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Numerical Simulation of Chemical Spills and Assessment of Environmental Impacts

NUMERICAL SIMULATION OF CHEMICAL SPILLS AND ASSESSMENT OF ENVIRONMENTAL IMPACTS

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ABSTRACT

A two dimensional chemical spill model has been developed by National Center for Computational Hydroscience and Engineering (NCCHE) to predict the trajectory and fate of chemicals in water body. A number of processes including transportation, volatilization, sedimentation, adsorption, degradation, etc. were simulated in this model. In this paper, the capabilities for simulating chemical spills and their transports in natural waters have been developed and tested in realistic surface waters. The model was first applied to simulate the flow fields in a reservoir with unsteady flows driven by wind and hydrology, and then it was applied to simulate the trajectory and fate processes of chemical spill in the reservoir. Based on numerical results and EPA's drinking water standard, polluted areas due to the chemical incident in the reservoir can be estimated.

In order to provide information for emergency management and response planning, the chemical spill model was applied to simulate lots of cases by changing flow discharges, wind directions and speeds. Using statistic analysis, the probability of each location that chemical concentration was higher than the Maximum Contaminate Level (MCL) was calculated, and the worst condition for some important facilities, such as water intake, recreation places, and reservoir outlet were studied. The calculated results provide useful information for chemical incident response and environmental impact analysis.

Key words: Chemical spill model, Statistic analysis, Environmental impact, Reservoir

1. INTRODUCTION

A large number and wide variety of chemicals are used in manufacturing facilities and transported near water bodies, raising potential dangers of chemical spill incidents. In recent years, the number of accidents by which large quantities of toxic chemicals are discharged into water bodies has increased. In November 1986, several tons of various pesticides (such as thiometon), solvents, dyes, and other raw and intermediate chemicals were flushed into Rhine River within a few hours due to a fire in a chemical storehouse at Schweizerhalle, Switzerland (Wanner et al, 1989). The accident led a massive kill of fish and other living organisms over 250 km along the river. In October 2000, a tanker, the Ievoli Sun, sank in the English Channel containing about 4000 tons of styrene, 500 tons of methyl ethyl ketone, and 1000 tons of isopropanol (French et al, 2006). This incident raised awareness of potential ecological risks of chemical spills. In November 2005, an explosion at a chemical factory in China's Jilin Province released about 100 tons of highly toxic benzene into the Songhua River, a tributary of the Amur (Kim and Murphy, 2006). The blasts created a 80 km long toxic slick in the Songhua River. As the slick travelled downstream, dead fish washed up on the banks and

many water supply facilities had to be shut down for a couple of days. In March 1993, About 65,000 gallons of toluene spilled from a ruptured line into the Ohio River while being pumped from a barge into a factory (New York Times, 1993). This incident caused a lot of potential environmental impacts on the Ohio River.

When a chemical accident occurs, it is imperative to know where the released chemical may go and what the chemical concentration in water is. Numerical model provides a useful tool for predicting the trajectory and fate of chemical spills in water body. National Center for Computational Hydroscience and Engineering (NCCHE) has developed a two dimensional hydrodynamic model, CCHE2D, to simulate the flow in natural water bodies. In recent years, its capability has been expanded to predict the fate and transport of chemicals in water. The processes of volatilization, photolysis, hydrolysis, adsorption, desorption, degradation, etc. were included in CCHE2D chemical module, and the interaction between sediment bed and water column was also considered (Jia et al 2002, Zhu 2006).

In this paper, a hypothetical chemical incident in a reservoir in USA was presented. It was assumed that 30 tons of toluene, one of toxic chemicals for human being and animals, was discharged into a river from a plant located 100 km upstream of the reservoir, and then transported through the river into reservoir. The CCHE2D model was applied to simulate the flow as well as toluene concentration distribution in the reservoir. Based on numerical results, the polluted areas due to the chemical incident in the reservoir, and the worst condition for some important facilities, such as water intake, recreation places, and reservoir outlet were estimated. These results provide useful information for chemical incident response and environmental risk analysis.

2. CHEMICAL SPILL MODULE DESCRIPTION

2.1 Governing Equations

In the current CCHE2D chemical module (Zhu 2006), the distributions of chemical concentrations in the water column and in the sediment lays were simulated. The processes of transportation, volatilization, sedimentation, adsorption, degradation, etc. were considered.

In the water column, the chemical concentrations can be described by the following mass transport equation:

$$\frac{\partial C}{\partial t} + u\frac{\partial C}{\partial x} + v\frac{\partial C}{\partial y} = \frac{\partial}{\partial x}(D_x \frac{\partial C}{\partial x}) + \frac{\partial}{\partial y}(D_y \frac{\partial C}{\partial y}) + \sum S_i \tag{1}$$

in which u and v = depth-averaged velocity components in x and y directions, respectively; C = depth-averaged chemical concentration in water column; D_x *and* D_y = dispersion coefficients; $\sum S_i$ = effective source terms, which include source terms due to external loading, volatilization, adsorption, desorption, degradation, and vertical diffusion at water-sediment interface.

In sediment layers, it is assumed that pore water may infiltrate in and out of those layers and thus induce additional chemical transfer. In the present module, a multiple-layer approach proposed by DiToro (2001) was used to simulate the chemical transport in sediment layers. The governing equations can be expressed as:

$$\frac{\partial h_j C_j}{\partial t} = \sum S_j \tag{2}$$

where C_j =concentration of chemical in sediment layers; h_j =depth of sediment layers; $\sum S_j$ is the effective source term. In the first sediment layer, $\sum S_j$ includes source terms due to external loading, vertical diffusion at water-sediment interface, degradation, and vertical

diffusion between the first and second sediment layers. In other sediment layers, $\sum S_j$ includes source terms due to external loading, vertical diffusion between neighboring sediment layers, and degradation in sediment layers.

2.2 Chemical Fate Processes Considered in the Chemical Module

Volatilization is the movement of chemical across the air-water interface as the dissolved neutral concentration attempts to equilibrate with the gas phase concentration. The rate of exchange is proportional to the gradient between the dissolved concentration and the concentration in the overlying atmosphere and the conductivity across the interface of the two fluids. The conductivity is influenced by molecular weight, Henry's Law constant and environmental conditions at the air-water interface. Based on the "two-film" theory, a formula was presented to calculate the volatilization rate (Wool et al. 2001).

The adsorption process occurs in the water column between dissolved chemical and particulate matter. Adsorption reactions are usually fast relative to other environmental processes, and equilibrium may be assumed. In the present model the processes of adsorption-desorption are assumed to reach equilibrium at each time step and a linear adsorption isotherm is applied to describe the kinetics of adsorption and desorption. The ratio between the concentrations of particulate and dissolved chemical is taken as a constant and defined as partition coefficient. Its value can be obtained from the experimental measurement or calculated based on the organic carbon partition coefficient (Karickhoff et al 1979).

Degradation encompasses the broad and complex processes of enzymatic attack by organisms on organic chemicals. A first order decay algorithm is used to simulate the degradation process of chemical, and constant decay rates are specified for chemical degradation in water and sediment systems. The degradation rate of a chemical in water or soil can be obtained based on the experimental measurements.

2.3 Numerical Solution

The chemical spill module was decoupled with the CCHE2D free surface flow and sediment transport finite element model (Jia et al 2002). The unsteady flow equations were solved using the time marching scheme. The velocity correction method was applied to solve the dynamic pressure and enforce mass conservation. Provisional velocities were solved first without the pressure term, and the final solution of the velocity was obtained by correcting the provisional velocities with the pressure solution (Jia et al 2002). The system of the algebraic equations was solved using the Strongly Implicit Procedure (SIP). Flow fields, including water elevation, horizontal and vertical velocity components, and eddy viscosity parameters were computed by CCHE2D and set as an input data file. The concentration distributions of chemical in the water column and sediment layers were obtained by solving mass transport Eq. (1) and (2) numerically.

This model has been verified using analytical solution and applied to a real chemical incident case in Rhine River, Switzerland (Zhu 2006).

3. MODEL APPLICATION

3.1 Study Area

In order to test the model capabilities for simulating chemical spills and their transports in natural waters, a realistic reservoir in USA was selected. The area of the reservoir is about 134 km^2 acres, and the averaged depth is about 3 meters. It serves as the

primary drinking water supply for a city, and it also provides recreational opportunities in the forms of campgrounds, parks, boat launches, multi-purpose trails, etc.

Fig. 1 shows the watershed of the reservoir and upstream rivers. Since the reservoir is connected directly or indirectly by many rivers or creeks in the watershed, the water quality in the reservoir is mainly affected by the water quality levels of the receiving water. There are 9 hydrology stations and 21 water quality stations in this watershed. The water levels, water discharges as well as some water quality constitutes at those stations are measured. These measured data can be used for model simulation.

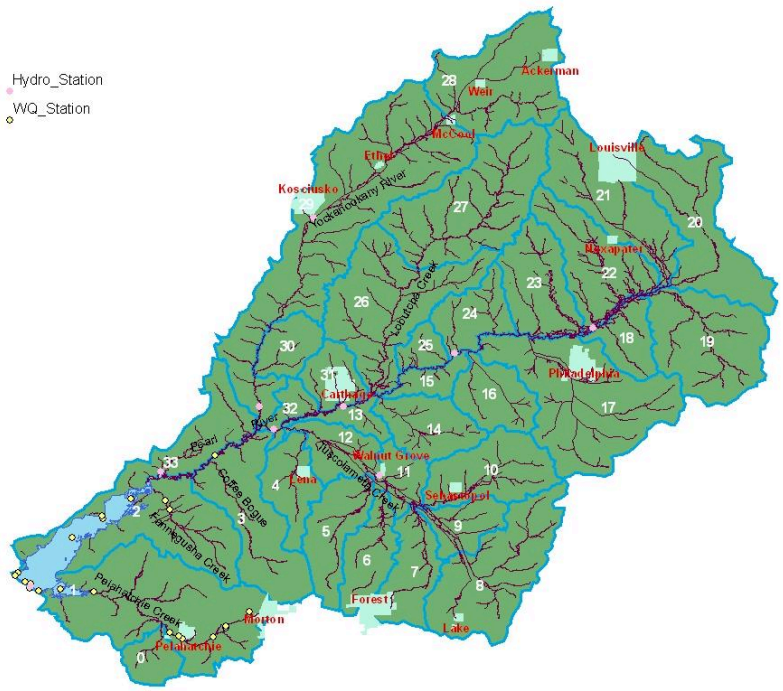


Fig. 1 Watershed of the reservoir and upstream rivers

3.2 TRI Facilities in the Watershed

The Toxics Release Inventory (TRI) is a publicly available EPA database that contains information on toxic chemical releases and other waste management activities reported annually by certain covered industry groups as well as federal facilities. This inventory was established under the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) and expanded by the Pollution Prevention Act of 1990.

Fig. 2 shows the TRI facilities distribution in the watershed. There are 26 TRI facilities in 10 sub-watersheds, including Areas 1, 5,6,7,10,17,21,28,29,33, and releasing 19 chemicals to water, air as well as other sites. The total release amounts of chemicals from those TRI facilities are listed in Table 1. In this study, the chemicals released to water and other sites are considered as potential pollutants, and chemical incidents may be occurred in the above mentioned 10 sub-watersheds.

Fig.3 shows the maximum release amounts of chemicals in Area 28. There are seven chemicals, including methyl ethyl ketone, methyl isobutyl ketone, toluene, xylene, lead, mercury, sulfuric acid, are released into water or other sites. In this study, it is assumed that the toxic chemical toluene is released into the river due to a hypothetical chemical incident occurs from a factory in this area.

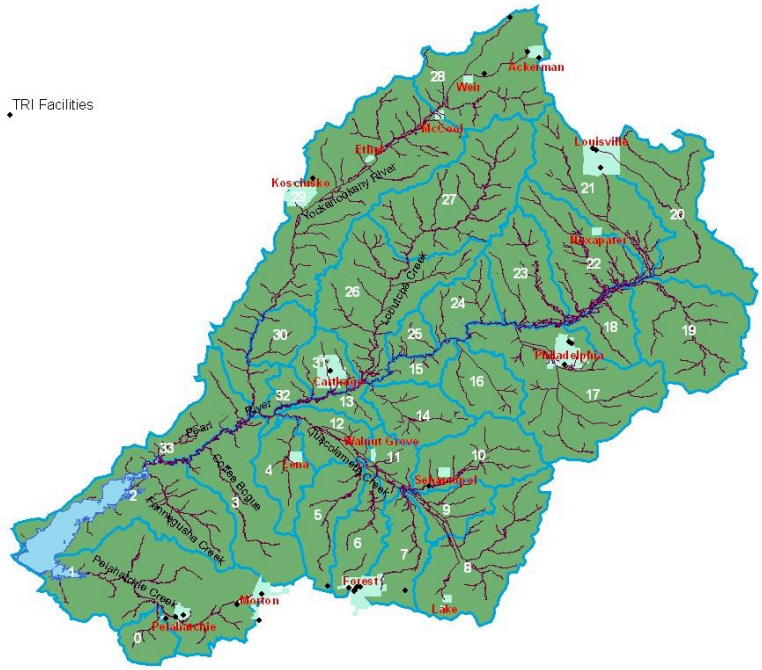


Fig. 2 TRI Facilities in the Watershed

Table 1 Total release amounts of chemicals from TRI facilities

Chemical Name	Release to water (lbs/year)	Release to air (lbs/year)	Release to land or other sites(lbs/year)
Ammonia	2057	197181	22590
Chromium	0	1577	444128
Copper	12	157	98228
Dioxin & Dioxin-like compounds	0	0.27	0.03205
Formaldehyde	0	53599	8060
Lead	2.6217	1768.538	151543.93
Manganese	41	2938	81934
Mercury	0	60	281
Methanol	0	182849	860
Methyl Ethyl Ketone	0	19878	998
Methyl Isobuty Ketone	0	11816	24625
Nickel	41	229	239915
Nitrate compound	2829270	0	0
Phenol	0	7169	498
Sulfuric acid (1994 & after acid aerosols only)	0	183480	0
Toluene	0	61420	7416
Xylene(mixed isomers)	0	16749	2805
Zinc compounds	0	4715	452128
1,1,1-Trichloroethane	0	37305	0

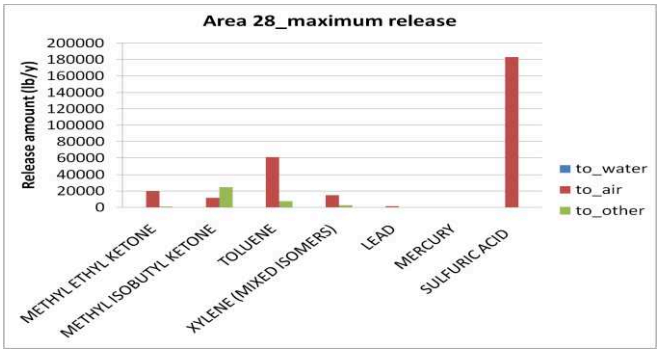


Fig. 3 Maximum release amounts of chemicals in each sub-watershed

Toluene is a flammable, colorless organic liquid with an aromatic odor like that of benzene. It is widely used as raw material in the production of organic compounds and as a solvent for paints and coatings. It is a very toxic chemical. In humans and animals, the primary effect associated with inhalation exposure to toluene is central nervous system depression. Exposure to high concentrations of toluene has produced hearing loss in rats. Hepatomegaly and impaired liver and kidney function have been reported in some humans chronically exposed to toluene. Toluene vapors may cause eye irritation and prolonged or repeated dermal contact may produce drying of skin and dermatitis. The Maximum Contaminant Level (MCL) of toluene in drinking water suggested by EPA is 1 ppm.

3.3 Numerical Simulation of Flow and Chemical Transport in the Reservoir

Fig.4 shows the computational domain of the Reservoir. The length is about 18 km and the width is about 4.8 km. Based on the bathymetry, the computational domain was discretized into a structured finite element mesh using the CCHE Mesh Generator (Zhang, 2007). In the horizontal plane, the irregular computational domain was represented by a 274 × 50 mesh.

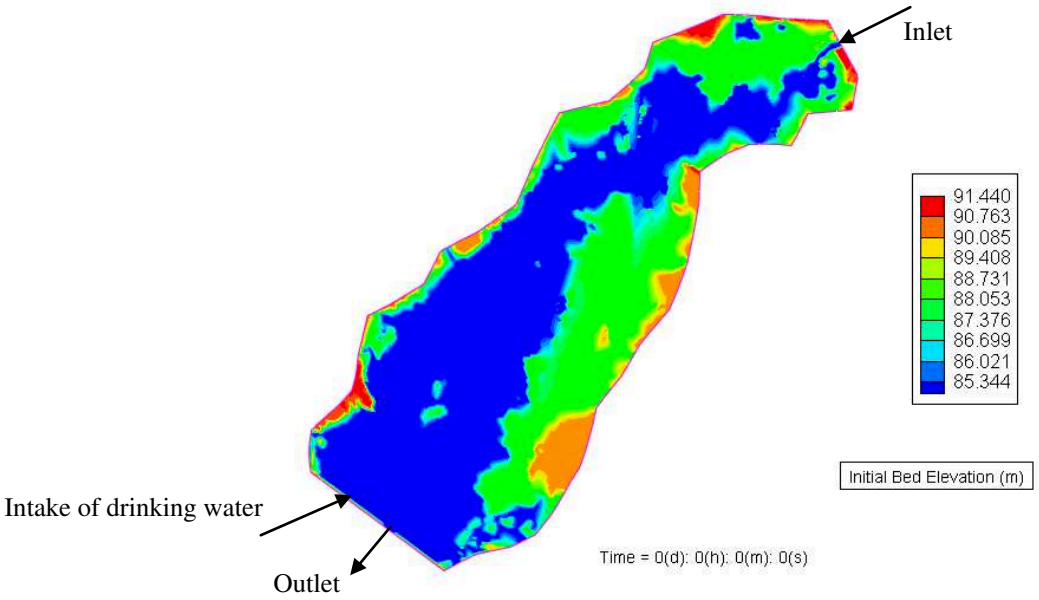


Fig. 4 Computational domain of the Reservoir

CCHE2D model was first applied to simulate the flow fields in the reservoir. Wind stress and upstream discharge are the most important driving forces for flow currents in the reservoir. The period from Jan 1 to 31, 2005 was chosen for model simulation. Fig. 5 shows the observed wind speeds and directions at the 10 m level during the simulation period. Fig. 6 shows the time series of flow discharges at inlet. Fig. 7a and Fig. 7b show the velocity vectors at the first day and second day, respectively.

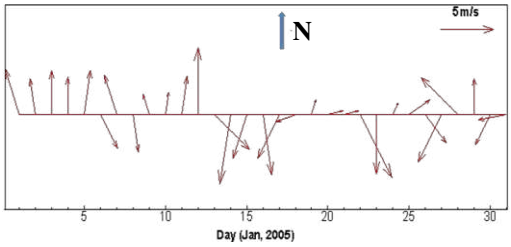


Fig. 5 Time series of wind speeds and directions(Jan. 1–31, 2005)

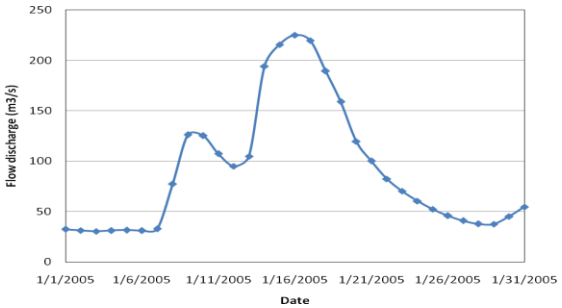
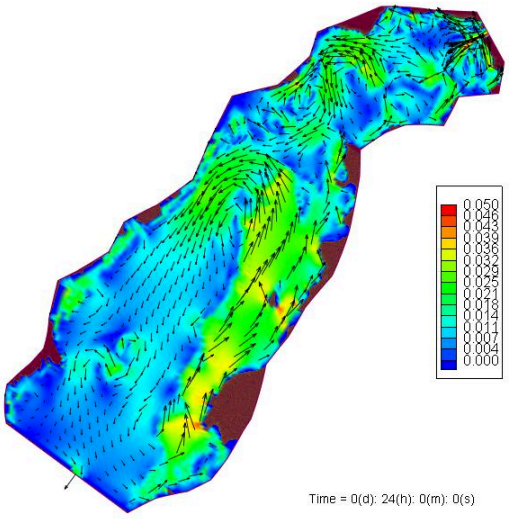
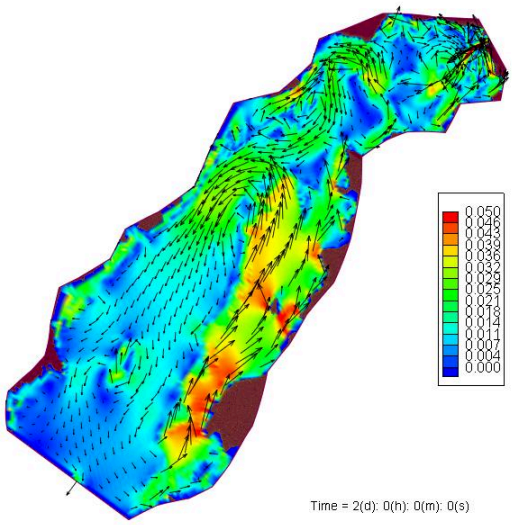


Fig. 6 Time series of flow discharges at inlet(Jan. 1–31, 2005)



a. At 24:00hr, 01/01/2005



b. At 24:00hr, 01/02/2005

Fig. 7 Numerical results of velocity vectors

Based on the environmental information in the watershed of the reservoir and upstream rivers, a lot of toluene has been used for solvent by a factory in the Area 28 shown in Fig. 4. It has potential dangerous for the studied reservoir due to an unexpected chemical incident. It was assumed due to a chemical incident at the factory, about 30 tons of toluene released into a nearby river, and then transported through the river to the reservoir.

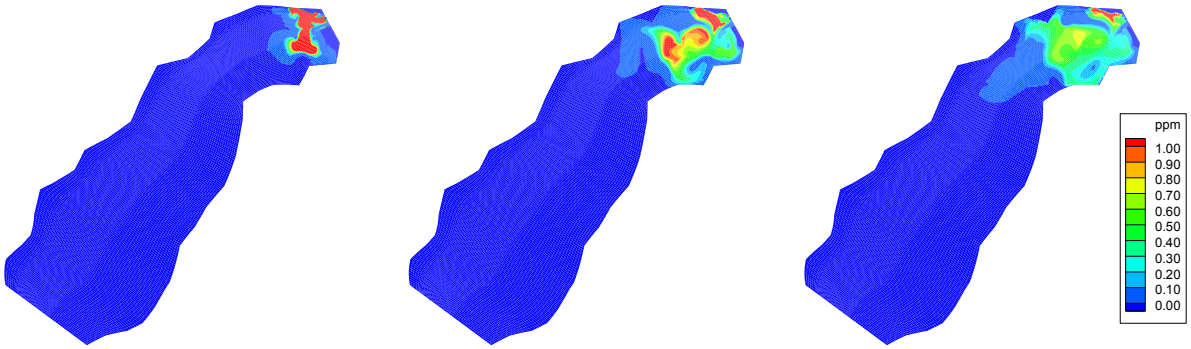
After obtaining the flow currents, the time series concentrations of toluene in the reservoir can be simulated using CCHE2D model. It is known that the density of toluene is smaller than water and the solubility of toluene in water is very low, so when toluene releases to water, it may spreading on the water surface first, and then transport and diffuse into water column. For this case, the processes of trajectory and fate of toluene in the river were not simulated. When transporting in the river, it was assumed about 1/3 of toluene lost due to evaporation, dissolution, decay, etc., and toluene slicks on the water surface had broken and mixed with water before it transported to the reservoir. So the surface processes including spreading, advection, evaporation, dispersion, etc, were not taken into account. It took about 12 hours for the remaining 20 tons of toluene completely discharged into the reservoir from

the inlet. The concentration of toluene in the reservoir can be obtained using CCHE2D model by solving the mass transport equation (Eq.1). The boundary condition of toluene concentration at inlet can be calculated by

$$C_0 = \frac{M_0}{Q_0 T} \tag{3}$$

in which, C_0 = toluene concentration at inlet; M_0 = total mass of toluene discharged into reservoir; T = time period for toluene completely discharged into reservoir from the inlet; and Q_0 = flow discharge at inlet.

Fig.8 shows the concentration distribution of toluene at first day, third day and fourth day after toluene discharged into reservoir, respectively. It can be observed that during the first four days, the upstream of the reservoir was the major polluted area, and the concentration was greater than the 1ppm of the Maximum Contaminant Level (MCL) suggested by EPA. After four days, the concentration in the whole reservoir was less than the MCL.



First day Third day Fourth day

Fig. 8 The concentration distribution of toluene in the reservoir (ppm)

4. STATISTIC ANALYSIS OF CHEMICAL SPILL IN THE STUDIED RESERVOIR

Since chemical spill incidents are random events, they are not predictable. In order to get useful information for spill response planning and environmental risk assessment, the chemical spill model was used to run lots of cases by changing flow discharges, wind conditions and spill amounts. These flow discharges and wind conditions were obtained based on frequency analysis of their time historical records. The hypothetical case presented in section 3 was uses for model simulation. Using statistic analysis, the probability (percentage) of each location that concentration is higher than the MCL can be obtained, and the worst condition for some important facilities, such as water intake, recreation places can be figured out. Based on EPA's water quality standard, polluted areas due to chemical incidents in the reservoir can be estimated. These results provide useful information for chemical incident response and environmental risk analysis.

Based on the recent 10 years time historical records of flow discharges obtained from USGS and wind speeds and directions obtained from National Climatic Data Center, the frequency distributions of flow discharges and wind rose diagram can be obtained (Fig. 9 and Fig. 10).

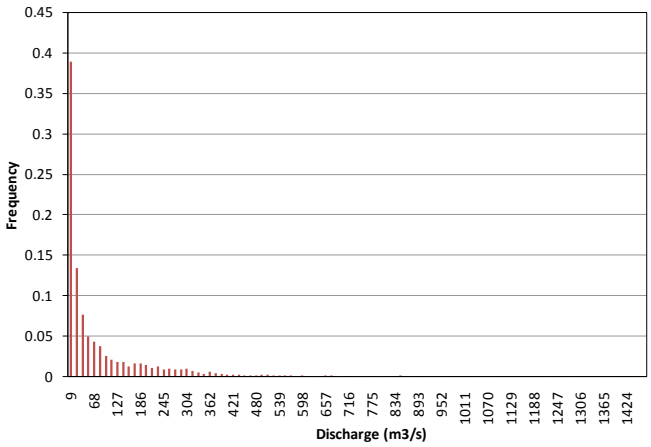


Fig. 9 Frequency distribution of flow discharge

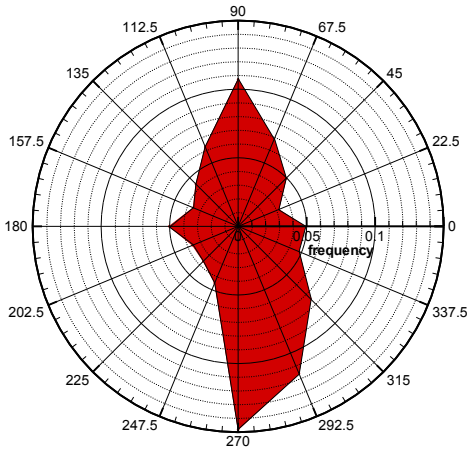


Fig.10 Daily averaged wind rose diagram

The flow discharges were classified as three groups based on the frequency distributions. Table 2 show discharges, water level, as well as their related frequencies of the three groups.

Table 2 Frequencies of three flow groups

Flow	High		Low		Mean	
	Value	frequency	Value	frequency	Value	frequency
Inlet discharge (m^3/s)	422	0.1	11	0.5	87	0.4
Outlet water level (m)	90.8	0.1	90.05	0.5	90.2	0.4

The wind directions and speeds were classified as 8 and 3 groups, respectively. The wind speeds, directions and their related frequencies of the total 24 groups are listed in Table 3.

Table 3 Frequencies of 24 wind condition groups

wind		High		Low		Mean	
directions	frequency	Value m/s	frequency	Value, m/s	frequency	Value m/s	frequency
East	0.0860	4.82	0.03	0.65	0.2	2.1	0.77
North	0.1789	10.03	0.01	0.65	0.11	2.76	0.88
Northeast	0.0969	10.03	0.01	0.65	0.15	2.21	0.84
Northwest	0.0896	5.86	0.02	0.65	0.12	2.76	0.86
South	0.2362	6.9	0.01	0.65	0.12	2.52	0.87
Southeast	0.1525	7.95	0.01	0.65	0.16	2.46	0.83
Southwest	0.0767	6.9	0.01	0.65	0.24	1.96	0.75
West	0.0831	5.86	0.03	0.65	0.19	2.0	0.78

Combining 3 flow discharge and 24 wind groups, there are 72 groups representing the whole possible flow-driven conditions. The CCHE2D model was applied to simulate flow fields as well as toluene concentrations for each group. Based on simulation results of those multiple model runs, some statistics were produced for environmental risk assessment.

Fig.11a shows the possible maximum toluene concentration at each location in the reservoir. The upstream of the reservoir near the inlet was the major polluted area, and the maximum concentration was about 17ppm, much higher than the MCL. At the outlet, the maximum concentration was about 3.4ppm, which means the hypothetical chemical incident may cause potential pollution for the river located downstream of the reservoir. The maximum concentration at the intake of drinking water was always less than the 1ppm of MCL, which means the hypothetical chemical incident may not affect the quality of drinking water. Fig.11b shows the earliest time that concentration might exceed MCL at each location. During the first one or two days, the most areas of upstream of the reservoir were polluted. It might take 4 days for the toluene concentration at outlet was greater than the MCL. These results could be used for guiding the operation of decontamination processes. Fig. 11c shows the maximum exposure time that concentration might exceed MCL at each location. At the upstream of the reservoir near the inlet, the maximum exposure time was about 2 days, it might greatly affect the fish and other biological population. Fig. 11d shows the probability of each location that toluene concentration was higher than the MCL. Among the total 72 cases, the occurring probability of each case was different. Those differences were treated as different weight factors when calculating the probability of each location shown in Fig. 11d. At the upstream of the reservoir near the inlet, the probability that toluene concentration was higher than the MCL was more than 90%, while at the outlet, the probability dropped to 10%.

Those results provide useful information to understand the worst conditions of each location, such as maximum concentration, maximum exposure time, etc.

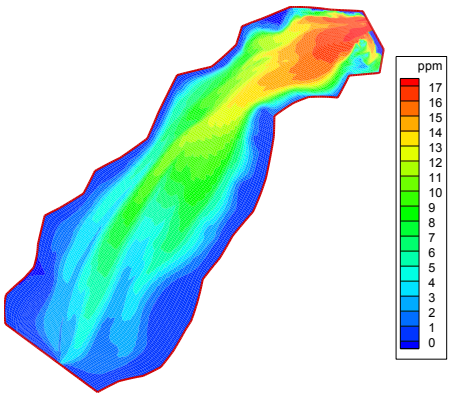
CONCLUSIONS

The CCHE2D model was applied to simulate flow fields as well as chemical concentration distributions of a hypothetical chemical incident in a reservoir. The hydrological information, weather conditions, as well as chemical release amounts within the reservoir-related watershed were collected. The time series of flow velocities and chemical concentrations in the reservoir were obtained. Based on numerical results and EPA's drinking water standard, polluted areas in the reservoir due to the chemical incident were estimated.

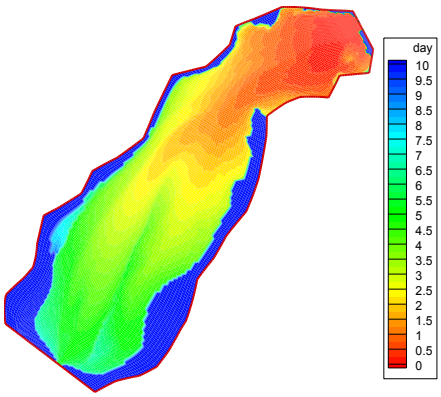
In order to provide information for emergency management and response planning, the numerical model was applied to simulate lots of cases by changing flow discharges, wind directions and speeds. Based on the simulation results of those multiple model runs, the following statistics were produced for environmental risk assessment:

- The probability at each location that chemical concentration is higher than the MCL
- The possible maximum chemical concentration at each location
- The earliest time that concentration may exceed MCL at each location
- The maximum exposure time that concentration may exceed MCL at each location

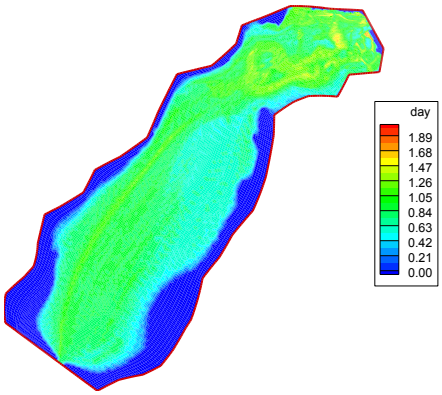
This model provides useful information for developing and implementing an emergency response plan, and they are also valuable for environmental impact assessment.



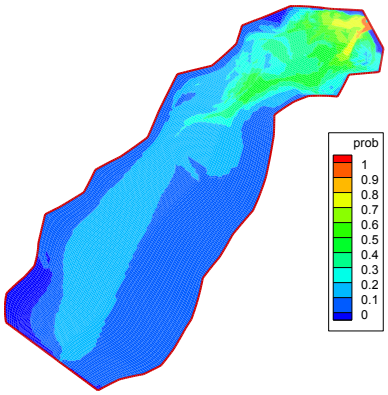
a. The possible maximum toluene concentration at each location



b. The earliest time that concentration might exceed MCL at each location.



c. The maximum exposure time that concentration might exceed MCL at each location



d. The probability of each location that toluene concentration Might be higher than the MCL.

Fig. 11 Statistic results of whole 72 groups

ACKNOWLEDGMENTS

This research was funded by US Department of Homeland Security (No. 4000055423). The suggestions and advices provided by and Dr. Yaoxin Zhang of the University of Mississippi and Mr. Dan Gaillet of the Pearl River Valley Water Supply District are highly appreciated.

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