

Numerical Modeling of Ozonation of Organic Chemicals in Surface Water

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ABSTRACT

Ozonation of organic chemicals generally can result in less toxic and more biodegradable products. It is proposed to use ozone as a potential decontaminant in case of chemical spill in surface waters. CCHE2D chemical model, a two-dimensional depth-averaged and process-based chemical fate and transport model, was developed for simulating multiple decontamination tests including two-chemical-reaction processes. In this study, toluene decontamination by ozone was selected as an example. Both chemicals' transport, fate and the reactions between these two are all taken into consideration. The model is also used to investigate the effectiveness of decontamination on the water quality by comparing the simulation results of a self-decay case with scenarios of ozonation. The hypothetical case demonstrated the model's capability to represent not only the chemical fate and transport but also the decontamination operations.

INTRODUCTION

Recently, there is a rising awareness of water infrastructure security. Surface water quality can be deteriorated by chemical spill incidents caused by natural or manmade disasters such as extreme flood, transportation accidents, willful dumping, etc. There is an increasing need to assess the environmental impact of the chemical spill incidents and evaluate the mitigation and control measures to counteract the negative effects. Numerical models have been extensively used as an assessment and evaluation tool. Some examples are the modeling of the chemical spill on the Rhine River in November 1986 (Mossman *et al.*, 1988); the simulation of the long-term impacts of heavy metals or PCBs in both fresh and coastal waters (Thomann *et al.* 1993, Ji *et al.*, 2002, QEA, 1999).

CCHE2D chemical model (Zhu et al., 2006) has been developed and validated to simulate chemical fate and transport. It is a two-dimensional depth-integrated and process-based model for simulating advection, dispersion, settling and erosion of sediments, partition between dissolved and particulate phases of chemicals, mass transfer between the water column and sediment bed, and chemical decay through volatilization, photolysis, hydrolysis, and biodegradation, etc. It was integrated with CCHE2D hydrodynamic and sediment transport model (Jia and Wang, 1999; Jia et al., 2002). The model uses a finite element numerical scheme and staggered quadrilateral meshes. It has been developed for simulating free surface flows, sediment/pollutant transport and channel morphological changes. The model has been verified and validated vigorously using analytical solutions, physical model data, and field data.

In this study, the CCHE2D chemical model was extended to simulate the reactions between two chemicals in addition to their individual fate and transport. The purpose of this new development is to study the decontamination measures in case of a chemical spill incident using numerical simulation. The selected study case here is the ozonation of spilled toluene resulted from a hypothetical spill incident.

Toluene (C_7H_8 or $C_6H_5CH_3$) is a common solvent and can be used as additive to gasoline, adhesive and cleaning agent, and raw material in production of benzene and polymers (ATSDR, 1994). By inhalation or ingestion, toluene can cause acute and chronic health problems, and pose as a cancer threat (ATSDR, 1994, USEPA, 1999). Toluene is a colorless, flammable, refractive liquid, slightly soluble in water (The Merck Index, 1989) with the solubility of 0.47 g/l at 20°C. The Maximum Contaminant Level (MCL) of toluene in drinking water suggested by EPA is 1 ppm. There are over 100 toluene spill incidents occurs since 2000 (NRC, 2009). One of the major incidents happened in March 1993, when 65,000 gallons of toluene was spilled into the Ohio River.

Ozone has been widely used to reduce the concentration of aromatic organic pollutants such as toluene, benzene, etc., in wastewater and drinking water. The advantage of ozonation is that it generally results in less toxic, more bio-degradable products. Ozone itself decomposes into oxygen if not consumed by the pollutants. In the drinking water industry, the only regulated ozonation by-product in United States (USEPA, 1998) and Europe (EU, 1998) is bromated, which is formed by the ozonation of bromide-containing waters. The reaction products of ozonation of toluene are not well documented in literature. Wibau et al. (1950) reported that formic, acetic, oxalic acids, carbon dioxide and water may be formed in the ozonation of toluene. Recently, Pi et al. (2005) proposed a reaction pathway for the reaction of ozone and some aromatic compounds, including toluene and the products of toluene ozonation would be short chain hydrocarbons, which are more bio-degradable and less toxic than toluene. Hence, it is proposed to use ozone to clean the spilled toluene in natural water body.

REACTION MECHANISM

In aqueous phase, ozone oxidizes toluene in two major mechanisms (Hoigne and Bader, 1976; Langlais et al., 1991, von Gunten, 2003): one is the direct oxidation

of toluene by ozone molecules; and the other is indirect oxidation by hydroxyl radical reactions. Toluene reacts with ozone in the following form:



in which, η is the stoichiometric ratio ranging from 1-2.5 with the maximum measured in the lab condition of 5 (Hoigne and Bader, 1983).

Toluene decays by ozone direct and indirect oxidation can be written as:

$$-dC/dt = k_T C_{ozone} C$$

$$-dC_{ozone}/dt = (\eta k_T) C_{ozone} C$$

in which, C is the toluene concentration, C_{ozone} is the ozone concentration, k_T is the overall rate constant.

Kuo and Chen (1996) carried out a traditional ozonation test at pH values varying from 3 to 11 at 25°C. The initial concentration of ozone is from 0.00013 to 0.0002 mol/l (6.24 mg/l to 9.6 mg/l), and toluene from 0.0005 – 0.002 mol/l (46 mg/l to 184 mg/l). The overall rate constant ranges from 2.34 l/(M s) to 29.41 l/(M s) (pH from 3.0 to 9.0). The oxidation kinetics is first-order with respect to the ozone concentration, and the reaction order in toluene varies with pH ranging from 0 to 1 (0 for pH over 10.0; 0.5 for pH between 7.0 and 9.0; and 1 for pH below 5.4). The measured stoichiometric ratio is 1 in their study. The oxidation rate is determined by both the direct and indirect mechanisms in distilled water (initial pH of 5.2-5.4) and other weak acids.

In natural waters, ozone can be consumed not only by the spilled pollutants but also by a lot of organic and inorganic compounds existing in the background. The rate of dissolved ozone consumption can be written as:

$$-dC_{ozone}/dt = w C_{ozone}$$

in which, w is the specific ozone utilization rate, a function of the pH and chemical composition of the water matrix.

Yurteri and Gurol (1988, 1989) did experiments using synthetic water samples from several rivers and groundwater. Various chemical consumptions have been tested (pH = 6.8 – 9.0; TOC (total organic carbon) 0.3-5.3 mg/l; alkalinity = 10 – 500 mg/l as CaCO₃). The temperature was controlled at 20±1°C. The initial ozone concentration was set around 10 mg/l. The experiments were carried out in a headspace-free reactor made of dark glass so that volatilization was limited. The specific ozone utilization rate was found to be

$$\log w = -3.98 + 0.66\text{pH} + 0.61 \log (\text{TOC}) - 0.42 \log(\text{alkalinity}/10)$$

in which, w is in /hr.

GOVERNING EQUATIONS OF THE MODEL

The chemical model simulates the ozonation of toluene by solving three transport equations simultaneously: two for the toluene transport in the water and bed respectively; and the third for the transport of ozone in the water. The transport equation in the water is written as:

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x}(uC) + \frac{\partial}{\partial y}(vC) = \frac{\partial}{\partial x}(E_{xx} \frac{\partial C}{\partial x}) + \frac{\partial}{\partial y}(E_{yy} \frac{\partial C}{\partial y}) + S_k + S_{load}$$

where C is depth-averaged concentration for either ozone or toluene (mg/l); u , v are depth-averaged velocities in x and y direction (m/s), respectively; E_{xx} and E_{yy} are components of dispersion tensor E (m^2/s); S_k is kinetic source term (mg/l/s); and S_{load} is the external loading (mg/l/s).

The kinetic source term for ozone is mainly due to the consumption of toluene and background organic and inorganic compounds.

$$S_{ozone} = wC_{ozone}$$

The kinetic source term for toluene comprises of chemical source/sink due to net settling or eroded sediment flux, vertical diffusion, decay (volatilization and biodegradation) and decomposition by ozonation.

$$S_{toluene} = S_{load} + S_{sed} + S_{v-diff} + S_{decay} + S_{ozonation}$$

where S_{sed} is chemical source/sink due to net settling or eroded sediment flux (mg/l/s); S_{v-diff} is vertical diffusion flux at the water-sediment interface (mg/l/s); and S_{decay} is chemical decay term (mg/l/s).

$$S_{ozonation} = k_T C_{toluene} C_{ozone}$$

It is assumed that the convection and dispersion in bed sediments are negligible. The governing equation for the bed sediments in the conservative form is:

$$\frac{\partial(C_s \times D_{sed})}{\partial t} = S_{load,s} - S_{sed} + S_{v-dif} + S_{decay,s}$$

where C_s is the toluene concentration in bed (mg/l); D_{sed} is the depth of sediment layer (m); $S_{load,s}$ is the external load to bed (mg/l/s); and $S_{decay,s}$ is the chemical decay rate in the bed (mg/l/s).

SIMULATION OF TOLUENE OZONATION SCENARIO

In this study, a hypothetical toluene spill incident was assumed to occur in a reservoir. The reservoir is about 18 km long and 4 km wide with the water depth of about 4 m in the main channel. It was assumed that 270 tons of toluene was spilled into the middle of the reservoir over a period of 12 hours due. In order to clean the spilled toluene, the following numerical ozonation operation procedures were designed:

1. Identify the highest toluene plume in the reservoir, which can be found out using the simulation results of the toluene spill incident.
2. Set up an ozone barrier in the reservoir close to the plume with high concentration of toluene. The ozone barrier shall move at a similar speed with the traveling velocity of the toluene plume so that when it passes by, toluene can be degraded more efficiently. The traveling

velocity of the plume can be estimated from the flow simulation results. The length of the ozone barrier is set about the width of the plume. Two barrier width and two ozone generation capacity were tested in this study, which makes four operations in total.

3. Analyze the efficiency of ozonation using the simulation results of the chemical model. Adjust the location and ozone generation capacity of the ozone barrier if necessary to achieve favorable cleaning effects.

Flow simulation was conducted first to obtain the flow field (flow velocity, water depth, and eddy viscosity). With the input of flow field, the CCHE chemical model then was used to simulate the fate and transport of toluene spill incident, which provides the temporal and spatial toluene concentration in the reservoir and also serves as the background level without ozonation. Finally, four ozonation operations were simulated and analyzed.

Flow Field Simulation

The simulation domain was discretized into a 70 by 174 numerical mesh. Steady flow condition was assumed with the flow discharge at upstream being 120 m³/s and water surface elevation at downstream 90.25 m. Manning's roughness coefficient was set as 0.025. Mixing length model was used for the turbulence closure. The steady flow was simulated at a time step of 20 seconds using CCHE2D model. Figure 1 shows the bathymetry of the reservoir, locations of inlet, outlet and toluene spill, and local flow field near the spill site.

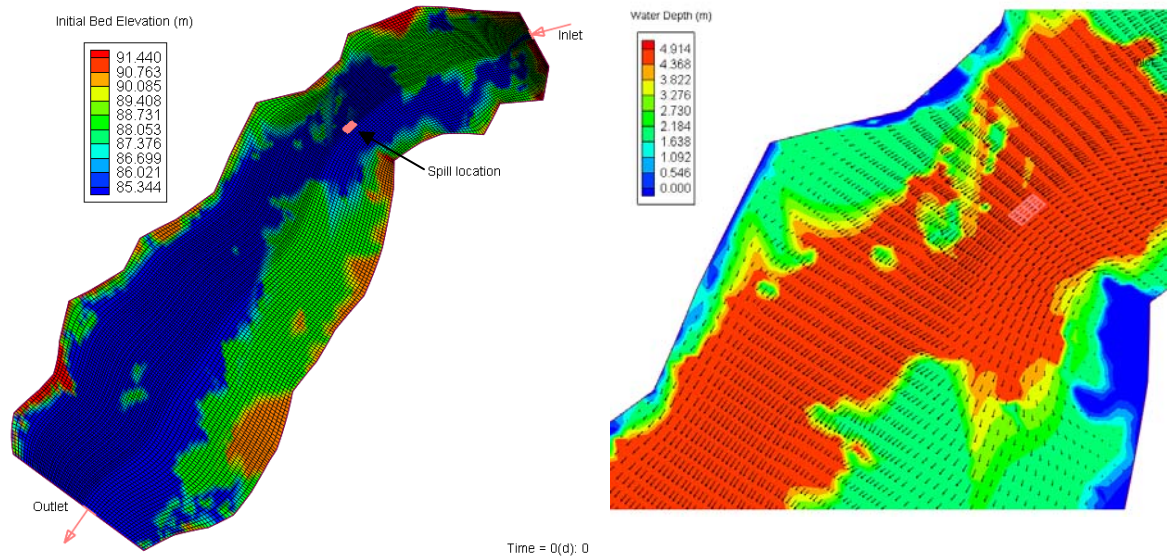


Figure 1 Numerical domain (left) and local flow field (right)

Simulation of Toluene Spill

The hypothetical toluene spill incident was simulated for 10 days. The parameters for simulating toluene decay processes and interaction with sediments are listed in Table 1.

Table 1 Parameters for simulating toluene

Biodegradation rate (s^{-1})	1.30787E-006
Partition coefficient	100
Vertical diffusion (m^2/s)	1E-007
Gas phase transfer rate (m/s)	1E-005
Henry's constant ($atm\ m^3/mol$)	0.00664
Suspended sediment concentration (mg/l)	10
Bed porosity	0.4

Toluene concentration still exceeds EPA's MCL at the end of 10 days although due to decay processes, it has decreased from 298 mg/l (at the end of first day after spill) to 7 mg/l (at the end of 10 days after spill) (shown in Figure 2).

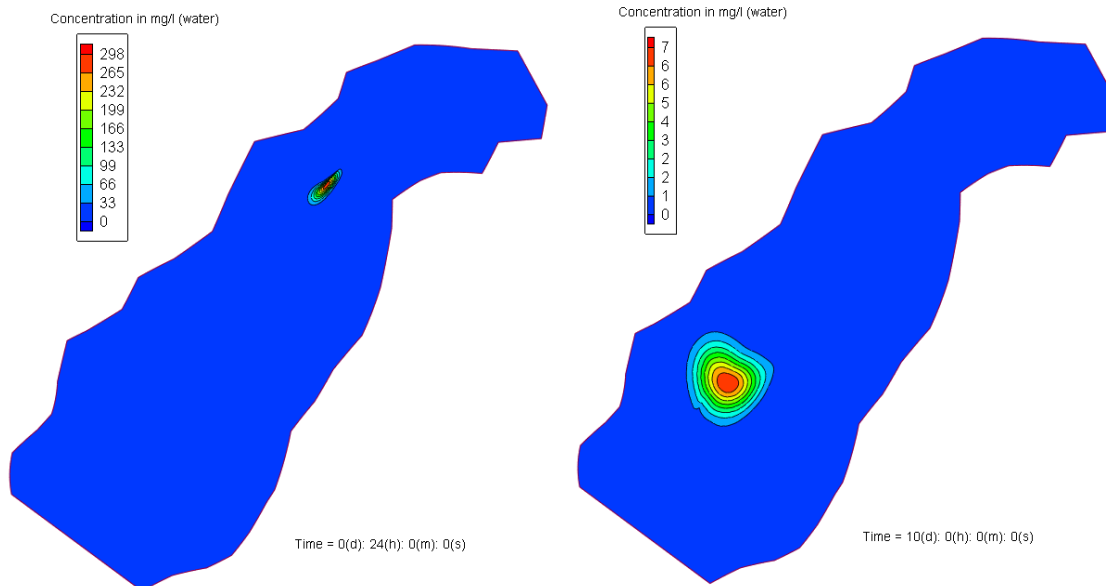


Figure 2 Toluene concentration distributions after the spill

Simulation of Ozonation Options

The hypothetical ozonation was designed to start right after all toluene was spilled into the reservoir, i.e. after 12 hours of the spill. Four options of ozonation barrier were summarized in Table 2. The barrier moves downstream with the toluene plume at an average speed of 0.013 m/s.

Table 2 Ozonation Operation Parameters

Options	1	2	3	4
Barrie width (m)	80	160	80	160
Ozone generation capacity (g/s)	650	650	1650	1650

The reservoir water is neutral with pH value of 7 and it is assumed that during the simulation period the water temperature is at 20°C. To simplify the problem, it is also assumed that the consumption of ozone was mainly by toluene. The overall rate constant of ozonation was set as 0.0002 s⁻¹. The stoichiometric ratio was set at 1. Four ozonation options were simulated using the same flow, environmental condition, and ozonation rate constant. The simulation results of Option1 and 2 are found to be similar and that's the case for Option 3 and 4, which suggests that ozone generation capacity is the dominant factor to increase the toluene removal rate. Figure 3 shows the toluene concentration distributions at the end of Day 3 after the spill. It can be seen that with higher ozone generation capacity, option 3 can clean the spill site faster.

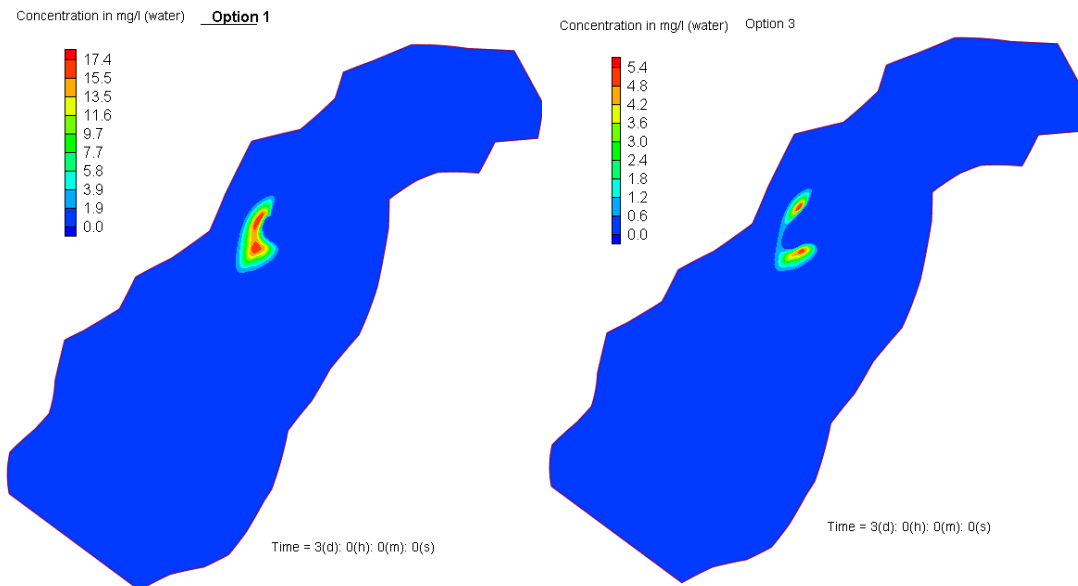


Figure 3 Toluene concentration distributions with ozonation

Total mass of toluene in the reservoir was calculated as ozonation went on to show the removal rates for each option (Figure 4). Again, Option 1 and 2 has the similar mass reducing pattern, which is also true for Option 3 and 4. In Option 3 and 4, the toluene mass reached zero after 100 hours, while it took about 200 hours in Option 1 and 2.

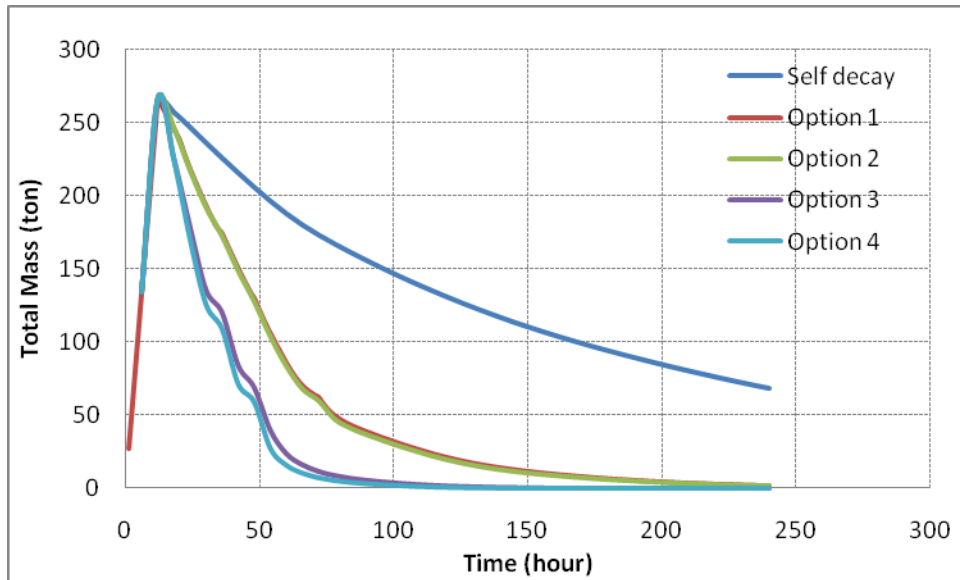


Figure 4 Toluene removal rate of four ozonation options

The water is considered safe if everywhere in the reservoir the toluene concentration is below the MCL (1 ppm). Figure 5 shows the days it took for each option to bring the water back to the safe level. After ten days, the toluene concentration still exceeds the MCL if no ozonation was conducted. Using Options 3 and 4, the water quality can recover the soonest within 5 days.

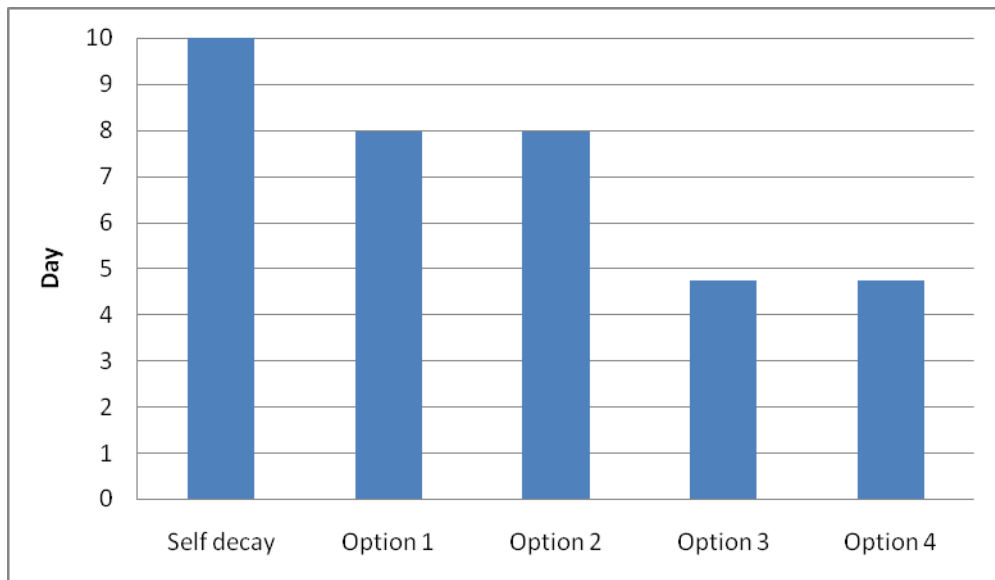


Figure 5 Toluene clean-up time

CONCLUSIONS

A hypothetical toluene spill incident in a reservoir was assumed and the clean-up operations by means of ozonation were designed and simulated using CCHE chemical decontamination model in this study. The process-based model simulates major decay processes of toluene in the surface waters including ozonation, volatilization, biodegradation and interaction with suspended sediments and bed sediments. As this study emphasizes on the simulations of toluene ozonation, the hydraulic condition was simplified as steady flow and toluene decay processes were represented using those from literature. The spatial and temporal concentration distributions of toluene and ozone were obtained from the simulation results.

The impact of ozonation on toluene distributions can be found by comparing the toluene transport scenarios with or without ozone. With ozone barrier moving with toluene plume, the toluene can be decontaminated at least twice as faster compared with that of self decay case. The model is also able to investigate the effectiveness of different ozonation options. It was found through the simulations of four options that the width of ozone barrier has very limited impact on the toluene removal rate. However, the ozone generation capacity plays an important role. With higher ozone generation capacity, the total mass of toluene decreases faster and the reservoir would be cleaned up in about half of the time compared with the lower capacity options.

Although this case study is hypothetical, it demonstrates that the model is a useful tool to help design and evaluate clean-up operations. Practical layout of ozone device needs more study in the future taking into account of factors such as device size, device movement, and cost etc.

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