Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 149 (2007) 707–719
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

# Simulation of the cumulative effects of chemical spills using a spatial–temporal dynamics analysis algorithm

Mihaela Dinca-Panaitescu [a], James Li [a,*], Serban Dinca-Panaitescu [b]

[a] *Department of Civil Engineering, Ryerson University, 350 Victoria Street, Toronto, Ontario, Canada M5B 2K3, Canada*
[b] *York University, Toronto, Canada*

Received 11 August 2006; received in revised form 9 April 2007; accepted 10 April 2007
Available online 19 April 2007

**Abstract**

Accidents in urban areas involving chemical spills demands development of not only feasible emergency strategies, but also a consistent framework to protect the environment and prevent accidents. This can be possible only by a sound understanding of the environmental impact of spills and their potential long-term effects. Furthermore, the impact assessment of chemical spills can not be done disregarding the spatial–temporal pattern of previous exposures reciprocally influenced by both chemical and environmental properties. In this context, this paper presents an analysis framework to quantify the cumulative effects of chemical spills at any given point of a certain area based on a "present" history of exposure coupled with chemical and environmental properties to predict possible scenarios of future exposure and estimate in advance potential alarming levels of pollution. In the present circumstances when increasing knowledge is required for an accurate prediction of spill migration through unsaturated soil, this paper proposes an algorithm capable of incorporating models of increasing complexities to simulate the single-spill events once new advancements in the field are taken. The algorithm developed is illustrated using a simple model with homogenous and steady-state conditions to simulate the single-spill events. A hypothetical case study was constructed to illustrate the analysis steps and the benefits of the algorithm.


*Keywords:* Chemical spills; Spatial–temporal dynamics; Cumulative effects; Terrestrial pollution

## 1. Introduction

Accidents in urban areas involving chemical spills demands development of not only feasible emergency strategies, but also a consistent framework to protect the environment and prevent accidents. This can be possible only by a sound understanding of the environmental impact of spills and their potential long-term effects.

Although for a significant period of time oil spills in oceans were at the forefront of public and political concern, through the years chemical spills in urbanized areas have gained equal importance in spill management efforts. A report by Environment Canada summarizing spill events in Canada over the period 1984–1995 concluded that of all reported spills, 48% are discharged to the land and that chemical spills make up more than 25% of reported spills significantly affecting land and groundwater [1]. Furthermore, the highest number of reported spill incidents occurs in the province of Ontario. This can be attributed not only to the industry concentration, but also to a good reporting system. Although the majority of these spills are minor and have marginal impact on the environment, there are some releases with the potential to input a greater quantity of hazardous substances to the environment than combined gradual minor releases of substances over many years. In certain cases, depending on the substances released, season or sensitivity of area, even relatively small spills can have a severe cumulative impact on the environment.

Spills data in Ontario are compiled using a computerized data management system called the Occurrence Report Information System (ORIS) and handled by the Spill Action Centre (SAC). SAC is responsible for receiving reports of spills and other urgent environmental events and initiating and coordinating an

* Corresponding author. Department of Civil Engineering, Ryerson University, 350 Victoria Street, Toronto, Ontario, Canada M5B 2K3.
Tel.: +1 416 979 5345; fax: +1 416 979 5122.
*E-mail address:* jyli@ryerson.ca (J. Li).

0304-3894/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2007.04.032

environmental response to these reports. Reported occurrences recorded on ORIS allow tracking the status of occurrences and preparing data summaries [2]. Descriptive statistics give information about annual and seasonal trends of spills in Ontario, spills distribution by region with associated volumes, the most frequent substances spilled in different regions with corresponding volumes, annual and seasonal trends of spills for top sectors, causes, reasons and sources of spills for top sectors, and estimated spill emissions in different media.

The spatial and statistical analysis of chemical spills is an essential preliminary step in identifying trends, sensitive areas with potential increased levels of pollution, primary causes of spills and some general guidelines for an effective prevention and control strategy. The increasing concern over chemical spills in urbanized areas has created an impetus for innovative research such as the spatial and statistical analysis of the chemical spills that occurred in Southern Ontario from 1988 to 2000 [3,4]. However, spills are not disparate events with only local or simply added effects on the environment. It is well established that certain chemicals, when discharged to the environment, can persist for a sufficiently long period of time, can travel considerable distances and can migrate among different media, including humans. At the same time, the environment is complex and continually changing, making it difficult to predict the fate of the spilled chemicals. Moreover, some attributes of chemicals in the environment cannot be measured directly and they can only be estimated by simulation models.

The impact assessment of chemical spills can not be done disregarding the spatial–temporal pattern of previous exposures reciprocally influenced by both chemical and environmental properties. This kind of approach is dictated in recent years by the increasing recognition and awareness of the link between human health and the environment. For spills that may not pose an immediate threat, the general public still wonders what the long-term effects of exposure to the spilled substance might be. Furthermore, if the public relies on the regulator to provide advice and help, how does the latter quantifies the risks resulting from accidental spills and how appropriate is the approach used?

In this context, this paper presents a general framework for a better assessment of the impact of chemical spills on the terrestrial environment. To achieve this purpose, an algorithm was developed to assess the cumulative effects of chemical spills on a selected area taking into account the spatial–temporal adjacency of other spill events. Within this algorithm, the effect of any single-spill event on the terrestrial environment can be simulated by a four-dimensional (4-D) model based on certain assumptions on chemical and soil characteristics. The complexity of this model depends on the complexity of phenomena considered to simulate the transport and fate of the chemical spilled and also on the level of complexity considered when conceptualizing the terrestrial environment where the spills occur. At present, it is recognized that the existing data on chemicals spilled is not of sufficient quality to predict accurately the behaviour of the chemical in complex terrestrial environment. In the context of these constraints, a useful approach would be to develop a framework capable of incorporating models of increasing complexities once new advancements are taken. Soil maps and information on terrain slopes could help for a better assessment of fate and transport of the chemical spilled. In this paper, a simple model was chosen to simulate the single-spill events assuming steady-state and homogenous conditions. The model for a spill event was chosen to illustrate the applicability of the algorithm; modeling the spills migration representing one of the multiple steps of the algorithm. The following sections describe the algorithm and illustrate the algorithm using a hypothetical case study.

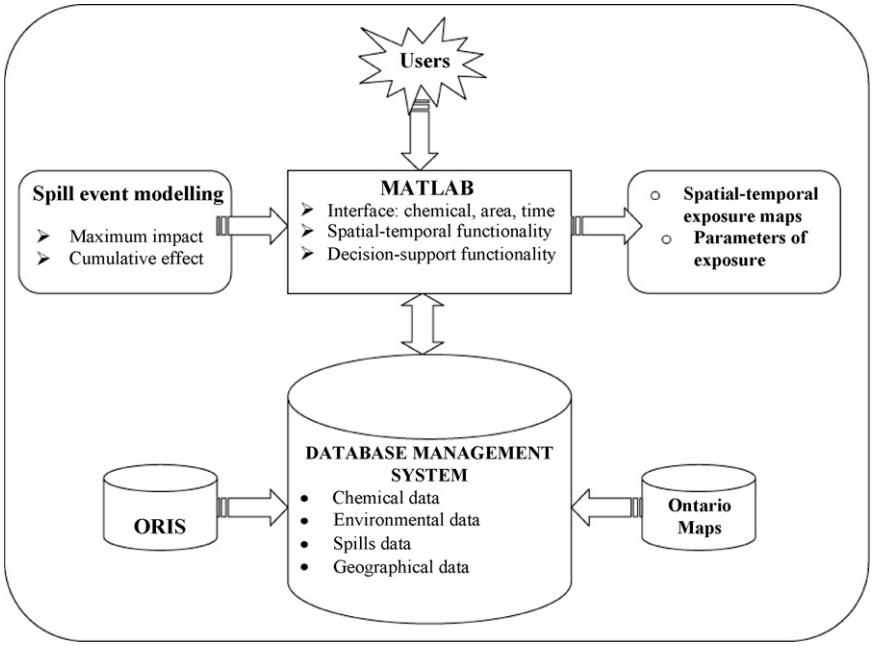


Fig. 1. Spatial–temporal spills analysis system architecture.

## 2. Algorithm development

In this paper, an algorithm is proposed to assess the accumulated impact of chemical spills in an area of interest. Depending on the data available and the required analyses, this algorithm can be used with different analysis models of increasing complexity to simulate the fate and transport of a single or multiple spills. Once a model is chosen for the analysis, different scenarios can be developed for spills of different quantities and frequencies in space and time. Based on the spatial–temporal dynamics of spills within and adjacent to the area of interest, this algorithm can estimate the level of pollution at any chosen point of the selected area. Furthermore, this algorithm can be used to predict the combined effect of previous and future spills so a possible "alarming" level of pollution could be detected in advance and the corresponding response action is developed.

### 2.1. Components of the spills analysis algorithm

The major components of the spatial–temporal spills analysis algorithm are: spill event modeling, Microsoft ACCESS database management system, databases (ORIS, maps), Matlab platform and the output in the form of spatial–temporal exposure maps and parameters of exposure (Fig. 1). The database component incorporates geocoded data from the ORIS, maps of the Ontario municipalities with their geographical coordinates and chemical and environmental data. ORIS database was designed primarily for the Ministry to develop and modify pollution abatement programs and spill prevention initiatives as trends or concerns are identified. The ministry also shares data with other agencies, such as Environment Canada and the International Joint Commission on the Great Lakes, to assist in identifying and evaluating common environmental concerns.

A spill event is modeled as a 4-D concentration function depending on the chemical and environmental parameters. Matlab offers advanced capabilities of handling multi-dimensional arrays required by the 4-D spatial–temporal models. It also offers GUI capabilities that allow users to easily interact with the system for selecting the geographical region, the area of analysis, the chemical of interest and the environmental and chemical parameters. The output is in the form of dynamic 3-D exposure maps that depict the cumulative effect of single or multiple spills and could be used as a decision support tool in the spills management process.

### 2.2. Spill database

#### 2.2.1. Data source

The Ontario Spill Action Centre (SAC) provides a province-wide, toll-free system staffed by environmental officers on 24-hour basis. This corresponds to the SAC responsibility for initiating and coordinating environmental actions to reported spills and other urgent environmental matters. The Ryerson University's research team compiled the chemical spill event data from 1988 to 2000 from the SAC spill database and created a geocoded chemical spill database. The locations of spills were identified by geocoding the addresses where chemical spills were reported to have occurred. With the support from the Toronto and Regions Conservation Authority, the Ryerson University's research team conducted a mapping study of chemical spills in the Etobicoke Creek watershed of Toronto [3]. However, the database used for the above-mentioned mapping study does not contain detailed information on the chemicals spilled. Most of the recorded chemicals were assigned a general description such as wax, liquid, paint. As a result, this may cause serious impediment for a more realistic assessment of spill effects incorporating both chemical and environmental characteristics. It will be desirable if the technical names of spilled chemicals can be reported.

#### 2.2.2. Database design

A database was designed using Access Database Management System (DBMS) that keeps the structure of the spill records previously compiled by the Ryerson University's research team [4]. It uses a set of specific data to simulate the cumulative impact of spills in a certain area.

The database consists of three related tables. The first table defines the chemical and soil parameters; the second one defines the regions in Ontario with their geographical coordinates and holds the maps; and the third one records the chemical spills characteristics.

The first table stores the physical and chemical parameters to simulate the fate of a spill event include volumetric water content ($L^3/L^3$), soil bulk density ($M/L^3$), pore-water velocity (L/T), longitudinal dispersivity (L), chemical half-life in soil and water (T), and the first-order degradation rates in soil and water (designated in the algorithm as FODRS and FODRW) (1/T). As these parameters have a large degree of variation in their values, the analysis algorithm counteracts this impediment by allowing users to interactively modify the parameter values for the simulation of different environmental conditions.

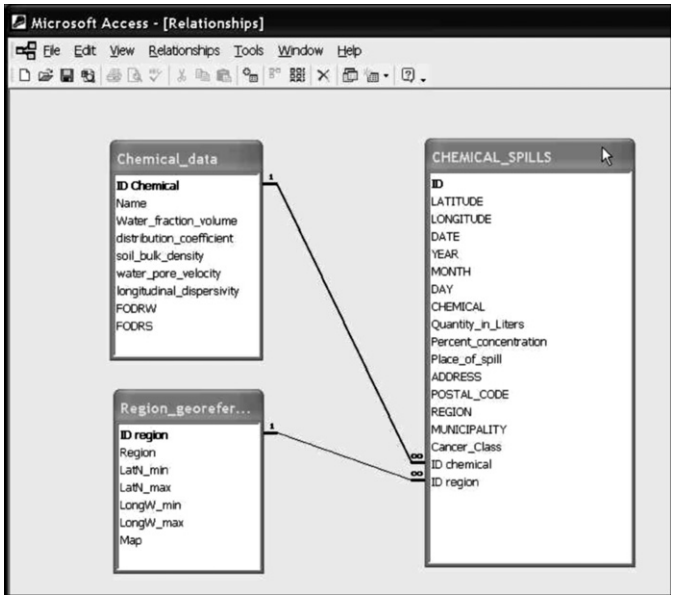


Fig. 2. Relationships between chemical, spill, and location characteristics.

The second table stores the geographical coordinates of the maps of the territorial-administrative regions of Ontario. This table could be easily linked with a Geographic Information System (GIS) to create high-resolution maps of soil and local topographic characteristics for the spill analysis model.

The third table stores spill information provided by ORIS: the type and quantity of spill, the date of occurrence and the location of the spill in geographical coordinates and, where available, postal address and code.

As illustrated in Fig. 2, this relational database has the above-mentioned three tables linked through the Chemical ID and Region ID and data can be retrieved or modified (for the chemical and soil parameters) through the interface designed in Matlab.

### 2.3. Interactive interface for chemical and space selection

An important step in the general framework of the algorithm is the selection of a chemical of interest with its relevant properties and an area of study where the accumulated effects of those spills for the selected chemical are to be assessed. In order to fulfill this step of the algorithm, the following sub-steps are set up.

#### 2.3.1. Region selection

An area of study has to be extracted from the region including the area of interest. In order to display the region, the maps of Ontario municipalities are stored in the database along with their geographical coordinates. The region where the area of study is included can be retrieved from the database using a pop-up selection button so that the map of selected region with its geographical coordinates is displayed (Fig. 3). The region maps are not scale-restricted since the analysis algorithm is scale-independent.

#### 2.3.2. Chemical selection

The next sub-step is to retrieve from the spill database a chemical of interest with all its records. Furthermore, the locations of those spills of the selected chemical are mapped within the borders of previously selected region (see black squares in Fig. 4).

#### 2.3.3. Chemical/environmental parameters selection

For each selected chemical, an interface was designed to interactively modify different chemical and environmental parameters considered in the single-event modeling. This option is essential since most of the parameters have a large range of variability. Fig. 5 shows the values for linear alkylbenzene sulfonates (LAS) used in the case study [5–7].

#### 2.3.4. Time interval selection

The time interval of analysis can be selected by entering the first and last day. This way, only those spills occurring in the specified time interval are selected from the database and displayed on the map of previously selected region.

#### 2.3.5. Area selection

Within the borders of the previously selected region, any area of study can be selected either by zooming on the regional map or by introducing the geographical coordinates of the area to be analyzed (Fig. 6). For a better sense of the area size, the metric dimensions of the considered area are also displayed as illustrated in Fig. 4 ($X_{max}$, $Y_{max}$).

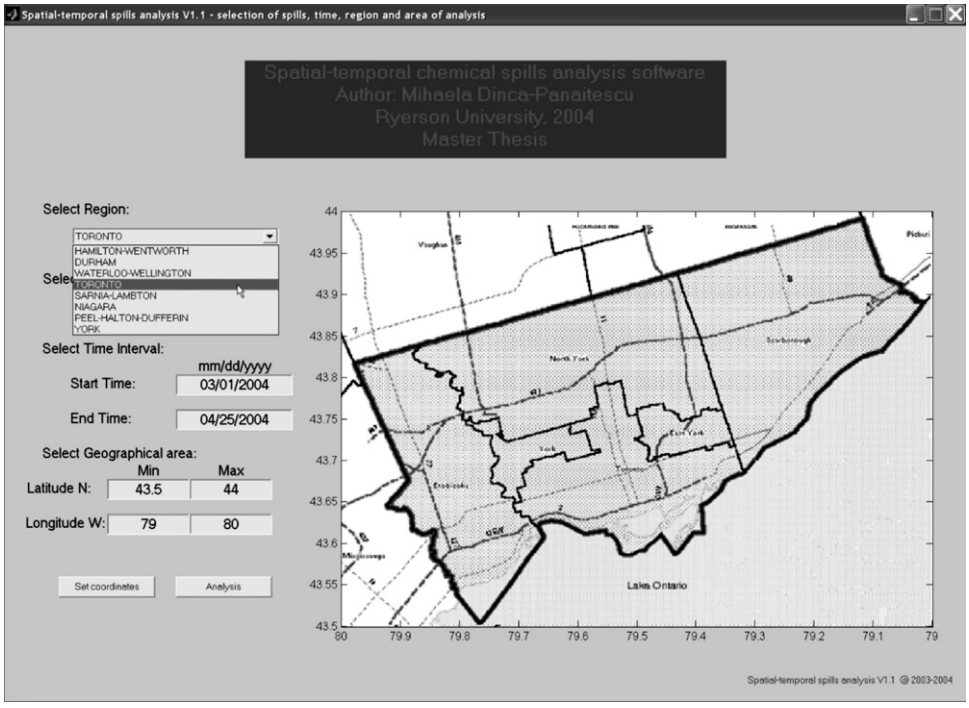


Fig. 3. An interactive interface for region selection.

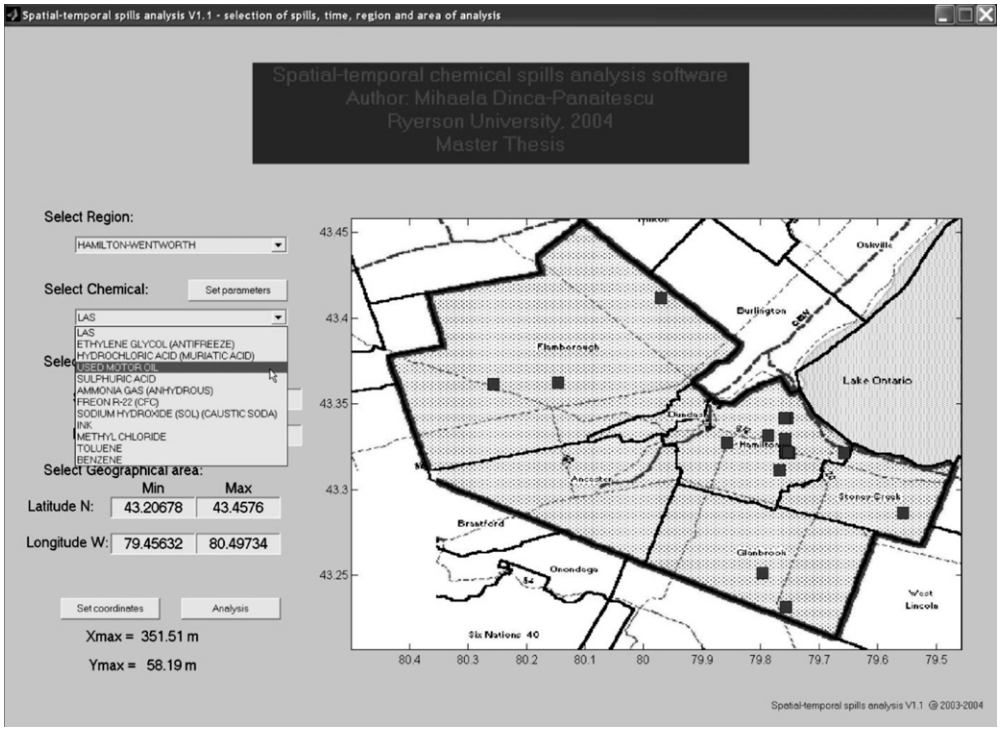


Fig. 4. An interactive interface for chemical selection.

### 2.3.6. *Inclusion of spatial–temporal adjacent spills*

The algorithm also takes into consideration those spills potentially affecting the area of study. One example is the spills (in a selected area) that have occurred earlier but their effects are still present at the moment of the analysis. Another example is the spills (in the specified time interval) located in the vicinity of the area borders that could affect this particular area. To do so, the maximum persistence and the maximum impact area of a single spill event must be assessed. The analysis space is extended with maximum impact radius and the time interval of analysis is extended with the maximum persistence to consider all those spills occurred before the initial time of analysis within maximum persistence time.

The dimensions of the area selected for analysis depend on the spatial scale of the spilled chemical. The advantage of this algorithm is that any kind of spills can be analyzed regardless the impact area by selecting the appropriate scale for each chemical.

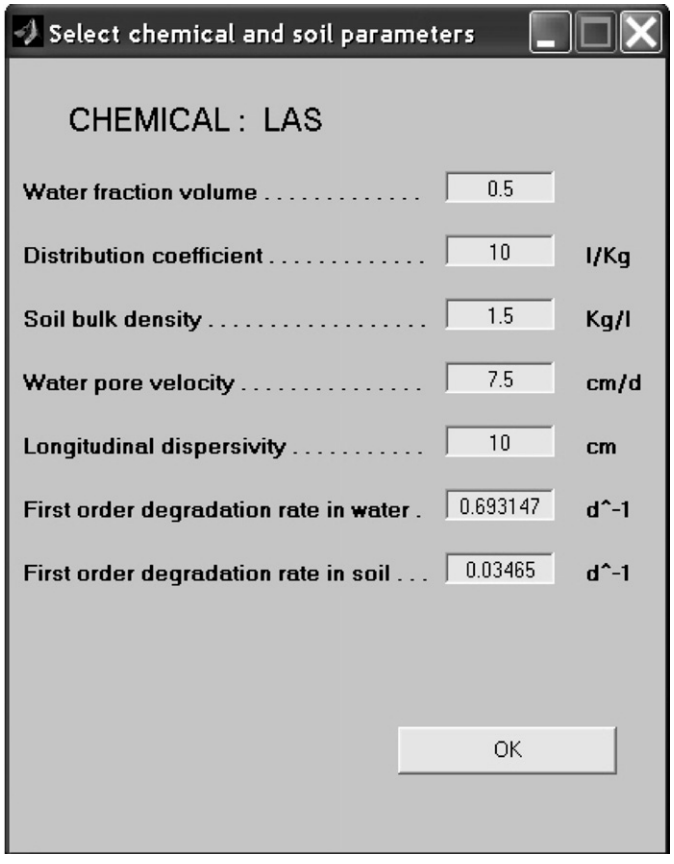


Fig. 5. An interactive interface for chemical parameters.

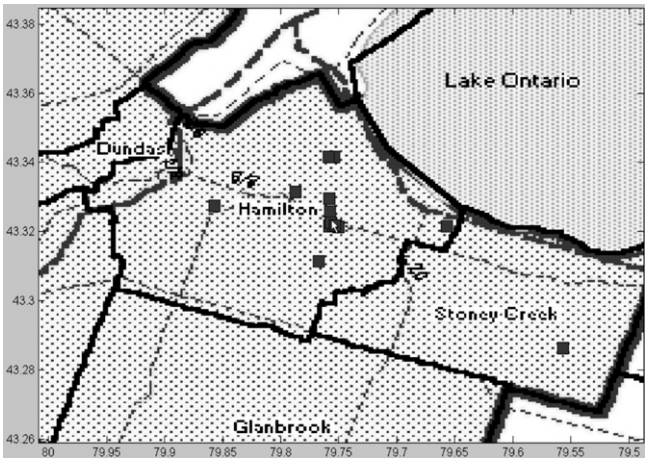


Fig. 6. Interactive interface: area selection.

### 2.4. Algorithm steps

#### 2.4.1. Modeling of the effect of a single spill

The algorithm consists of various sub-steps. The first step is to choose an appropriate model to simulate the chemical movement through the unsaturated zone. Each spill event is simulated as a spatial–temporal evolution of a concentration function further implemented as a Matlab function into the subsequent steps of the algorithm.

The selection of the model has to be done in the present context in which there is not yet an approach that incorporates a validated 3-D model capable of accurate prediction of spill migration, and a procedure that takes into account the spatial–temporal pattern of spill accidents into real-world proximity conditions. Under these circumstances, a rational framework would be one capable of incorporating models of increasing complexity once new advancements in the field are taken. The algorithm incorporates a simple model to simulate the concentration function for any single-spill event with the possibility of incorporating more sophisticated models once required or justified by the situations considered.

The model considers the case of involatile and soluble substances released at the initial time $t_0$ into a homogenous soil profile lying in the horizontal $(x, y)$ plane and beneath the surface considered with $z=0$ and $z$ positive downwards. Steady-state conditions are assumed with water and dissolved chemicals moving in a downward vertical direction at a constant pore-water velocity.

The processes modelled include advection, diffusion and dispersion, sorption on solids particles of soils, and biodegradation. The following general solute transport equation is used to describe the convection–dispersion representation adapted to the type of chemicals considered in this simulation [8–16]:

$$\frac{\partial c}{\partial t} + v'\frac{\partial c}{\partial z} + \lambda c = D'_x\frac{\partial^2 c}{\partial x^2} + D'_y\frac{\partial^2 c}{\partial y^2} + D'_z\frac{\partial^2 c}{\partial z^2} \tag{1}$$

where $c$ is the solute concentration ($ML^{-3}$)

$v'$ is retarded velocity ($LT^{-1}$):

$$v' = \frac{v}{R} \tag{2}$$

$v$ is the average pore-water velocity ($LT^{-1}$)

$R$ is retardation factor (dimensionless)

$$R = 1 + \frac{K_d\rho_b}{\theta} \tag{3}$$

$\rho_b$ is soil bulk density ($ML^{-3}$), $K_d$ is distribution coefficient ($L^3M^{-1}$), $\theta$ is volumetric water content ($L^3/L^3$).

$$\lambda \text{ is defined as : } \quad \lambda = \frac{k}{R} \tag{4}$$

$k$ is overall first-order degradation rate ($T^{-1}$)

$$k = \frac{k_w + k_s\rho_b K_d/\theta}{R} \tag{5}$$

$k_w$ is first-order degradation rate in water ($T^{-1}$), $k_s$ is first-order degradation rate in soil ($T^{-1}$)

$D'_i$ is retarded $i$-dispersion coefficient ($L^2T^{-1}$):

$$D'_i = \frac{D_i}{R} \text{ with } i = x, y, z \tag{6}$$

$$D_i = \alpha_i v \text{ is hydrodynamic coefficient} \tag{7}$$

where $\alpha_i$ is the dispersivity (L)

The solute transport equation with the initial condition adopted after Charbeneau [13] is given by

$$c(\tilde{r}_0, 0) = \frac{M}{\theta R}\delta(\tilde{r}_0) \tag{8}$$

where $r_0$ is defined as a point $(x_0, y_0, z_0)$

Eq. (8) is solved using the Fourier method [13] and the general solution for solute transport equation with the initial condition that a mass $M$ be released at $t=0$ at the point $\tilde{r}_0 = (x_0, y_0, 0)$ is given by:

$$c(x, y, z, t) = \frac{M/(\theta R)\ \exp[-(z - v't)^2/ 4D'_z t - (x - x_0)^2/4D'_x t - (y - y_0)^2/4D'_y t]}{(64\pi^3 D'_x D'_y D'_z t^3)^{1/2}} \times e^{-\lambda t} \tag{9}$$

The spill event is described as a 4D (3D-space plus time dimension) concentration function (Eq. (9)) depending on the following parameters grouped in two categories:

(a) chemical parameters: mass released, degradation rates and distribution coefficient;
(b) environmental parameters: volumetric water content, pore-water velocity, and hydrodynamic coefficients.

The concentration function will be further implemented into the algorithm as a Matlab function to describe the spatial–temporal evolution of any spill event.

*2.4.1.1. Implementation of the concentration function.* The concentration function was conceived as a 4-D object, having as input data the soil and chemical parameters described in the previous section. This 4-D representation has the advantage that it facilitates the development of spatial–temporal analysis models, which incorporates the relevant information into a single object.

Fig. 7 presents the spatial–temporal evolution of a single spill. The concentration function is displayed at different moments in time on a grey colour scale. For a better visualization of the function, the outer boundary that represents the minimum concentration level is displayed in black. This 4D representation offers the possibility of tracking and visualizing the history of a spill event simultaneously in time and space.

#### 2.4.2. Calculation of the maximum impact area and maximum persistence

An essential step of the algorithm is to calculate the maximum impact area and maximum persistence for that spill of maximum quantity occurred in the area of analysis. Any spill that occurred outside of this area but within a distance shorter

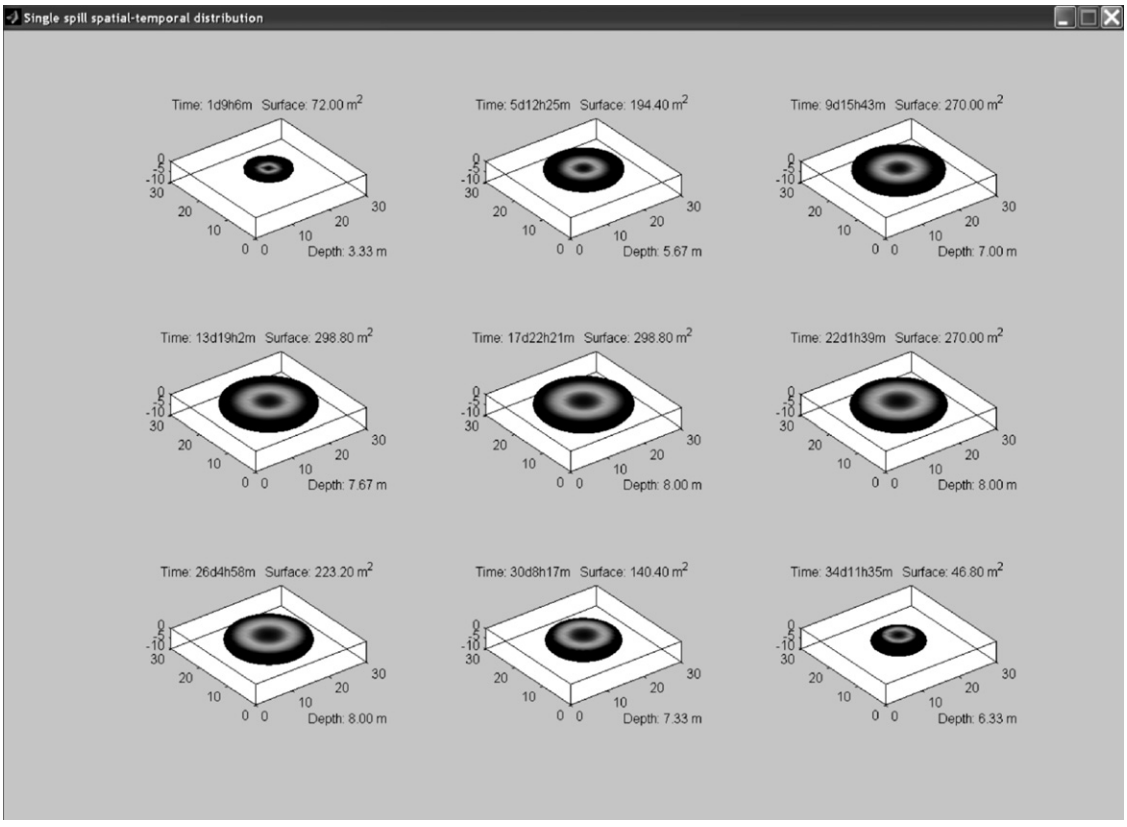


Fig. 7. Concentration function: single-spill spatial–temporal evolution.

than the calculated maximum impact radius will be considered as having potential effect on the area of analysis. Similarly, any spill that occurred prior to the time interval of analysis with the calculated maximum persistence will be also considered as having potential effect on the time interval of analysis. This assures that the potential effects of those spills occurring in the spatial vicinity of the area of analysis and in the temporal vicinity of the time interval of analysis were taken into account. In practical terms, the maximum persistence and maximum radius of impact for the maximum spills are assessed and the 4D-object assigned

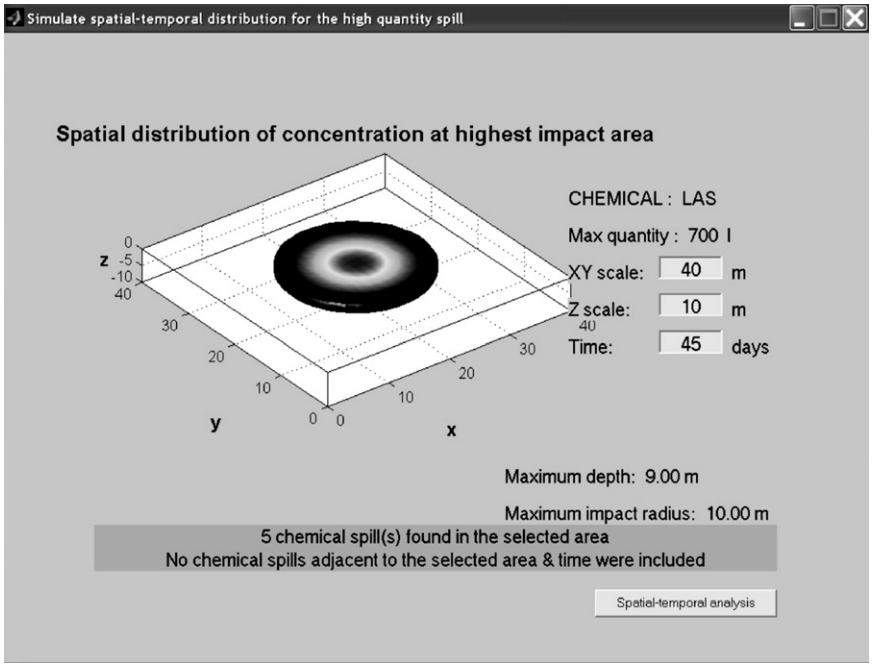


Fig. 8. Calculation of the maximum impact area and maximum persistence.

to the area and time interval of analysis is extended with these two parameters.

The database is first queried to retrieve the spill event of maximum quantity that occurred within the selected geographic area for which the simulation will be performed. Eq. (9) is solved by a Matlab function which in turn will retrieve the selected chemical and soil parameters. This function returns a 4D-object that is dynamically displayed while calculating the impact area and impact depth for every moment of time. The scales in $x$, $y$, $z$, and $t$ can be changed to capture the entire phenomenon.

As indicated in Fig. 8, the spatial distribution of concentration is eventually plotted for the moment at which the maximum impact occurred and the corresponding maximum impact radius and maximum impact depth are displayed.

An additional simulation is performed to include in the analysis those adjacent spills that could potentially have an effect on the selected area & time interval of the analysis. The selected area will be extended in all directions with the maximum impact radius and the time interval of analysis will be extended before the start time with the previously calculated maximum persistence. The database is queried with these new spatial–temporal limits and the detected spills will be included in the analysis.

All these spill data are then used to define the 4D-object dimensions (spatial and temporal scale) which will be used to compute the maximum concentration for all selected spills. This 4D-object, whose dimensions are defined by the two parameters of the maximum spill impact (i.e., maximum persistence and maximum radius of impact), is assigned to each spill. This way, the whole spatial–temporal evolution of the concentration function is captured within the 4D-object.

#### *2.4.3. Spatial–temporal dynamics of the cumulative effects of chemical spills occurred over a period of time*

For the selected area, an empty 4D-object is created with $x$ and $y$ dimensions corresponding to those of the area and $z$ and time dimension defined by the maximum impact depth and the maximum persistence of the cumulative spill effect. For each spill which has occurred within the selected area, its geographical coordinates are retrieved from the database, and its $x$ and $y$ are calculated relative to the area of analysis. Within the big "empty" 4D-object assigned to the selected area, the concentration 4D-objects are placed at different ($x$, $y$) positions corresponding to the place where each spill occurred and placed on time-axis at different moments of occurrence relative to the initial time of analysis. For adjacent spills, only those assigned 4D-objects included in the area of study are taken into account in the calculation of the cumulated effects. This way, the spatial–temporal dynamics of all spills occurring within and adjacent to the spatial–temporal unit of analysis is described by a single 4D-object incorporating smaller 4D-objects describing individual spill events. This single 4D-object is used furthermore to assess the cumulative effects of a certain scenario of pollution.

By entering the time $t$ (days from the start time of analysis), depth ($Z$) and the ($X$, $Y$) coordinates on the selected layers, users can focus the analysis at one point in the 4-D space. For better positioning, users can select the ($X$, $Y$) coordinates graphically directly on the image. The spatial distribution of concentration is simultaneously displayed. For the selected point in space, the temporal evolution of concentration is plotted, showing the current value (corresponding to the selected time) and its position versus a maximum admissible value when it is assigned to the selected chemical.

The impact calculations based on the above algorithm are divided into two categories: the maximum spill effects describing the overall impact of a scenario of pollution within the selected area and the maximum spill effects describing the level of pollution at a selected point within the area of study.

In the first category, the following spill effects are calculated to describe a certain scenario of pollution within the selected area:

- maximum impact area;
- maximum concentration;
- maximum impact depth.

In the second category, for any selected point within the area of analysis, the following effects are computed based on the temporal evolution of point concentration over the period of analysis:

- maximum concentration;
- current concentration;
- concentration ratio ($C/C_{\text{limit}}$) if the chemical of interest has been assigned a maximum admissible limit ($C_{\text{limit}}$);
- the time period when the concentration exceeds this limit.

For the assigned limit of maximum admissible concentration, the moments of time and the number of times this threshold is surpassed could also be determined.

## 3. Case study

A hypothetical case study was constructed to illustrate the analysis steps and the benefits of the algorithm. This consists of a study area of about 15,000 $m^2$ where many LAS spills occurred in different quantities and at different times and locations. The data set containing the spill characteristics is obtained by querying the database and is shown in Table 1.

An analyst may analyse what will happen in that particular area for a specific time interval (e.g., between March 8th and April 30th) and search for the following answers:

1. What is the maximum concentration of LAS in soil and when does it occur?
2. Does the concentration exceed a maximum admissible value? If yes, for how many days?
3. What is the maximum depth where the cumulated effects of spills propagate within soil?
4. If a spill of a certain concentration is released today in this area, what will be its potential effect in the near future?

The spatial–temporal analysis model calculates the spill effects as shown in Fig. 9. To get the 2D and temporal concentration dynamics, one could enter the time and select the

Table 1
Case study data set

Microsoft Access - [Query1 : Select Query]

File Edit View Insert Format Records Tools Window Help

| LATITUDE | LONGITUDE | DATE | CHEMICAL | Quantity_in_Liters | REGION |
|---|---|---|---|---|---|
| 43.322 | 79.758 | 19/02/2004 | LAS | 200 | HAMILTON-WENTWORTH |
| 43.32151 | 79.75703 | 10/03/2004 | LAS | 350 | HAMILTON-WENTWORTH |
| 43.32165 | 79.75773 | 12/03/2004 | LAS | 350 | HAMILTON-WENTWORTH |
| 43.32181 | 79.75713 | 17/03/2004 | LAS | 320 | HAMILTON-WENTWORTH |
| 43.32165 | 79.75753 | 20/03/2004 | LAS | 100 | HAMILTON-WENTWORTH |
| 43.32161 | 79.75783 | 02/04/2004 | LAS | 360 | HAMILTON-WENTWORTH |
| 43.32141 | 79.75703 | 18/04/2004 | LAS | 250 | HAMILTON-WENTWORTH |

position corresponding to the maximum value. The instance of maximum concentration usually corresponds with the moment of the maximum spill in the selected area. The peak value represents the density of the liquid spill before reaching the soil. The concentration then drops drastically once in contact with soil. For this case study, the maximum concentration is reached on the 18th day of the analysis period.

Furthermore, it could be easily estimated the time period when the concentration exceeded a maximum acceptable limit, in this case being 38 days. The algorithm calculated the maximum impact depth where the chemical could still be found. Fig. 10 shows the moment when the maximum impact depth is reached. This also illustrates an instance where two spills occurring at different moments and locations, however adjacent, have a cumulative effect in the selected point.

Another simulation essential to the spills assessment is the maximum impact area. Fig. 11 shows the moment when the spills spread to the maximum extent in the selected area and time interval of analysis. It can be noticed that an adjacent spill (in the lower left corner), which is located outside of the selected area, brings its influence to the total concentration in the selected point.

Further, this algorithm could be used to predict the potential contamination level given the current distribution of concentra-

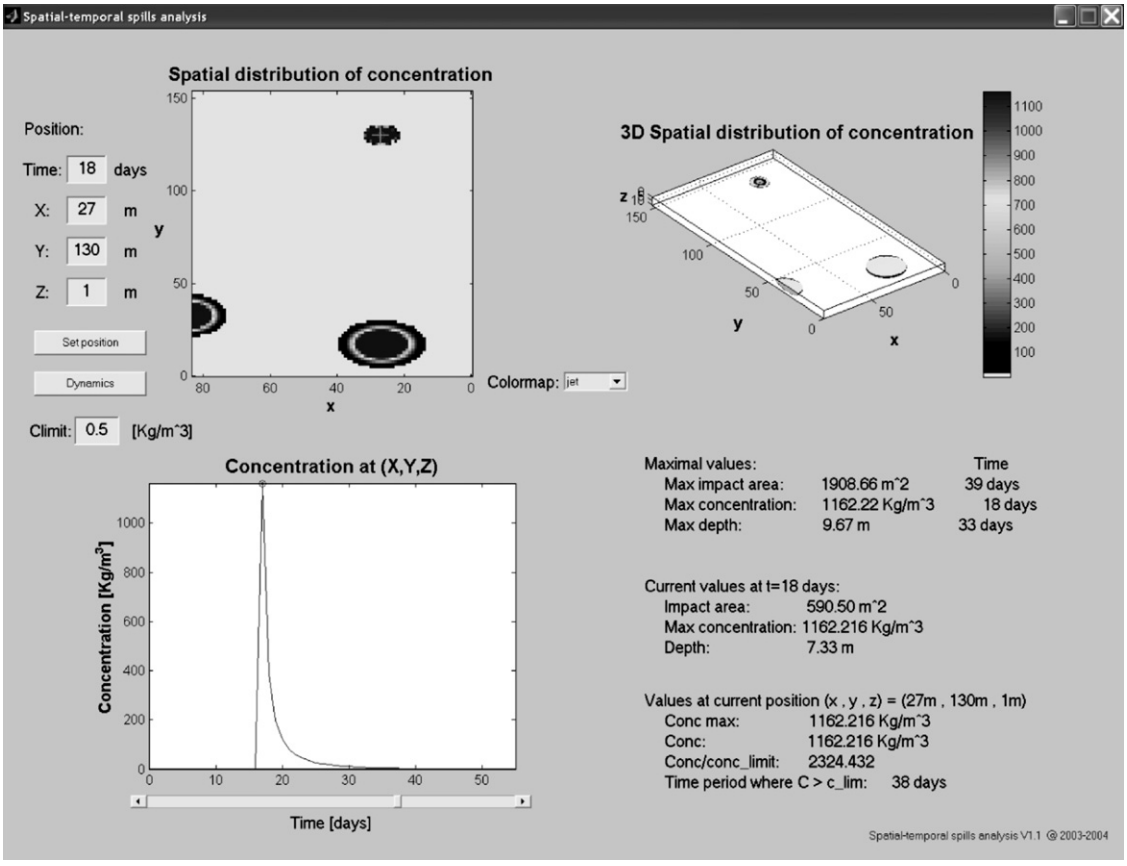


Fig. 9. Spatial–temporal dynamics: the maximum concentration.

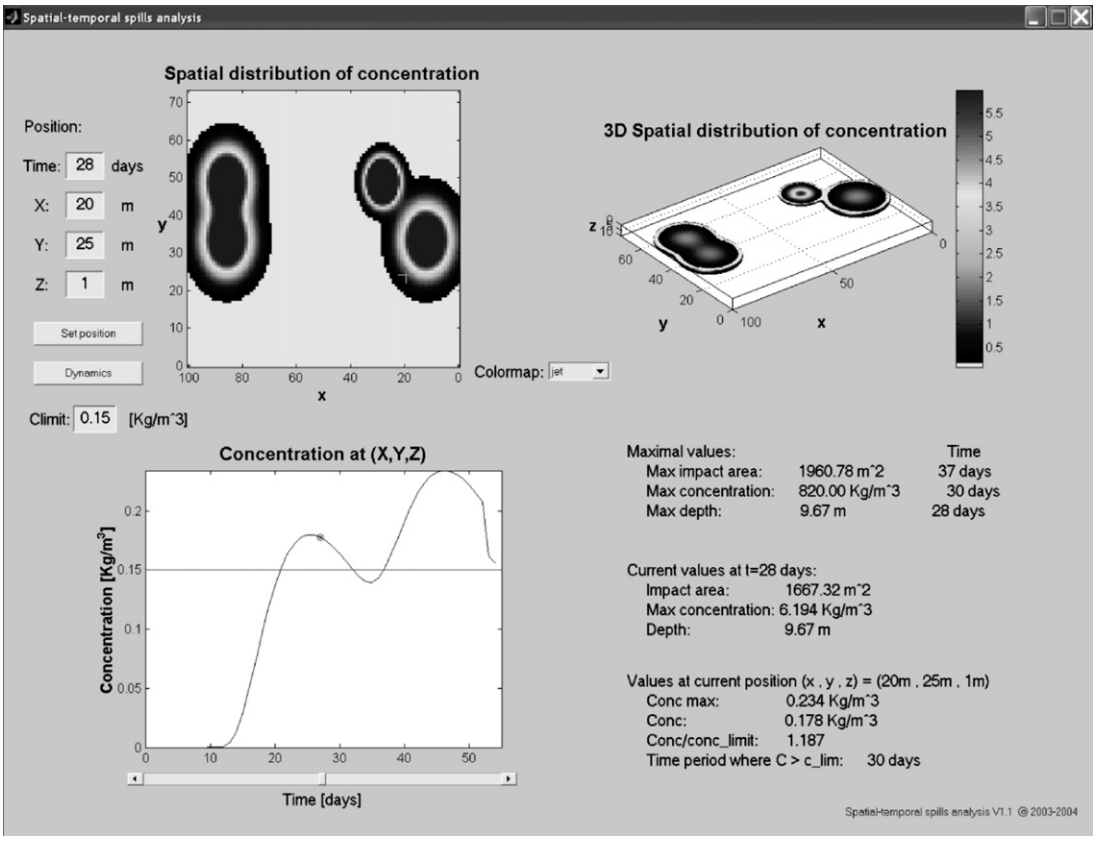


Fig. 10. Spatial–temporal dynamics: the maximum impact depth.

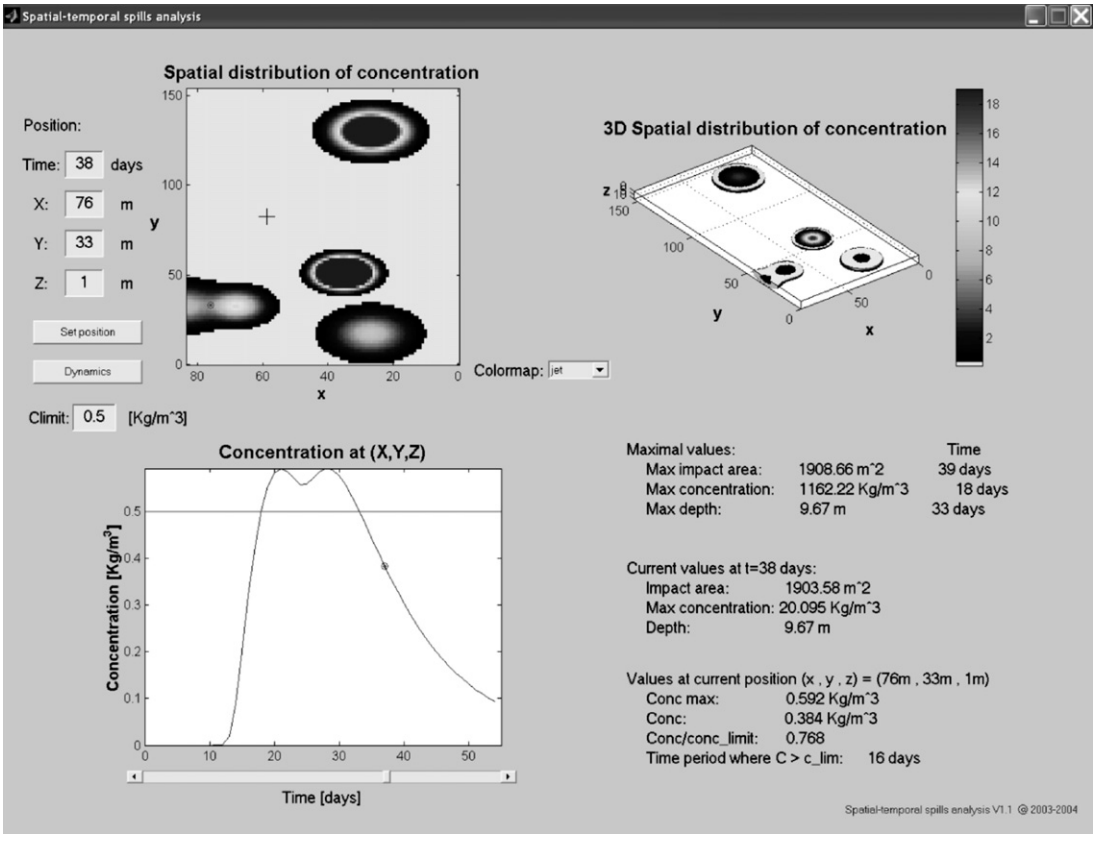


Fig. 11. Spatial–temporal dynamics: the maximum impact area.

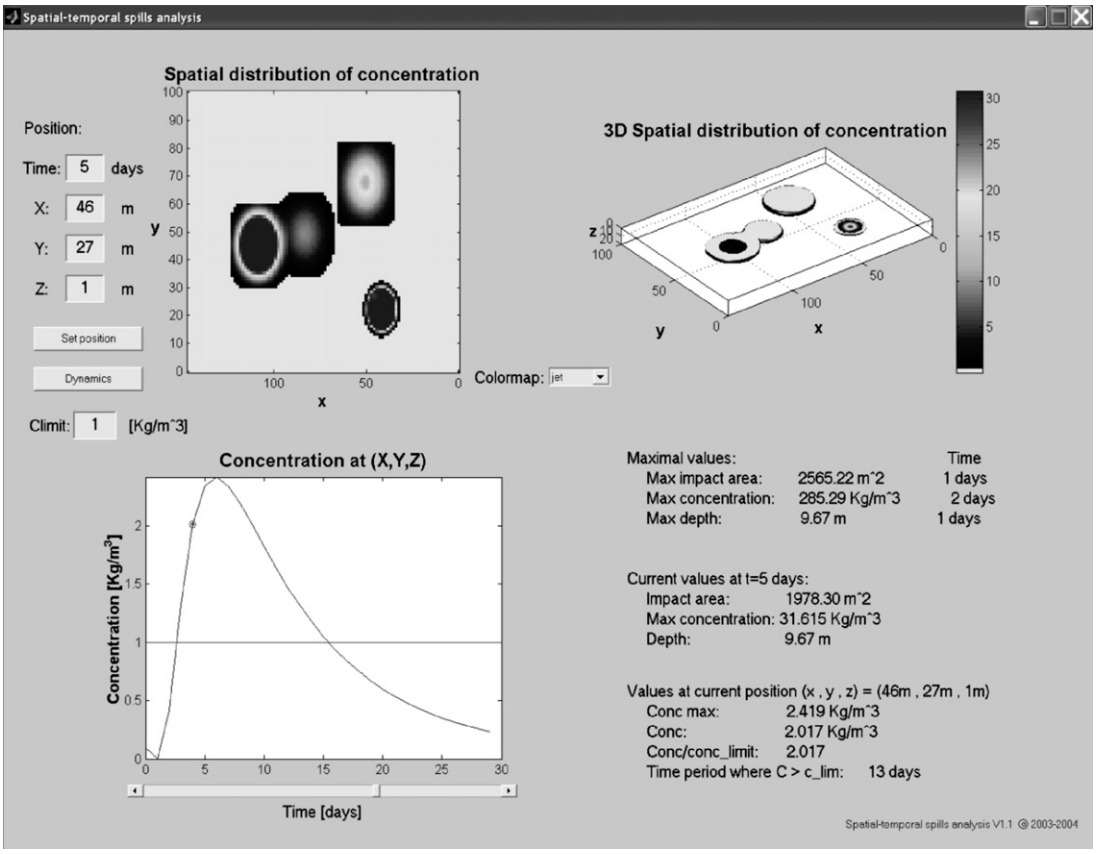


Fig. 12. Spatial–temporal distribution of concentration before the new spill event.

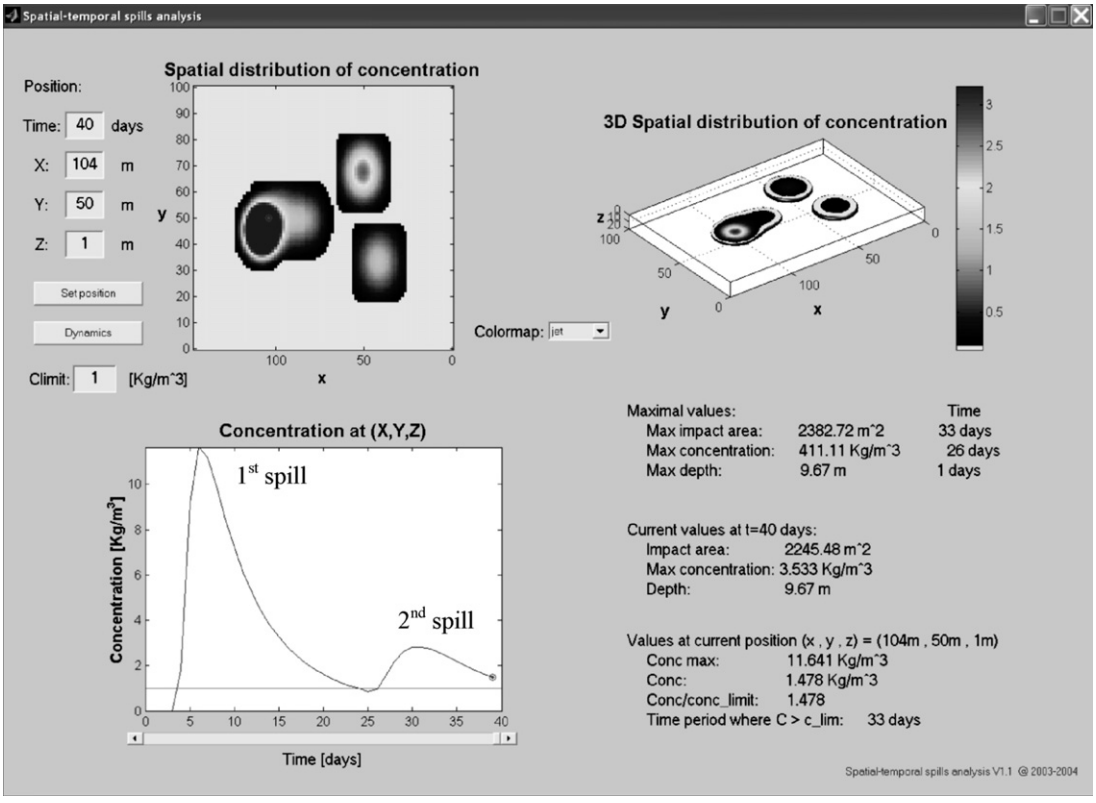


Fig. 13. Spatial–temporal dynamics of concentration distribution 5 days after the new spill event.

tion, quantity and location of a new spill. Fig. 12 represents the concentration distribution before a new spills event. Once a new spill is reported, the algorithm estimated the concentration profile in the future. Fig. 13 displays the predicted distribution for five days after the new event. This prediction capability of the model can bring clues guiding the response strategy.

## 4. Limitations of the algorithm and future development options

The precision of this new tool is dependent on the complexity of the fate and transport model incorporated into the algorithm, and the variety of receptors and exposure routes considered. The complexity of scenarios developed with the algorithm and hence the complexity of analysis is directly influenced by how exhaustive this model is with respect to types of phenomena considered, types of chemicals and levels of heterogeneity in conceptualization of the environment.

The analysis is also limited by the availability and accuracy of the spill and chemical data. This algorithm is useful for those situations when spills are accurately documented in term of location, quantity, chemical types and time of occurrence.

The algorithm is currently conceived for a daily temporal scale in order to match the time-scale of the spill database. However, the algorithm can analyze spills of short persistence in the range of hours only after certain modifications, which are not addressed at this moment.

A matrix of standardized responses appropriate to certain real spill situations can be developed based on a consistent database, which has to comprise classes of chemicals with those physical–chemical processes relevant to each type and also chemical parameters required to model these processes. Additional specific digital information about the environment (e.g., soil maps, information on terrain slopes, locations of environmentally sensitive areas, detailed land use, biota or demographic data) should be compiled in order to facilitate exposure assessment. Furthermore, coupling this algorithm with risk modules sheds light on risk evaluation, which is very important in the case of toxic chemical spills.

Another domain where the new tool can bring insights is environmental equity. Due to its capacity of comprising different types of chemicals and different characteristics of the environment, and also of estimating cumulative effects from multiple sources of pollution, this general framework can be used to identify those populations bearing a disproportionate environmental risk, with valuable clues for policy-makers.

The proposed algorithm represents a first step in the process of developing a decision-making tool which could respond to a large spectrum of situations faced by a spill management team.

## 5. Conclusions and recommendations

This paper responds to the present challenges of spill management in Canada by addressing each of the follow-up, rehabilitation, and prevention phases in an articulated way. During the follow-up phase, environmental and/or human health investigations are conducted to estimate potential long-term implications of a spill event. This is generally done by focusing on a singular event while ignoring the influences of the other events from its spatial–temporal vicinity. In real situations, spills happen with different spatial–temporal dynamics in a continuously changing environment. Therefore, when the impact assessment of chemical accidents is attempted, the overall effects of spills in an area of interest should be considered. Furthermore, this area is not a closed system, but a system embedded in a larger one and receiving influences from what happens in the latter system. In this context, the proposed algorithm offers the opportunity for a more accurate impact assessment in conditions closer to real-world situations as it quantifies the cumulative effects of chemical spills occurring within and adjacent to an area of analysis.

Using this algorithm, the level of contamination can be determined in any chosen point in an area of interest based on the spatial–temporal dynamics of spills within and adjacent to this area. This could be of great help to detect the "hot" spots of pollution. Moreover, given that the algorithm provides estimation of the maximum impact area and of the maximum depth where accumulated effects of a certain scenario of spills could propagate, this brings valuable clues on the extent of the problem and also on groundwater vulnerability.

Furthermore, this paper also offers helpful insights from a rehabilitation-phase perspective. The proposed algorithm has the option to outline the temporal evolution of concentration at any selected point within the area of study. If the chemical considered has been assigned a limiting concentration, the algorithm can determine the moments of time and number of times this threshold is surpassed. Coupled with the concentration profile across the depth of the soil system, this could be used as guideline to discriminate among the potential locations for sampling and alternatives for recovery. Furthermore, as the most likely and the worst-case accident scenarios can be identified, a planned recovery system can be developed. This will decrease the remediation time, which in turn will reduce the overall costs.

The algorithm also makes contributions to prevention strategy due to its power of prediction. Identifying the frequency, potential consequences and impacts of spill events in advance can reduce their likelihood and magnitude. Using this algorithm, real scenarios can be developed for any specified spatial boundaries and time periods based on the spatial–temporal pattern of the events within and adjacent to the considered windows of space and time. Starting from these scenarios mirroring present situations, new events can be simulated to construct potential future scenarios. For each of these scenarios, the "alarming" levels of pollution can be predicted and identified in space and time. Additionally, the algorithm can be used to compare these scenarios and identify those factors giving clues for a better-designed prevention system.

Another advantage of this algorithm is its flexibility. Models of various complexities can be implemented into the algorithm to simulate single-spill events. This flexibility responds to the real-world situations characterized by an overwhelming complexity and dynamism, which cannot be comprised by the present state of insufficient theoretical knowledge and/or

experimental validation. In this context, a logical solution is to design a framework that could be up-dated on the track, once new knowledge or certain conditions create the climate for improvement. Furthermore, this algorithm can be adapted to different types of chemicals and, more than this, it can be used to simulate and assess scenarios amalgamating spills of different types. This could be of value for actual situations when different chemicals with significantly different properties bring their "contributions" to a certain spatial–temporal "unit" of the world.

## References

[1] Environment Canada, Summary of Spill-events in Canada, 1984–1995, 1998.
[2] Ontario Ministry of the Environment, Spill Action Center Summary Report of 1993 Spills, PIBS 2744E01, 1994.
[3] J. Li, Spill Management for the Toronto AOC: The Etobicoke Creek Watershed Spills Mapping Study, Report Prepared for Conservation Toronto and Region, ON, 2003.
[4] J. Farah, Analysis of Reported Chemical Spills in the Southern Ontario Region, Bachelor of Science's Thesis, Department of Civil Engineering, Ryerson University, Toronto, ON, 2002.
[5] M. Holysh, S. Paterson, D. Mackay, M. Bandurraga, Assessment of the environmental fate of LAS, Chemosphere 15 (1986) 3–20.
[6] R.J. Larson, Structure–activity relationship for biodegradation of LAS, Environ. Sci. Technol. 24 (1990) 1241–1246.
[7] R.J. Larson, T.M. Rothgeb, R.J. Shimp, T.E. Ward, R.M. Ventullo, Kinetics and practical significance of biodegradation of LAS in the environment, J. Am. Oil Chem. Soc. 70 (1993) 645–657.
[8] D.R. Nielsen, M.T. van Genuchten, J.W. Biggar, Water flow and solute transport in the unsaturated zone, Water Resources Res. 22 (9) (1986) 89S–108S.
[9] W.A. Jury, H. Fluhler, Transport of chemicals through soil: mechanisms, models, and field applications, Adv. Agron. 47 (1992) 41–201.
[10] C. Zheng, G.D. Bennett, Applied Contaminant Transport Modeling: Theory and Practice, Van Nostrand Reinhold Ed., NY, USA, 1995.
[11] J.L. Schnoor, Environmental Modeling: Fate and Transport of Pollutants in Water, Soil, and Air, Environmental Science and Technology, Wiley/Interscience Series, 1996.
[12] P.B. Bedient, H.S. Rifai, C.J. Newell (Eds.), Groundwater Contamination, Prentice-Hall, NJ, USA, 1999.
[13] R.J. Charbeneau, Graundwater Hydraulics and Pollutant Transport, Prentice-Hall, NJ, USA, 2000.
[14] S.C. Hern, S.M. Melancon (Eds.), Vadose Zone Modeling of Organic Pollutants, Lewis Publishers, MI, USA, 1986.
[15] Mackay, Multimedia Environmental Models: The Fugacity Approach, Lewis, Chelsea, MI, 1991.
[16] T.R. Ellsworth, W.A. Jury, A three-dimensional field study of solute transport through unsaturated, layered, porous media. 2. Characterization of vertical dispersion, Water Resources Res. 27 (5) (1991) 967–981.