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RESEARCH ARTICLE

A real-time, dynamic early-warning model based on uncertainty analysis and risk assessment for sudden water pollution accidents

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Abstract A real-time, dynamic, early-warning model (EP-risk model) is proposed to cope with sudden water quality pollution accidents affecting downstream areas with raw-water intakes (denoted as EPs). The EP-risk model outputs the risk level of water pollution at the EP by calculating the likelihood of pollution and evaluating the impact of pollution. A generalized form of the EP-risk model for river pollution accidents based on Monte Carlo simulation, the analytic hierarchy process (AHP) method, and the risk matrix method is proposed. The likelihood of water pollution at the EP is calculated by the Monte Carlo method, which is used for uncertainty analysis of pollutants' transport in rivers. The impact of water pollution at the EP is evaluated by expert knowledge and the results of Monte Carlo simulation based on the analytic hierarchy process. The final risk level of water pollution at the EP is determined by the risk matrix method. A case study of the proposed method is illustrated with a phenol spill accident in China.

Keywords Water quality · Early warning · Risk assessment · Monte Carlo simulation · Analytic hierarchy process

Introduction

With rapid economic development and the growth of human activities, environmental problems have become one of the most serious issues confronted by society. Among these problems, sudden water pollution accidents frequently occur, especially those that affect upstream sources of drinking water (rivers and lakes), such as factory explosions (Zhang et al. 2011), traffic accidents (Hou et al. 2013), and capsized ships (Duarte et al. 2013), which can adversely affect people's health in downstream areas through pollutant advection and diffusion. These accidents possess the following features: (1) they are sudden or unpredictable, (2) they are uncertain or difficult to predict accurately with changes in hydrological and meteorological conditions, and (3) they are catastrophic or leading to grave social consequences.

When a severe water pollution accident occurs in the upstream reaches of a river that threatens downstream area with raw-water intakes (herein called early-warning point or EP), there is a strong need to continually evaluate and report the pollution risk until the pollutant plume no longer threatens the water intakes. There are four key questions of interest about river pollution concerning the downstream EPs as follows: (1) how large is the concentration of the pollutant now and how large will it be in the future? (2) What will the peak value of the pollutant be? (3) When will the pollutant arrive at the EP, and how long will it take for it to no longer pose a threat? (4) Can the water treatment plant (WTP) at the EP remove the pollutants and produce safe drinking water?

Several available water quality models, early-warning models, and early-warning systems could be applied to answer these four questions for eliminating or decreasing the impacts of water pollution accidents. In previous research, sudden water pollution warning models were designed to quickly assess emergency situations, particularly on predicting pollutants' concentrations at locations downstream from a pollution site. Many studies have been conducted to establish mathematical models by employing the principles of mass balance, chemical thermodynamics, and transport phenomena, along with sufficient knowledge of the physical–chemical properties of chemicals and the hydrological and sedimentation characteristics of the receiving environment (Di Toro et al. 1983; Brown

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and Barnwell 1987; Runkel 1998; Connolly et al. 2000). In recent years, several models for organic chemicals have been developed to simulate and predict the transport of organic chemicals in water (Warren et al. 2002; Malve et al. 2003; Wang et al. 2012). Various systems have been researched and developed to produce early warnings and trigger emergency responses to sudden water pollution accidents. For example, a water quality early warning system was implemented by the Ohio River Valley Water Sanitation Commission (ORSANCO) to monitor the water quality of the Ohio River in the US (Grayman et al. 2000). An emergency early warning system designed by researchers in Germany, Austria, and seven other countries for the Danube River was established to provide risk assessment and emergency response to water pollution incidents (Jansky et al. 2004). River Spill is a GIS-based software package that calculates the time of travel and concentration of contaminants in streams and rivers (Samuels et al. 2006). Combined with its GIS spatial environment to communicate propagation risks and locate response resources, SMIS 2.0 is a state-of-the-art, 3D hydrodynamic, chemical spill modeling system tool that possesses improved capability to predict spills and chemical transport (Camp et al. 2010). These systems offer valuable tools for response, planning, and training to protect regional sources of surface drinking water. They can also manage and display data with GIS. However, most of the existing research about sudden water pollution models or early warning systems possess the following limitations: (1) they mainly focus on modeling the transport of contaminants in water; (2) they mainly focus on raw water and the water environment, and rarely on drinking water quality; (3) they employ water quality models with limited consideration of the uncertainties caused by boundary conditions, model parameters, and the physical properties of the river; and (4) they do not involve real-time, effective risk assessment.

Various uncertainty analysis and risk assessment methods for hydrologic and water quality modeling have been developed over the years. The uncertainty analysis methods are mainly applied to evaluate or predict water quality characteristics. Among these methods, stochastic differential equations are commonly used to describe the changes in water quality characteristics of a system using the actual distribution of the observed (or perceived) values of model coefficients instead of their average values to investigate the statistical properties of equations and a variety of possible outcomes (Wendroth et al. 1999; Whitehead et al. 1981; Finney et al. 1982; Hamed and El-Beshry 2004). Other studies on uncertainty analysis have been conducted based on black system theory via artificial neural networks, fuzzy theory, and gray system theory (Maier and Dandy 1996; Huang and Xia 2001; Fan et al. 2003).

Risk assessment methods have also received considerable attention in early warning models of human health, natural hazards, and environmental pollution accidents (Merkhoher 1993). The four-step risk assessment framework for human health (US National Research Council 1983) and the risk assessment methodology for process plants (Salvi and Debray 2006) are two examples of risk assessment methodologies. These methods facilitate risk planning by governments or factories to prevent sudden accidents and decrease risks to an acceptable level. In the field of water pollution, risk assessment is also widely used and most research focuses on in-advance risk assessment, that is, on assessing the impact/consequence and the occurrence probability of pollution (Xu et al. 2004; Liu et al. 2013). Jiang et al. (2012) developed a real-time, generic "four-step-three-mode" method for river chemical spills. This method links risk areas threatened by chemical spills into rivers to geographic information systems (GIS) and models on the basis of risk assessment in real time. Bi and Si (2012) presented a dynamic risk assessment framework of oil spill accidents based on numerical simulation. Most previous risk assessment methods for dealing with pollution accidents tend to focus on the assessment of impacts/consequences, and uncertainty analysis has not been incorporated into these methods.

The introduction of uncertainty analysis and risk assessment methods greatly improve the capacity of early warning for sudden water pollution. However, that type of research was limited by the following issues: (1) they do not combine the likelihood of pollution with the possible consequences of accidents in downstream areas, thus do not produce a comprehensive risk assessment; (2) they do not emphasize the impact of pollutants on the capacity of WTPs, which provide drinking water to cities, and (3) they do not provide a continuous, dynamic analysis to report pollution alarms for the EPs.

Because of the current lack of an efficient warning model for sudden water pollution, the primary objective of the present study is to develop a real-time, dynamic early-warning model for sudden water pollution, based on uncertainty analysis and risk assessment. The model is applicable to sudden water pollution accidents that occur upstream of water intakes that have not yet being polluted. The model produces a comprehensive risk assessment that combines the likelihood of pollution and the possible consequences of pollution on the basis of the uncertainty of pollutant advection/diffusion downstream. The Monte Carlo (MC) method, analytic hierarchy process (AHP), and 1D water quality simulation are combined to support the model, which is tested with a sudden water pollution accident that occurred in the Qiantang River, China.

Methodology

Definition of risk

Pollution risk

There are different definitions of pollution risk in the technical literature. In the early days, pollution risk was often defined as the likelihood/probability that pollution will occur, or the impact/consequence of the pollution, as follows:

$$Risk = L \quad or \quad Risk = I \tag{1}$$

where L is the likelihood/probability of a pollution event occurring, I is the impact/consequence caused by the pollution event.

In some cases, pollution risk was also defined as "a combined measure of the degree of detriment to society or the aquatic ecosystem caused by a defined event (or combination of events), and the probability of that event occurring" (EUREAU 1999; McIntyre et al. 2003). Therefore,

$$Risk = L \otimes I \tag{2}$$

where $\otimes$ is the product operator of the likelihood L and the impact I. Pollution risk is usually categorized into a small number of levels because neither the likelihood nor the impact of pollution can be estimated with accuracy and precision. Risk matrix is frequently used to define the various levels of risk as the product of the harm likelihood categories and harm impact categories. This is a simple and common mechanism to increase the visibility of risks and assist decision making (Henriksen et al. 2009). Equation (2) is an in-advance risk assessment method and cannot evaluate past accidents.

EP risk

In practice, after a severe water pollution accident has occurred in a river basin upstream, a emergency response plan will be quickly launched. Several emergency sampling sites will be deployed temporarily along the river to monitor the concentration of leaked pollutants. Before the pollutants travel to the EP, there is still enough response time to evaluate the potential risk of the accident for the downstream EP. Based on the potential risk, some decision will be made for the EP or river reaches. A schematic of a river pollution accident and its emergency response is shown in Fig. 1, which is adapted from the earlier paper of Grayman and Males (2002).

For realizing real-time and dynamic risk assessment at the downstream EPs, and considering the uncertainty of the transport of pollutants, the pollution risk at a given EP is redefined as follows:

$$EPRisk = L \otimes I \tag{3}$$

where L is the likelihood that pollution will occur at a given EP (hereinafter called EP likelihood) when a sudden water pollution accident has occurred upstream. This value is

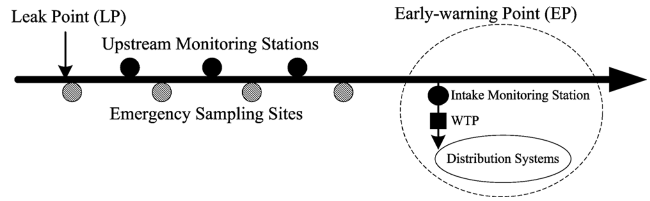

Fig. 1 Schematic representation of river pollution and its emergency response. *WTP* water treatment plant

quantitatively evaluated by the uncertainty analysis method, using information about the accident and numerical simulation of pollutant concentration that is compared with the alarm threshold of a pollutant (set by national standards, or by commonly-recognized criteria, or user-defined concentration of pollutant based on the treatment capacity of the water treatment plant at the EP); I is defined as the potential impacts of river pollution at the given EP (hereinafter called EP Impact, over the entire area served by the WTP). It includes social, economic, and environmental losses caused by the pollution accident; $\otimes$ is an operator applied to L and I based on the risk matrix. Generally, there may be one or more downstream EPs along the river that might be affected by pollution spills.

Framework for EP-risk assessment based on uncertainties

Risk assessment is one of the most important components in the analysis of sudden water pollution accidents. It is a tool used by managers to monitor and implement activities to cope with harmful events. When a sudden water pollution accident occurs in an upstream river reach, confirming the risk at the downstream EP involves uncertain information. Therefore, a four-step model (hereinafter called EP-risk model) was developed for risk assessment of sudden water pollution accidents (Fig. 2).

The first step is implemented by pollutant transport simulation based on uncertainty analysis, and considering water quality data, hydrological data, and meteorological data that is updated with time. The EP likelihood L (step 2) and EP impact I (step 3) at the downstream EPs were obtained from the simulation results of step 1. Step 4 is used to assess the EP risk using risk assessment methods. In practice, steps 1 to 4 can be executed continuously and their execution is triggered by new input data. Therefore, the EP-risk model can be used as a dynamic approach to evaluate the real-time EP risk.

Based on the four-step EP-risk model depicted in Fig. 2, a generalized form/framework of EP-risk model for river pollution accident is proposed based on Monte Carlo (MC) simulation and the analytic hierarchy process (AHP; see Fig. 3).

In this study, the probability distribution of the peak concentration and the duration of the pollution (the duration in which the pollutant concentration exceeds the given alarm threshold) at the EP can be obtained by a set of random MC

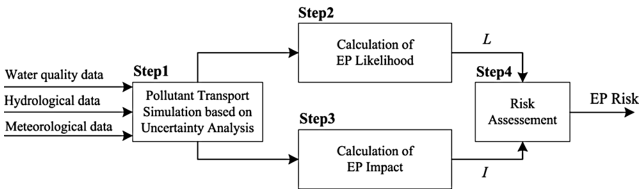

Fig. 2 Schematic of a four-step EP-risk early warning model

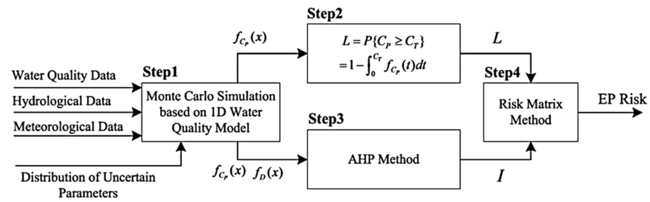

Fig. 3 A generalized form of the EP-risk model for river pollution accident. C_P is the peak concentration of pollution at the EP, D is the duration of pollution at the EP, $f_{C_P}(x)$ and $f_D(x)$ is the probability density function of C_P and D, respectively, and C_T is the alarm threshold at the EP

simulations based on a 1D water quality model. The EP likelihood is calculated based on the probability distribution of the peak concentration. The analytic hierarchy process (AHP) combined with risk matrix method was employed to assess EP risk. The concrete steps of the methodology graphed in Fig. 3 will be described in the next sections.

Step 1: MC simulation based on 1D water quality model

MC simulation

Uncertainty in a water quality simulation model is inevitable because of the difficulty in fully capturing all the nuances (i.e., hydrological information and parameter values) present in river transport. Although there is extensive knowledge available on water quality processes from laboratory experiments, the extrapolation of this knowledge to models of the real environment has consistently proven to be difficult.

The MC method is the most commonly used probabilistic technique to propagate uncertainty in simple or complex models. The MC method is effective in characterizing risks and uncertainty in circumstances in which a considerable amount of data that describe system dynamics is available (Vose 2008). Numerous studies related to the practical applications of the MC method for risk assessment have been conducted (Harris and Jones 2008; Lee et al. 2011; Qu et al. 2012). A typical Monte Carlo simulation of a physical process has four stages as follows (Raychaudhuri 2008):

1. Static model generation

   Every Monte Carlo simulation starts by developing a deterministic model which closely resembles the real scenario (in our case, pollutant transport in the river). This deterministic model represents mathematical relations which use the values of the input variables, and transforms them into the desired output.
2. Input distribution identification

   When the deterministic model is adopted, the risk components are added to the model. As mentioned before, since the risks originate from the stochastic nature of the input variables, the underlying distributions, if any, which govern the input variables need to be identified. This step needs historical data for the input variables. There are standard statistical procedures to identify input distributions.
3. Random variable generation

   After the underlying distributions for the input variables are identified, a set of random numbers (also called random variables or random samples) are generated from these distributions. One set of random numbers, consisting of one value for each of the input variables, will be used in the deterministic model to provide one set of output values. This process is repeated by generating more sets of random numbers, one for each input distribution, and collect different sets of possible output values. Usually, the number of sets of inputs (iterations) is large, and how large it should be depends on characteristics of the phenomenon being simulated. The generation of multiple sets on input values for model simulations constitutes the core of Monte Carlo simulation.
4. Analysis and Decision Making

   After a sample of output values is collected from the simulation, statistical analysis is performed on those values (in our case, the probability distributions of peak concentration and pollution duration at the EP). This step provides statistical confidence for the decisions that the analyst makes after running the simulation.

The MC simulation has been widely used in water quality modeling and risk assessment. Deway proposed a stochastic dissolved oxygen river model by using the MC method (Dewey 1984). Sohn et al. developed a Bayesian MC method for assessing and reducing the uncertainty of groundwater flow and chemical pollutants prediction (Sohn et al. 2000). Arabi proposed a computational framework for analyzing the uncertainty in model estimates of water quality benefits of best management practices (BMPs) in two small watersheds in Indiana (Arabi et al. 2007). Grayman and Males proposed a risk-based modeling of early warning systems for river pollution accidents (Grayman and Males 2002). The MC simulation technique is used to generate random spills events (different locations, substances, magnitudes and duration, etc.) to test early warning systems, and to aid in development of EWS policies and design criteria. However, it remains largely in-advance (or a priori) method of analysis but not a real-time early-warning model. This work implements the MC method as a real-time analysis tool.

In the study, MC simulation is used when a specific river pollution accident has occurred upstream. A set of random parameters (flow velocities, decay rate coefficient, and diffusion coefficients, etc.) is first generated as inputs to the 1D water quality model. After a user-defined number of iterations, one set of output values (such as concentration of river pollutant) is provided to calculate the probability distributions of peak concentration and pollution duration at the downstream EP. The latter two probability distributions are then calculated as the output of the MC simulation for the next risk assessment stage. Figure 4 shows the flowchart of MC simulation based on 1D water quality model.

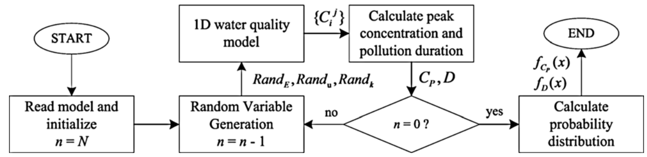

Fig. 4 Flowchart of MC simulation based on 1D water quality model. N is the total number of iterations for MC simulation

1D water quality model

The diffusion and distribution problem of pollutants in water is essentially a complex 3D problem that is difficult and time consuming to solve. For a long river, its depth and width are very small compared with its length, so the pollutants discharged into the river will be mixed in the cross section after they flow at a certain distance away from the leak point. For many rivers (especially river segments), the problem of calculating water quality can therefore be simplified as a 1D chemical transport problem, which assumes that the pollution concentration in the cross section is homogeneous and changes only with the flow direction.

A common finite-difference form of 1D river chemical transport is as follows (Zhang et al. 2011):

$$C_i{}^{j+1} = C_i{}^j + \left(E_i \frac{C_{i+1}{}^j + C_{i-1}{}^j}{\Delta x^2} + u_i \frac{C_{i-1}{}^j}{\Delta x}\right)\Delta t - \left(E_i \frac{2C_i{}^j}{\Delta x^2} + u_i \frac{C_i{}^j}{\Delta x}\Delta t + K_i C_i{}^j\right)\Delta t \tag{4}$$

where C_i^j (mg/m^3) is the cross-section average concentration of pollutant at section i (i=1, 2, .., M, M is the total number of sections in the river) at time j (j=1, 2, …, P, see Eqs. (6–7)); E_i (m^2/s), u_i (m/s), and K_i (s^{-1}) are the diffusion coefficient, the vertical flow velocity, and the decay rate coefficient at section i on the river; Δx (m) is the distance step in the x-direction, and Δt (s) is the time step.

Based on Eq. (4) and simplifying assumptions, the pollutant concentration of any section in the river at any moment C_i^j can be estimated by the time series of pollutant concentration $\{C_1^j\}$ at the first (upstream) section (leak point), and the model parameters E_i, u_i, and K_i. In most previous studies, E_i, u_i, and K_i are simplified as constants E, u, and K, which are obtained by the parameter calibration method (for example, least squares method) using historical data and then taken as certain parameters of Eq. (4) for model calculation. Due to the complexity of pollution and water environments, E, u, and K are taken as uncertain parameters for evaluating the unknown pollutant concentration C_i^j in this study.

As shown in Fig. 3, the water quality data, hydrological data, and meteorological data from upstream monitoring stations and emergency sampling sites can be used in the EP-risk model. In this paper, the flow-velocity data from upstream monitoring stations is used to estimate the possible distribution of the vertical flow velocity u (see MC simulation); the pollutant concentration data from emergency sampling site at the first section (leak point) is used to predict the time series of pollutant concentration $\{\{C_1^j\}\}$, which is an important boundary-condition input to the 1D water-quality model, and can be obtained by polynomial curve fitting with a least-square calculation on the basis of the limited pollutant concentration data from emergency sampling points after the pollution accident has occurred.

The simplified 1D water quality model used in this paper has its limitations. For example, the simplified model cannot address issues related to multispecies contaminant fate and transport in the river systems. Also, the simplified model only addresses the soluble component of the spill, not suitable for the LNAPL (or DNAPL) risks and their unique mass transfer characteristics. In order to better describe the proposed EP-risk model and reduce computational complexity, the simplified model is used. It should be noted that besides the simplified 1D water quality model, other water quality models can be alternatives to be applied in the EP-risk model. By doing so, the complexity and the computation burden of model calculation may increase dramatically.

Generation of the random variable of model parameters

Due to the complexity of pollution and water environments, the model parameters E, u, and K are taken as uncertain parameters in this study. The probability distribution of E, u, and K can be characterized by their cumulative distribution functions (CDF), $F_E(x)=P\{E<x\}$, $F_u(x)=P\{u<x\}$, and $F_K(x)=P\{K<x\}$ for $x\in R$ (R is the set of real numbers), or corresponding probability density functions (PDF) $f_E(x)$, $f_u(x)$, and $f_K(x)$ for $x\in$ R.

The CDF or PDF of E, u, and K can be determined by experience, or identified by numerical methods, for example, maximum likelihood, which are used to fit the data to one theoretical discrete or continuous distribution. The methods for fitting PDFs are discussed in other papers (see for example, Raychaudhuri 2008).

After the underlying distributions for the uncertain parameters of the water quality model are determined, random variables are generated from these distributions by the inverse transformation method that uses the inverse of the PDF to convert a random number between 0 and 1 to a random value (Raychaudhuri 2008). The generated random variables are denoted by $Rand_E$, $Rand_u$, and $Rand_K$, which are taken as the model parameters of a single iteration in MC simulation. Equation (4) is redefined as follows:

$$C_i^{j+1} = C_i^j + \left(Rand_E \frac{C_{i+1}{}^j + C_{i-1}{}^j}{\Delta x^2} + Rand_u \frac{C_{i-1}{}^j}{\Delta x} \right) \Delta t - \left(Rand_E \frac{2C_i^j}{\Delta x^2} + Rand_u \frac{C_i^j}{\Delta x} \Delta t + Rand_K C_i^j \right) \Delta t \quad (5)$$

Calculation of the probability distributions of C_p and D

Based on Eq. (5), the peak concentration C_P and the pollution duration D at the EP are calculated as follows:

$$C_P = \max_{j=1,2,\ldots,P} \left\{ C_i^j|_{EP} \right\} \quad (6)$$

$$D = \operatorname*{count}_{j=1,2,\ldots,P} \left\{ C_i^j|_{EP} \geq C_T \right\} \quad (7)$$

where $C_i^j|_{EP}$ is the concentration of the nearest section from the intake within the EP at time j; C_T is the alarm threshold at the EP; P denotes the time at which the pollutant plume has thoroughly passed through the EP, which can be estimated by the experience, or the trend of $C_i^j|_{EP}$.

The results of the output variables of the 1D water quality model C_P and D after MC simulation are typically subjected to statistical analysis. Aggregating the output values into groups by size and displaying the values as a frequency histogram provides the approximate shape of the probability density function of an output variable.

Define $Frequency(h)$ as the total number of the observations in the hth bin, satisfying $N = \sum_{h=1}^{H} Frequency(h)$ (H is the total number of the bins), the density of the statistical variables in the hth bin is s follows:

$$Density(h) = \frac{Frequency(h)}{s \cdot N} \quad (8)$$

where s is the width of the bin; N is the total number of the output values (the total iterations times of MC simulation).

Base on Eq. (8), the density distribution of C_P and D are calculated, which can be fitted to a probability distribution if s is small enough and N is large enough. The fitted PDF and corresponding CDF of C_P and D can be expressed as follows:

$$F_{C_P}(x) = P\{C_P \leq x\} = \int_0^x f_{C_P}(t) dt \quad (9)$$

$$F_D(x) = P\{D \leq x\} = \int_0^x f_D(t) dt \quad (10)$$

Step 2: calculation of the EP likelihood

In this study, the EP Likelihood, L, is defined as the probability that the peak concentration C_P be greater than or equal to the alarm threshold C_T in the given EP based on the results of MC simulation, as follows:

$$L = P\{C_P \geq C_T\} = 1 - P\{0 \leq C_P < C_T\} = 1 - \int_0^{C_T} f_{C_P}(t) dt \quad (11)$$

or resorting to an approximate statistical expression,

$$L = \frac{\operatorname*{count}_{i=1,2,\ldots,N} \{C_{Pi} \geq C_T\}}{N} \times 100\% \quad (12)$$

where C_{Pi} is the peak concentration of ith iteration of MC simulation.

Equations (11) and (12) imply that the higher the probability of peak pollution, the higher the likelihood of pollution at the EP is.

Step 3: calculation of the EP impact

The analytic hierarchy process (AHP) method is adopted in this study to evaluate the EP impact during a water contamination accident. AHP provides a flexible tool to analyze complex problems (Golden et al. 1989). It simplifies problems by building a criteria and subcriteria hierarchy structure with a series of pairwise comparisons to evaluate the performance of alternatives against criteria and criteria weights (Saaty 1980; Saaty 1990). The AHP method has been used in a wide range of applications (Tiwari and Banerjee 2001; Chiang and Lai 2002; Ocampo-Duque et al. 2006; Bertolini et al. 2006; Martin-Ortega and Berbel 2010; Naddeo et al. 2012).

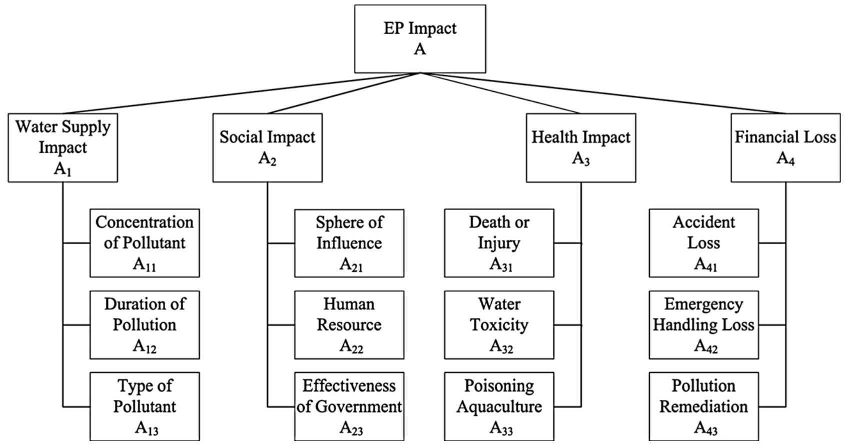

Fig. 5 Hierarchy tree to evaluate the impact of pollution at the EP during a water contamination accidents

The EP impact is decomposed into specific events in a way that the events of a certain level will cause the events of the level above it. Events at the bottom level of the diagram describe categories of causes that contribute to increase the adverse consequence. Based on the relative importance of contributing events, the global weight of each event in the entire consequence can be obtained. The water supply impact, social impact, health impact, and financial losses are the events that directly contribute to the EP impact shown in Fig. 5.

The concentration of pollutant, the duration of pollution, and the type of pollutant are considered to affect the treatment capacity of the water supply system at the EP. Three events influence the social impacts of river pollution as follows: the sphere of influence, human resources, and the effectiveness of government action. Health impacts measure the negative effects to human health, such as death, injury, water toxicity, and aquaculture poisoning. Financial losses include emergency handling losses, accident losses, and pollution remediation. It should be noted that the evaluations of the events considered in this study are limited to the EP area, but not the entire river basin as done in other studies. Furthermore, the AHP method is used to evaluate the potential impact of the events, but not the current impact of the events.

For evaluating the global EP impact, the degree of impact and weight of each event are determined by experts based on their knowledge, from historical data, or from MC simulations. If criteria A consists of n subcriteria A_i $(i=1, 2,\ldots, n)$ in the next rank, the expression of the judgment matrix for criteria A is described as follows (Saaty 1980):

$$B = \begin{bmatrix} b_{11} & b_{12} & \ldots & b_{1n} \\ b_{21} & b_{22} & \ldots & b_{2n} \\ \vdots & \vdots & b_{ij} & \vdots \\ b_{n1} & b_{n2} & \ldots & b_{nn} \end{bmatrix} \tag{13}$$

where b_{ij} denotes the relative importance between subcriteria A_i and A_j $(i,j=1,2,\ldots,n)$, with the constraints that $b_{ij}=1/b_{ji}$, for $i\neq j$, and $b_{ii}=1$, for all i. The determination of b_{ij} is made based on the knowledge of experts and the consistency analysis of the judgment matrix B (Saaty 1980).

The local weight of subcriteria A_i is denoted as LW_i, and is calculated as follows:

$$\overline{LW}_i = \sqrt[n]{\prod_{j=1}^{n} b_{ij}}, \quad i = 1, 2, \ldots, n \tag{14}$$

$$LW_i = \frac{\overline{LW}_i}{\sum_{i=1}^{n} \overline{LW}_i}, \quad i = 1, 2, \ldots, n \tag{15}$$

If a subcriteria A_i consists of m sub subcriteria (hereinafter called event) A_{ik} $(k=1, 2,\ldots, m)$ in the next rank, and the local weights of each event A_{ik} are calculated by Eqs. (14) and (15), the global weight of each event A_{ik} is defined as follows:

$$GW_{ik} = LW_i \times LW_{ik} \tag{16}$$

The impact degree of A_{ik} is denoted as ID_{ik}, which is periodically evaluated by experts after the accidents, based on their subjective experience and the objective results from real-time, dynamic MC simulations. In this study, the impact degree ranges from 1 to 5, where 1 represents the smallest impact degree and 5 represents the greatest impact degree. For example, the impact degree of event "duration of pollution" ID_{12} is determined by the average value of the pollution duration D after MC simulation and the grading of experts; the impact degree of event "effectiveness of government" ID_{23} is determined by the experience of experts.

Table 1 Risk matrix for the EP risk

EP Impact level EP likelihood level	Small	Moderate	Severe	Catastrophic
Low	Low	Low	Low	Medium
Moderate	Low	Low	Medium	High
High	Low	Medium	High	High
Very high	Medium	Medium	High	High

After all impact degrees ID_{ik} and weights GW_{ik} are obtained, the quantitative value of the global EP impact is derived as follows:

$$I = \sum_i \sum_k GW_{ik} ID_{ik} \tag{17}$$

Step 4: calculation of the EP risk

Risk assessment is the identification and analysis of the likelihood and severity of the potential loss of a process. A variety of risk-assessment methodologies have been developed and used. Risk assessment methods are classified into qualitative, semiquantitative, and quantitative categories (Montague 1990). The risk matrix is a semiquantitative risk assessment method that includes two elements (i.e., likelihood of occurrence and severity of the consequences) to determine the risk. In this study, the risk matrix method was adopted to quantize the EP risk (Henriksen et al. 2009).

When a pollution accident occurs in an upstream reach of a river, a continuous, dynamic risk assessment of the given EP can provide additional time for WTPs or local governments to take remedial and protective measures and thus minimize losses. The EP risk levels (*low*, *medium*, *high*) obtained as products of EP likelihood levels (*low*, *moderate*, *high*, *very high*) and EP impact levels (*small*, *moderate*, *severe*, *catastrophic*) are defined, and illustrated in a two-dimensional risk matrix, as shown in Table 1. The EP likelihood levels are obtained by rating the values of the EP likelihood L, and the EP impact levels are correspondingly obtained by rating the values of the EP impact I.

The EP risk level *high* means not acceptable potential risk for the EP. If no mitigation actions or risk reducing treatments are taken (for example, control of pollution emissions, discharge of water from upstream reservoirs, and effective water treatment by WTPs) before the pollutants arrive at the intake, the WTPs at the EP have to stop their service to ensure safe water supply in the EP area. The EP risk level *medium* means acceptable potential risk for the EP, but the development of the accident must be monitored and analyzed on a regular basis, considering whether or not further response measures have to be implemented. The EP risk level *low* means acceptable risk for the EP. The WTPs are capable of dealing with the identified pollutant, but the accident must be monitored to ensure the detection of changing conditions that might increase the risk level.

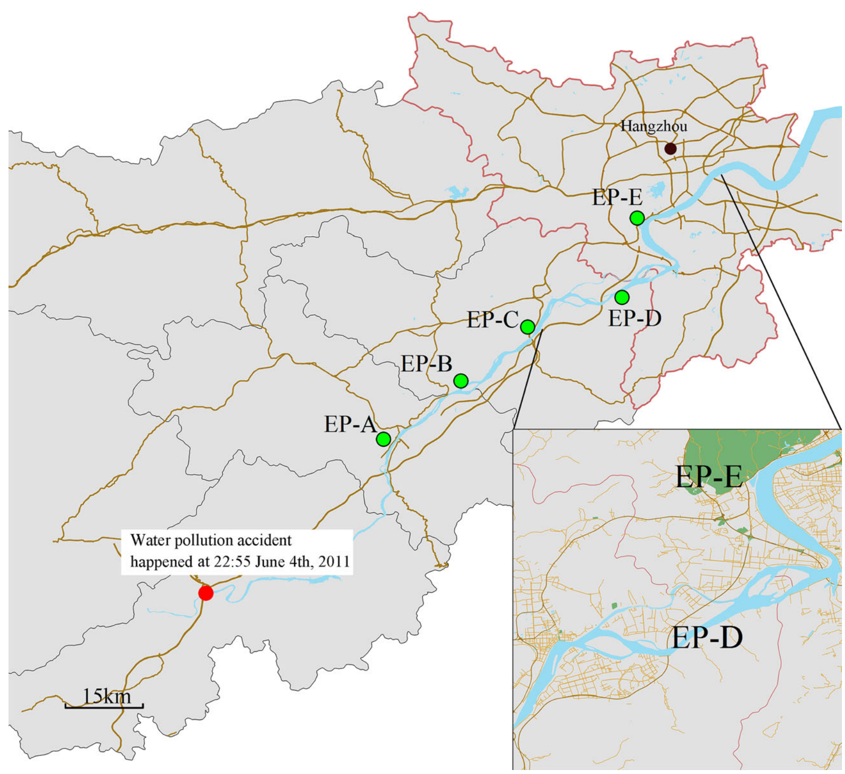

Fig. 6 The locations of the phenol leak point and five EPs along Qiantang River. The enlarged map is the key areas between EP-C and EP-E

Case study

General background

Qiantang River is situated in East China. Originating from Anhui Province and running through the northwest part of Zhejiang Province. It runs for 459 km (285 mi) through Zhejiang province, passing through the provincial capital Hangzhou, before flowing into the East China Sea through Hangzhou Bay. It is the main source of drinking water for several cities in Zhejiang, including the capital city of Hangzhou.

On the midnight of June 4, 2011, a tanker truck traveling along a highway rolled and leaked about 20 t (1 t=1,000 kg) of toxic chemical phenol, also known as carbolic acid. Because the accident site is near Qiantang River and it was raining heavily at the time, a large amount of phenol flowed into the river along the drains. The accident site is approximately 150 km (90 mi) upstream from Jiuxi Water Treatment Plant, which is the main source of drinking water for Hangzhou. Millions of people's lives were threatened by the accidental spill event.

After the spill occurred, an emergency response team was organized by the local government and eight water sampling sites were deployed temporarily along the Qiantang River from the accident site to Jiuxi, Hangzhou (with a sampling frequency of about one sample per hour at each site). The details of emergency response for the phenol spill has been presented in a previous paper by the authors (Hou et al. 2013). In this paper, the proposed EP-risk model is applied to evaluate the real-time EP risk of the phenol spill using MC simulation, AHP method, and risk matrix method.

MC simulation

The 1D river water quality model (Eq. 4) was used to simulate the chemical transport following the phenol spill accident. The river reach under study, which is 160-km long, was equally divided into 320 segments (0.5 km each).

The time series of pollutant concentration $\{C_1^j\}$ in the first section (at the accident site) are obtained by polynomial curve fitting with a least-square calculation using the pollutant concentration data from emergency sampling.

The vertical flow velocity u, vertical diffusion coefficient E, and decay rate coefficient K are regarded as uncertain parameters. The possible distributions of u, E, and K are important to the MC simulation.

The vertical diffusion coefficient E is mainly affected by flow conditions, section characteristics, and channel forms. Researchers have proposed some empirical formulas to estimate the vertical diffusion coefficient (McQuivey and Keefer 1974; Seo and Cheong 1998). In this study, the possible range of E is determined on the basis of the empirical formula proposed by Seo and Cheong (1998). The empirical and existing data of the calculation reaches are also considered.

The decay rate coefficient K is related to river hydraulics, pollutant characteristics, water temperature, bed roughness, and several other factors. In the MC simulation, the possible range of K is determined by empirical data and existing research results on hydrological parameters. Other factors are considered, such as pollutant characteristics, water temperature, and velocity. The report "National Technical Manual of Water Environmental Capacity Calculation" (CAEP 2003) was also used in the determination of K.

The possible distribution of the vertical flow velocity u is estimated by historical hydrological data.

It is herein assumed that (1) the vertical flow velocity u ranges from 0.1 to 0.8 m/s with a normal distribution, (2) the vertical diffusion coefficient E ranges from 100/s to 300 m^2/s with a uniform distribution, and (3) the decay rate coefficient K ranges from 0.05 to 0.15 day^{-1} with a uniform distribution.

Using the inverse transformation method based on their distribution characteristics, the random variables u, E, and K are generated and taken as the model parameters of a single

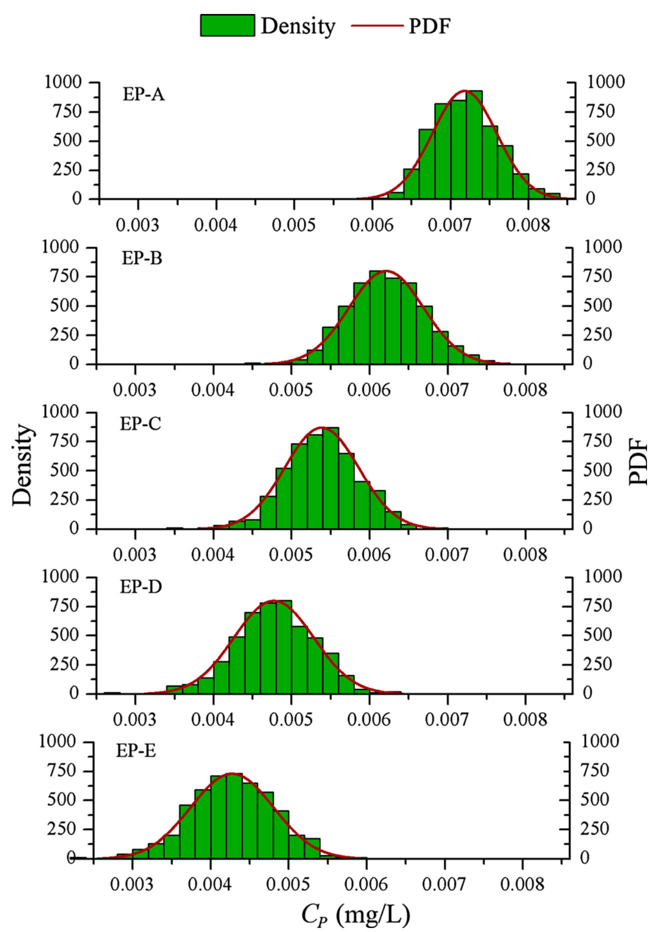

Fig. 7 Density and the fitted PDF of peak concentration C_P at the five EPs 36 h after the accident occurred

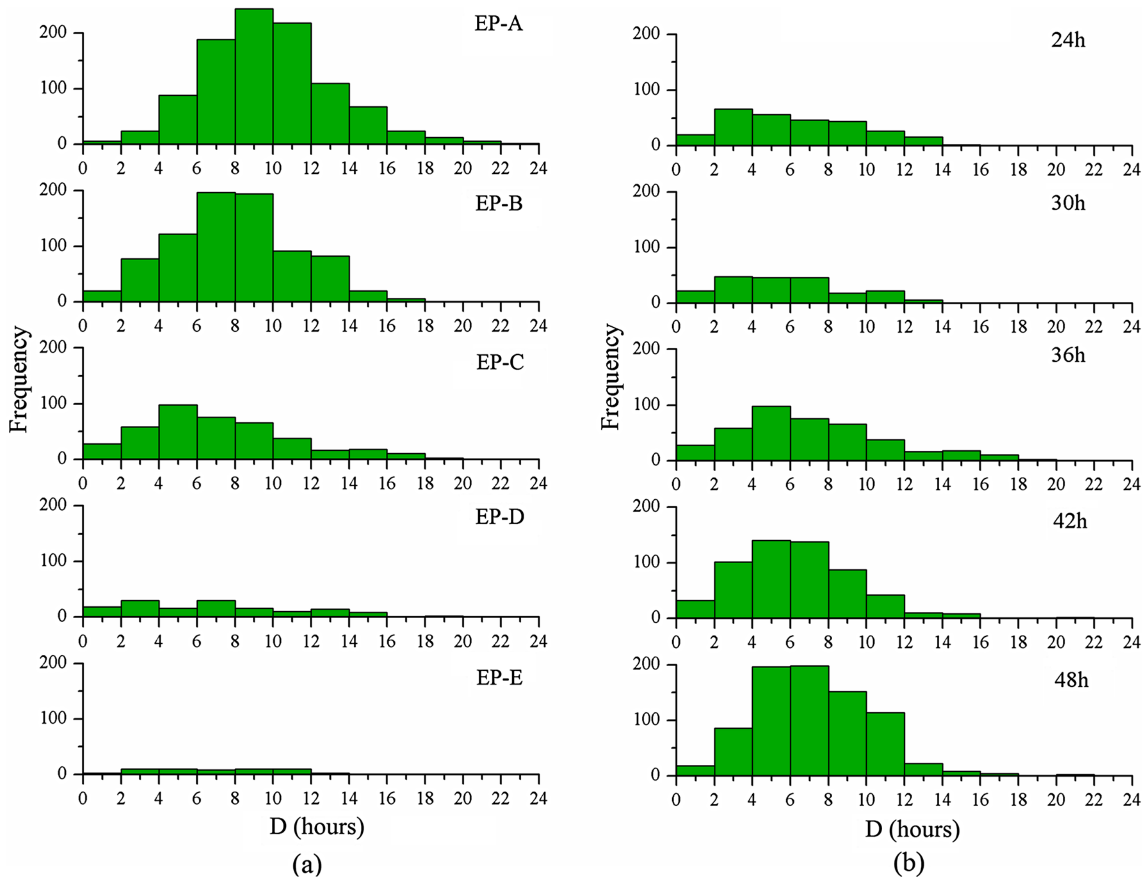

Fig. 8 Frequency histograms of pollution duration D. **a** Frequency histograms of pollution duration D at different EPs 36 h after the accident occurred; **b** frequency histograms of pollution duration D at the EP-C after different hours of the accident occurred

iteration in MC simulation. One thousand times of random iterations are conducted to obtain the statistical properties of peak concentration C_P and pollution duration D at the given EP. This number of MC iterations is a tradeoff between computing time and computational accuracy (see System Implement). For calculating D, the alarm threshold C_T is set

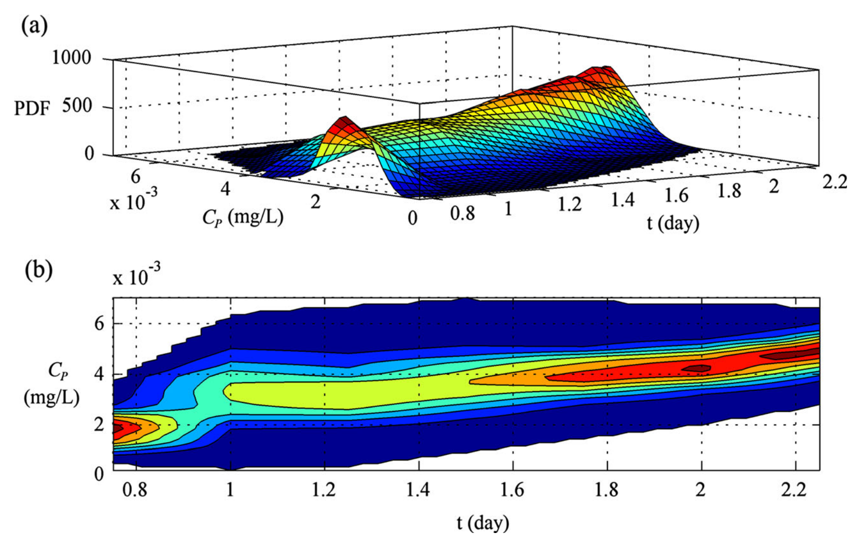

Fig. 9 **a** *Top* 3D diagram of the dynamic probability distribution of peak concentration C_P at the EP-E (Jiuxi). Each *horizontal section* presents the probability density function of the peak concentration at the corresponding time t (day) with one time MC simulation. **b** *bottom* Contour plot of the dynamic probability density function of the peak concentration C_P at the EP-E (Jiuxi)

Table 2 EP Likelihood L at the different EPs 18 to 54 h after the accident occurred

Time after accident (h) EP name	18	24	30	36	42	48	54
EP-A	5.2 %	95.2 %	94.6 %	99.0 %	100 %	100 %	100 %
EP-B	0	66.0 %	60.0 %	81.0 %	95.8 %	99.6 %	100 %
EP-C	0	27.6 %	20.8 %	41.0 %	56.2 %	80.0 %	95.0 %
EP-D	0	10.2 %	6.4 %	14.2 %	18.2 %	32.2 %	61.2 %
EP-E (Jiuxi)	0	2.2 %	1.6 %	5.2 %	5.9 %	8.0 %	25.6 %

to 0.005 mg/l, which is the criteria for volatile phenol in China's environmental quality standards for surface water (2002).

In this case, five EPs were used for testing of the MC simulation as follows: EP-A, EP-B, EP-C, EP-D, and EP-E (Jiuxi). The locations of the five EPs are shown in Fig. 6.

Figure 7 shows the relationship between the location of the EP and the PDF of C_P. The simulation results for C_P at different EPs 36 h after the accident occurred were used. In Fig. 7, the abscissa represents the peak concentration C_P, and the ordinate is the density and the fitted PDF of the corresponding peak concentration C_P. The different curves show the PDF of C_P at different EPs located at different lengths from the accident site. Figure 7 shows that the farther the distance from the accident site is, the smaller the maximum of the peak concentration C_P is.

Figure 8a shows the relationship between the frequency of D (pollution duration) and the location of EP in one MC simulation. It can be concluded that in this case, the longer distance between EP and the accident site is, the smaller the probability of longer pollution duration is. Because the pollution duration D is defined as the duration of the pollutant concentration being larger than the given alarm threshold at the EP (see Eq. (7)), as the spill moves downstream the peak concentration C_P is gradually attenuated, approaching and even becoming less than the alarm threshold C_T (0.005 mg/l). Therefore, the probability of longer pollution duration D decreases with distance from the accident site.

Figure 8b shows that as time goes on, the frequency distributions of D at the same EP vary. The reason is because more and more pollutant sampling data, hydrological data, and other useful information are obtained, which change the model inputs to the MC simulation. The more information about the accident is used, the better the accordance of water quality model with actual conditions is, and the higher the confidence of the prediction that can be obtained.

To demonstrate the different outputs from the MC simulation at different moments, a 3D diagram of the dynamic probability distribution of peak concentration C_P at the EP-E is presented in Fig. 9. The three dimensions are current time t, peak concentration C_P, and the PDF of C_P, respectively. In this case, Fig. 9 shows that as time goes on, the range of peak concentration decreases gradually, and the distribution of the peak concentration is relatively concentrated. The 3D diagram of dynamic probability distribution provides insight into the development trends of the accident and is helpful in making good decisions for emergency response.

Risk assessment

Assessing the risk level of a given EP is helpful for the emergency response agencies in taking mitigation actions and communicating effectively with the public. The EP-E is the key area of the accident because Jiuxi WTP is the main drinking water supplier to the City of Hangzhou. If the EP-E is under threat, the emergency agencies must take immediate measures because water supply pollution or shortage will result in serious effects to the city. In this study, the EP likelihood at the EP-E is calculated first, the impact weight and degree of each event in the AHP tree is then evaluated by experts, and the final risk level is determined using the risk matrix method.

Table 3 Calculation of the local weights of events A_1–A_4

		A_1	A_2	A_3	A_4	LW_i	CR
Water supply impact	A_1	1	4	1/3	5	0.29	0.06<0.1
Societal impact	A_2	1/4	1	1/5	2	0.11	
Health impact	A_3	3	5	1	5	0.53	
Financial loss	A_4	1/5	1/2	1/5	1	0.07	

CR consistency ratio, *LW* local weight

Table 4 Calculation of the local weights of events A_{11}–A_{13}

		A_{12}	A_{12}	A_{13}	LW_{1k}	CR
Concentration of pollutant	A_{11}	1	3	2	0.54	0.07<0.1
Duration of pollution	A_{12}	1/3	1	2	0.27	
Type of pollutant	A_{13}	1/2	1/2	1	0.19	

CR consistency ratio, *LW* local weight

Table 5 Calculation of the local weights of events A_{21}–A_{23}

		A_{21}	A_{22}	A_{23}	LW_{2k}	CR
Sphere of influence	A_{21}	1	5	4	0.65	0.08<0.1
Human resource	A_{22}	1/5	1	1/4	0.10	
Effectiveness of government	A_{23}	1/4	4	1	0.25	

CR consistency ratio, *LW* local weight

EP likelihood

The EP likelihood L is defined as the probability of the peak concentration C_P being greater than or equal to C_T at the given EP based on the results of MC simulation (see Eqs. (11–12)).

Table 2 shows the EP likelihood L at five EPs at different times after the accident occurred at an upstream location in the river. Obviously, EPs closer to the spill site have a greater probability of pollution (exceedance criteria event) than EPs farther downstream. As time goes on, the values of EP likelihood L become larger, that means the possibility of pollution at the five considered EPs increases.

EP impact

Based on the AHP method, the EP impact at different EPs is evaluated continuously after the accident. The EP-E (Jiuxi) is used to exemplify the impact weight and impact degree of each event, and then calculating the EP impact I, which is used to obtain the final risk level at EP-E (Jiuxi).

Firstly, the impact weight of each event is determined by experts using AHP hierarchy tree (Fig. 5). The relative importance between two events in the same hierarchy is identified with the judgment of experts. The calculation of the local weights of events A_1–A_4 is shown in Table 3. The health impact is the main contributor to the EP impact. The water supply impact is also important, whose local weight is 0.29. The social impact contributed 0.11 to the EP impact, and the local weight of financial losses is 0.07. Similarly, the calculation of the local weights of water supply events A_{11}–A_{14}, social events A_{21}–A_{24}, health events A_{31}–A_{34}, and financial events A_{41}–A_{44} is shown in Tables 4, 5, 6, and 7. The *CR* in Tables 3, 4, 5, 6, and 7 means the consistency ratio. If CR<0.1, the weight calculation result is acceptable; otherwise, the judgment matrix has to be modified and recalculated (Saaty 1980). The global weight of each event is obtained by Eq. (16).

Table 6 Calculation of the local weights of events A_{31}–A_{33}

		A_{31}	A_{32}	A_{33}	LW_{3k}	CR
Death or injury	A_{31}	1	5	5	0.69	0.07<0.1
Water toxicity	A_{32}	1/5	1	3	0.21	
Poisoning aquaculture	A_{33}	1/5	1/3	1	0.10	

CR consistency ratio, *LW* local weight

Table 7 Calculation of the local weights of events A_{41}–A_{43}

		A_{41}	A_{42}	A_{43}	LW_{4k}	CR
Accident loss	A_{41}	1	3	2	0.53	0.03<0.1
Emergency handing loss	A_{41}	1/3	1	1/3	0.14	
Pollution remediation	A_{43}	1/2	3	1	0.33	

CR consistency ratio, *LW* local weight

In the dynamic risk assessment process, the impact weight of each event is predetermined by experts, but the impact degree of each event should be modified occasionally by experts based on the results of dynamic MC simulation and the real-time monitoring data/information. In this case, we take the time 24 h after the accident as an example to investigate the calculation of the impact degree ID_{ik} (Table 8). The EP impact I at the EP-E 24 h after the accident occurred is obtained as 2.00 based on Eq. (17).

EP risk

After the EP likelihood L and EP impact l are determined, the real-time, dynamic risk level are obtained based on the risk matrix method.

In this case, the EP likelihood levels *low*, *moderate*, *high*, and *very high* are classified into nonoverlapping categories L<5 %, 5 %≤L<15 %, "15 %≤L<40 %," and "L≥40 %," and the EP impact levels *small*, *moderate*, *severe*, and *catastrophic* are classified into "I<0.5," "0.5≤I<1.5," "1.5≤I<3.0," and "I≥3.0."

Taken the time 24 h after the pollution spill occurred as an example, the EP likelihood L is equal to 2.2 % (Table 2), and the EP Impact I is equal to 2.00 (Table 8). Hence, the EP likelihood level is evaluated as *low*, and the EP impact level is evaluated as *severe*. Based on the risk matrix for the EP risk,

Table 8 Calculation of the EP impact I

A_i	A_{ik}	GW_{ik} = LW_i *LW_{ik}	ID_{ik}	EP impact I
Water supply impact	Concentration of pollutant	0.1566	3	2.00
	Duration of pollution	0.0783	2	
	Type of pollutant	0.0551	3	
Social impact	Sphere of influence	0.0715	3	
	Human resource	0.011	1	
	Effectiveness of government	0.0275	4	
Health impact	Death or injury	0.3657	1	
	Water toxicity	0.1113	2	
	Poisoning aquaculture	0.053	1	
Financial loss	Accident loss	0.0371	3	
	Emergency handing loss	0.0098	3	
	Pollution remediation	0.0231	4	

ID impact degree, *GW* global weight, *LW* local weight

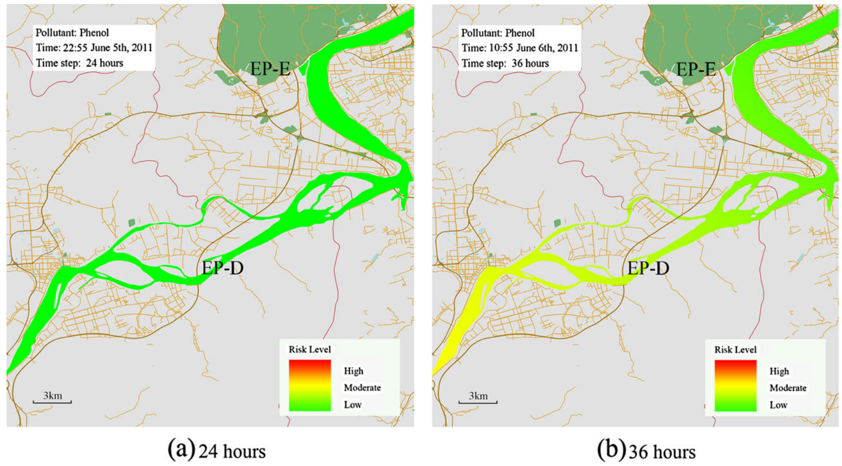

Fig. 10 Map display of the EP Risk levels in the key area after **a** 24 h and **b** 36 h of the accident occurred

the final risk level at the EP-E 24 h after the accident occurred is evaluated as *low*. It means a low-risk level at the EP-E with a low likelihood of pollution in the future. Using the same risk assessment method, the risk level at the EP-E 36 h after the pollution accident occurred is modified as *medium* because of the rising likelihood of pollution. The identified results of EP risk are used for the early warning of potential threats, for decision making of emergency-response agencies, and for disseminating event messages to the public. One type of visual display of the EP risk is shown in Fig. 10. Different colors denote different levels of EP risk.

System implement

System integration

The EP-risk model is integrated into an early-warning information system named DEWS (Hou et al. 2013). The data from upstream monitoring stations and emergency sampling sites are stored into the database of DEWS and can be accessed by the EP-risk model service. When the data is ready and the model parameters (for example, alarm threshold C_T, distribution of uncertain parameter E, u, and K, and iterations of the MC simulation) are determined, the MC simulation can be triggered to calculated the EP likelihood $L$and the distribution of pollution duration D. A user interface with the results of the MC simulation and real-time monitoring information is provided to the experts in the emergency response team to input or modify the impact degrees of 12 AHP events (see Table 8) to obtain the EP impact I and final EP risk level for further decision making. The impact degree ranges from 1 to 5, where 1 represents the smallest impact degree and 5 represents the greatest impact degree.

Computing time/early-warning interval

During a spill event, it is essential that information be processed quickly and that predictions be provided to downstream EPs promptly so that appropriate actions can be taken before the contamination reaches the intakes. A complex MC simulation may need long computing time, and the more iterations of MC simulations are implemented, the more accurate the result estimates would be. Once again, there is a tradeoff between computing time and the computational accuracy of

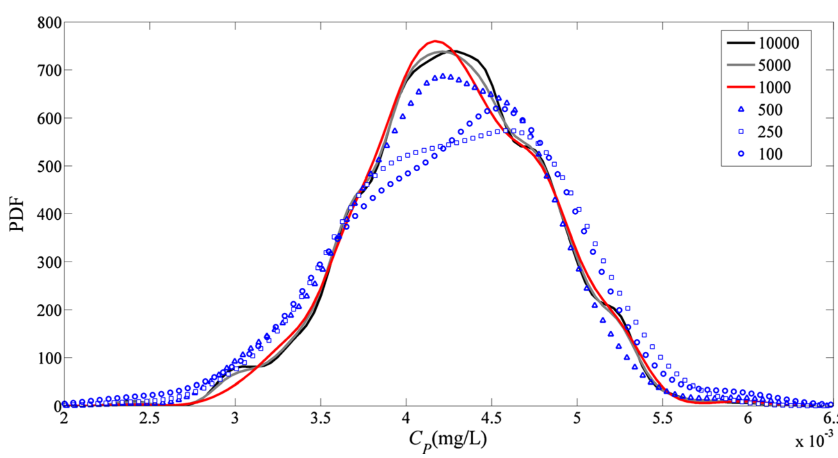

Fig. 11 PDF curves of C_P with different number of iterations used in the MC simulation

an MC simulation, which is exacerbated by the need to communicate results promptly for emergency response.

A test was conducted to assess the worth of iterations (k=1, 2, …, N) of MC simulation for the real-time early warning system. Figure 11 shows that the PDF curves of C_P at the EP-E after 36 h are different for 100, 250, 500, 1,000, 5,000, and 10,000 iterations of MC simulation. It can be seen that the results for 100, 250, and 500 iterations are not stable compared with 5,000 and 10,000 iterations of MC simulation. The 1,000 iterations of MC simulation (the red curve) is relatively acceptable and represents a reasonable tradeoff value with which to achieve accurate results with acceptable computing time.

With the available computational engine (Intel core i7 3520@2.90, 8G RAM), each iteration costs about 13 s and each MC simulation with 1,000 iterations cost about 3.61 h. Therefore, the recommended early-warning interval is 4 h in this case. Certainly, the computing time and early-warning interval can be shorten in the future by providing more computing capacity or with parallel computing schemes.

Discussion

This paper has described a real-time, dynamic early-warning model, named EP-risk model, for coping with sudden water pollution accidents. This model outputs the risk level for any chosen key downstream area (EP) with raw-water intakes by calculating the likelihood of pollution and evaluating the impact of pollution at the EP. A generalized form of EP-risk model for river pollution accident based on MC simulation, AHP method, and risk matrix method was proposed and tested with a phenol spill accident. The proposed method has the following capabilities during a sudden water-pollution accident: (1) calculates the probability distribution of peak concentration and pollution duration at chosen EPs, (2) predicts the likelihood of pollution (exceedance-criteria of pollutant) at chosen EPs, (3) evaluates the impact or consequence of potential pollution at chosen EP, and (4) assesses the risk level of EP combing the likelihood and impact of potential pollution at chosen EPs for further decision making.

Compared with previous early-warning models for sudden water quality accidents, the proposed method provides a convenient tool with different capabilities to determine the risk level for those areas that are exposed to pollution threats and have urgent needs of evaluating their carrying capacity during pollution events on a real-time basis. Considering the various uncertainties in riverine environments, the continuous data updating from sampling and monitoring station coupled with recursive MC simulation provides more reliable probabilistic water pollution predictions for decision makers than water quality models with fixed model parameters. The proposed method is theoretically reasonable and practically feasible. The effectiveness of the proposed method require further testing in view of the small number of severe water contamination events that are known or reported.

Future research efforts concerning the proposed method include the following: (1) dynamically optimizing the distribution of model parameters based on real-time data; (2) reducing the influence of the subjective factors in the AHP method, for example, by uncertainty analysis or fuzzy theory; (3) improving the credibility of the classifying strategies of the risk matrix; and (4) reducing the computing time of MC simulations.

The EP-risk model is a general framework for dynamically evaluating the risk level at the EP during sudden water pollution accidents. Various water-quality models and risk assessment methods can be applied in the EP-risk model. Correspondingly, the complexity and computation burden of model calculation may increase. The exploration of combing other water quality models, uncertainty analysis theories, and risk assessment methods into EP-risk model for more reasonable risk assessment during a sudden water-pollution accident has important significance and high research value.

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