloroform	3	×	0.5	52	881000	269000
Cyclohexane	2	×	0.5	240	6400	11800
Ethylbenzene	2	×	0.5	39	81000	48000
Ethylene glycol[a]	4	×	0.5	10000	0	0
Ethylenediamine	1	×	0.5	1400	28000	35000
Furfural	3	×	0.5	1057	8000	13500
Formaldehyde	1	×	0.5	4	16033000	5804000
Hydrochloric acid	3	×	0.5	510	32000	41000
Isopropanol	1	×	0.5	2128	12000	19000
Methanol[c]	1	×	0.5	3702	3600	7500
Methyl ethyl ketone	1	×	0.5	40000	0	0
Naphthalene	7		0.5	26	930	1760
Phenol[b]	4		0.5	1	32600000	11300000
Sodium hydroxide 25% solution	8		0.5	40380	0	0
Styrene	2		0.5	47	64000	39000
Tetraethyl lead[a]	7	×	0.5	2	103000	85000
Toluene	2	×	0.5	102	24000	23000
Trichloroethylene	3		0.5	170	190000	120000
Triethylamine	1	×	0.5	3200	4900	9500
Xylene (mixed isomers)	2	×	0.5	34.7	94000	52000

[a] Modeled as solid, but commonly shipped as a liquid.
[b] Modeled as liquid, but commonly shipped as a solid.
[c] Modeled as liquid, commonly shipped as gas or liquid.

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