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CUMULATIVE EFFECTS OF CHEMICAL SPILLS USING A SPATIAL-TEMPORAL DYNAMICS ANALYSIS ALGORITHM

By

Mihaela Dinca-Panaitescu

Bachelor of Science

University of Bucharest, Romania

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ABSTRACT

Cumulative effects of chemical spills using a sptial-temporal dynamics analysis algorithm

Mihaela Dinca-Panaitescu, MASc., 2004

Environmental Applied Science and Management, Ryerson University

The increasing number of accidents 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, the thesis proposes a general 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 designated as relevant to predict possible pictures of future exposure and estimate in advance potential alarming levels of pollution. To achieve this purpose, the following objectives are set up. The first objective is to develop a four-dimensional model to simulate a single-spill event based on certain assumptions about chemical and soil characteristics. The second objective is to develop an algorithm to assess the cumulative effects of chemical spills on a selected area using the model for a single-spill event while taking into account the effects of those spills of the spatial-temporal zone adjacent to the study area.

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Dedications

This work is dedicated with the kindest love to my husband and my son.

To my husband whom I owe the most important personal and professional achievements

To my son who so admirably accepted to be privated of so many story-telling nights, so that his mom being "the best of the whole world"

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CHAPTER 1 INTRODUCTION

1.1 BACKGROUND

The increasing number of accidents 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 were at the forefront of public and political concern, through the years chemical spills have gained equal importance in spill-prevention 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 (EC, 1998). 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 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.

The increasing importance of chemical spills creating an impetus for future research is also suggested by the spatial and statistical analysis of the chemical spills that occurred in Southern Ontario from 1988 to 2000 (Li, 2003; Farah, 2002). Spills data were provided by 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 environmental response to these reports. Reported occurrences recorded on ORIS allow tracking the status of occurrences and preparing data summaries (SAC, 1994). The database contains spill information entered under a number of data fields including location, chemical name, quantity, cause, source, sector, and other relevant information. Descriptive statistics give information about annual and seasonal trends of spills in Southern 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 can be drawn based on this kind of information. However, spills are not disparate events with only local or simply added effects on the environment where they occur. 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, so that the chemical fate is correspondingly complex. Moreover, some attributes of chemicals in the environment cannot be measured directly and they can only be estimated by using models.

In these conditions, 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

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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 quantify the risks resulting from accidental spills and how appropriate is the approach used?

In this context, the thesis proposes an algorithm 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 designated as relevant to predict possible pictures of future exposure and estimate in advance potential alarming levels of pollution.

1.2 PURPOSE AND OBJECTIVES

The purpose of this thesis is to develop a general framework for a better assessment of the impact of chemical spills on the terrestrial environment. To achieve this purpose, the following objectives are set up. The first objective is to develop a four-dimensional model to simulate a single-spill event based on certain assumptions about chemical and soil characteristics. The second objective is to develop an algorithm to assess the cumulative effects of chemical spills on a selected area using the model for a single-spill event while taking into account the effects of those spills of the spatial-temporal zone adjacent to the study area.

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1.3 OUTLINE

The thesis is structured in the following manner. Chapter 1 presents the magnitude of the problem and justifies the impetus for future research. This chapter continues with a general description of thesis purpose and objectives. The next chapter reviews literature and exposes in detail the conceptualization of the soil environment, the main mechanisms of solute transport and fate associated with certain chemical and environmental properties, and the mathematical framework to address those processes undergone by chemicals once spilled into environment. Chapter 3 presents in detail the model proposed to simulate a single-spill event and the algorithm created to assess the cumulative effects of chemical spills based on spatial-temporal dynamics in four-dimensional space. The thesis ends with some conclusions and recommendations to improve and extend the research.

CHAPTER 2 LITERATURE REVIEW

Protection of the natural environment ranks as a major challenge for our industrialized society. One aspect of this challenge receiving increased attention in recent years from both regulatory agencies and the general public is the occurrence of spills. In Canada, environmental regulation is generally addressed by the traditional "command and control" approach. A complex set of laws is in place in Ontario to regulate emissions from industry with the final objective of minimizing and preventing adverse environmental and human health effects. However, in spite of the regulatory framework, accidents do happen as the consequences of the routine operations and processes taken for granted as part of our modern economy. These accidents can result in unintended releases of materials with potentially harmful effects on environmental health, human health or both. Depending on the nature of the release, industrial accidents can pose serious threats and also become issues of very high profile from a public point of view. For those spills that may not pose an immediate threat, the question of what the long-term effects of exposure to the spilled material might arise. This leads us to wonder how much harm/risk to environment and human health results from accidental spills and how appropriate are the approaches used by regulator to quantify the risk.

In order to determine the nature and extent of environmental damage caused by spills with direct implications on the decision-making process, it is essential to approach the problem in a framework comprised of certain properties of the environment where the spills occur, representative properties of the chemicals spilled, and also the spatial-temporal history of spill-environment interactions.

This chapter is designed to review the general principles driving the conceptualization of the soil environment and the phenomena undergone by different chemicals once spilled into the medium considered. Therefore, the general concept of a porous medium is exposed and, in this context, the main

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mechanisms of solute transport and fate are revised with significant chemical and soil properties influencing these processes. Furthermore, the mathematical framework to address the processes described and some general approaches used in modeling are discussed.

2.1 DESCRIPTION OF VADOSE ZONE

Subsurface water has been traditionally classified by groundwater hydrologists as shown in figure 1 below:

Figure 1 Vertical distribution of water content and classification system (Charbeneau, 2000)

There are two major zones: the unsaturated and saturated zones. *Saturated zones* called aquifers may be classified as unconfined with a free water table where pressure is atmospheric or confined with an overlying aquitard of impervious where pressure is greater than atmospheric (Bear, 1979).

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The unconfined aquifer is in direct contact with the unsaturated zone and its thickness varies from a meter or less to many 10s of meters.

The unsaturated zone also called *vadose zone* or *variably saturated zone* denotes the land region between the soil surface and the groundwater table, where water or liquids coexist with the gaseous phase. In the vadose zone, liquid and gaseous constituents are attenuated and transformed during their exchange in both directions between the soil surface and water table. The unsaturated zone is recognized as a key factor in the protection and improvement of groundwater quality.

In the vadose zone, water contents are less than soil porosity, and the soil water pressure (or metric) potential is negative, and less than atmospheric pressure. The concept of negative pressures in the unsaturated zone is an analog of chemical and thermodynamic energies. The thickness of the unsaturated zone ranges from a meter or less to several 10s of meters. It has been traditionally divided into three zones: *root zone* below the earth surface; *intermediate zone*, and *capillary zone* (or *fringe*) above the water table. In the capillary zone, the capillary forces draw water upward from the water table producing a zone that is wetter than the intermediate region of the unsaturated zone. The height of this zone varies with the size of pores. For fine-grained silts and clays, the capillary zone thickness is on the order of several meters. In the case of coarse-grained soils such as coarse sands and gravels, the capillary zone has a thickness of a centimeter or few millimeters. In the unsaturated zone, regions of localized saturation of soils may exist due to semipervious soils becoming saturated and causing the more pervious soils to be saturated. Such localized saturated zones are called *perched groundwater or perched aquifers*. Generally, such zones are only a few meters thick (Guymond, 1994).

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2.1.1 POROUS MEDIA AND PHASES

The soil may be viewed as a mixture of solid particles, liquid, and gas. These are called phases. Figure below depicts a conceptualization of a slice of porous media.

Figure 2 Porous media slice (Guymon, 1994)

Liquid and dissolved compounds are stored in the solid matrix or may move relative to a fixed datum. In general, the soil matrix is considered as nondeformable since most unsaturated flow problems can adequately be dealt with based on this assumption. Due to the complexity of the phenomena at the pore scale, when considering liquid or gas movement in soil, a macroscopic view of the system is taken.

Liquid phase

Water is an excellent solvent capable of weathering a great number of minerals and compounds. Stored water and that flowing through the porous medium slowly dissolve minerals associated with the solid phase and which appear in the liquid phase as ions. Besides water, other liquids generally consisting of pollutants associated with industrial activity are important in unsaturated flow problems.

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Gaseous phase

The gaseous phase is fluid and able to move through the soil. There are situations when the gaseous phase may be as significant as the liquid phase as it is the case of a volatile organic component. The dominant component of the gaseous phase is air in the soil pores. Air is a solvent for volatile substances similar to water for soluble materials. In general, the volatile pollutants associated with unsaturated flow problems are so dilute that they may be considered as completely miscible in the air.

Solid phase

The solid phase in soils is primarily composed of mineral soil particles: gravels, sands, silts, and clays. Solids and interconnected pores form a *solid matrix* called a *porous medium*. Organic material can also be attached to the mineral grains further contributing the bulk of the soil solid phase. Live organisms such as micro and macrofauna may be attached to soil particles or may exist separately in the liquid phase.

Porosity and related properties of soils

The fundamental interest in a porous medium is its ability to hold and transmit water. The most important of the number of terms related to this ability is medium porosity.

Porosity and void ratio

Porosity and void ratio describe the ratio of voids or pore volume to a reference volume.

Soil porosity:

$$n = \frac{V_v}{V} \quad \text{where } V = V_s + V_v$$

V_v is the volume of voids

V is the total (bulk) volume

V_s is the volume of solids contained within total volume

Porosity of a soil is generally a function of particle size. Course grain particles, particularly for well-graded soils, have a packing arrangement that results in a small void space while small particles such as clays and silts can develop a structure that results in relatively large void spaces. Clays and silts have porosities in the range of 0.4 to 0.5 while gravels have porosities in the range of 0.15. Finer grained soils, however, can have porosities with a wide variation depending on age, depositional characteristics, and organic content. Porosities may range as high as 0.8 or more.

Soil density

The actual soil density or dry density is defined as the dry mass of soil divided by the volume of solids:

$$\rho_s = \frac{M_s}{V_s} = \frac{W_s}{gV_s}$$ where g is the gravitational constant

Bulk dry density is defined as the mass of dry soil divided by the total volume (volume of solids plus volume of voids) as follows:

$$\rho_b = \frac{M_s}{V} = \frac{W_s}{gV}$$

Fluid content

The most common measure of water content used by soil scientists is volumetric water content defined as the ratio between water volume and total volume (Charbeneau, 2000):

$$\theta = \frac{V_w}{V}$$

where V_w is the volume of water

Water content must lie within the range $0 < \theta < n$

The maximum water content possible is equal to the porosity of the soil.

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2.1.2 SOIL WATER IN THE VADOSE ZONE

For unsaturated soil above the water table, part of the pore space is filled with water while the rest is filled with air. The sum of the volumetric water and air contents is equal to the total porosity:

$$\theta_w + \theta_a = n \; .$$

Both the volumetric water content and the water saturation are macroscopic parameters. This means that they cannot be applied to individual pores on the microscopic scale. It is important to understand the distribution of water at the pore scale within a mass of soil. For an initially dry soil, water added will be adsorbed as a film on the surface of the soil grains called *pellicular water* (Bear, 1972). Pellicular water is held strongly by van der Waals forces and can have a suction pressure of tens of atmospheres. The suction pressure is a thermodynamic measure of the energy state of the water within the soil. If water continues to be added, it will be accumulated at the contact points between grains that represent the smallest pore-space openings in the soil; this accumulating water is referred to as *pendular water*. The pendular water (pendular rings) is held at the contact points by *capillary forces* (Charbeneau, 2000).

Figure 3 Pellicular and pendular distributions of water (Charbeneau, 2000)

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These forces are caused by the presence of surface tension between water and air phases within pore space and they impinge water to move into the smallest pores. For low water content conditions, water movement in soil is slow, having to pass over the thin films of adsorbed water as moving from one pendular ring to the next. As the water content increases, the pendular rings grow, and the thickness of the pellicular water film increases. The saturation at which a continuous wetting phase forms moving freely is called the *equilibrium wetting phase saturation*. Above this critical saturation, the saturation is called *funicular* and flow of water is possible (Charbeneau, 2000).

Figure 4 Funicular saturation at intermediate water content (Charbeneau, 2000)

As the water content continues to increase, the air becomes isolated in individual pockets in the larger pores, and flow of the air phase is no longer possible. The saturation at which this process happens is called *insular saturation* (Charbeneau, 2000).

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Figure 5 Insular saturation at high water content (Charbeneau, 2000)

If the air is under positive gauge pressure, these air pockets will eventually dissolve, and complete water saturation will be achieved. Under normal conditions in the unsaturated zone, however, full water saturation is not achieved because of residual or entrapped air (Charbeneau, 2000).

When considering flow processes in an unsaturated porous medium, there are two aspects associated with the interface between water and air phases and with the presence of the solid phase. The first issue concerns the medium *wettability*. For mineral soils, there is more interfacial energy associated with air-solid phase interfaces than with water-solid phase interfaces. Thus, minimizing the total amount of air-solid interface minimizes the overall system energy, and the soil surface is preferentially covered with water. For this system, water is the wetting phase and air is the nonwetting phase, with respect to the soil. The second issue concerns the pressure difference across a curved surface. The interface between air and water phases acts as a membrane under tension, and a force balance shows that the pressure in the air phase is greater than that in the water phase, given the curvature of the interface (Adamson, 1978). The mean radius of this curvature decreases with increasing capillary pressure (the pressure difference between air and water), and thus with elevation above the water table. This implies that the interfaces are present in smaller and smaller pores with increasing elevation, so that the water phase saturation decreases while the air phase saturation increases. At higher elevations above

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the water table, water is retained in the smaller pores while the larger pores contain air.

2.1.3 SOIL SOLUTION. PHYSICO-CHEMICAL OBSERVATIONS

The liquid in the vadose zone is a solution of water and dissolved solid and gaseous constituents. Soil water properties are intimately linked to the chemical and physical properties of the solid phase on which it is sorbed. The amount of soil water, the mineralogical composition and particle-size distribution of the solid phase are important factors influencing the degree of this linkage. Water being a strong dipole, it is readily influenced by the net surface charge density of the soil particles and by different types of dissolved constituents. Due to the net surface charge on the soil particles, an electric field is created, this way affecting the distribution of cations and anions within the water films and also changing the properties and configuration of the water close to particle surfaces. However, controversy exists about the extent to which physical properties of water are affected by interactions with the solid phase, as well as about the impact of these effects on macroscopic soil behaviour (Parker, 1986). The excess surface-charge of soil particles is neutralized by an electrical "double layer" whose thickness is affected by the total electrolyte concentration and the mineralogical composition of soil particles. The relative rates of water movement depend on the thickness of the water film. Water-solute-particle surface interactions become increasingly important as the soil becomes progressively drier. These interactions are significant when water contents in the vadose zone are reduced to thin water films of only 10-20 molecules thick compared with water saturation conditions when water lenses are $10^3 - 10^4$ molecules thick (Parker, 1986).

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2.2 MECHA   ~S OF CHEMICAL TRANSPORT AND FATE IN THE VADOSE ZC

A better assessment and control of the exposure to chemicals spilled onto a terrestrial environment and of the health risks induced by this exposure strongly depend on a better understanding of the fate and migration of chemicals. The terrestrial environment is a dynamic system consisting of interdependent abiotic and biotic factors linked by physical, chemical, and biological processes. Chemicals introduced into this system use these linkages to migrate within and between the various media where they are transformed and degraded while moving. The ultimate disposal of chemicals in soil is determined by the dynamic, spatial-temporal interaction among different processes grouped into certain categories: transport, sorption, transformation/degradation, and volatilization.

2.2.1 MECHANISMS OF SOLUTE TRANSPORT IN VADOSE ZONE

Once introduced into the terrestrial environment, chemicals in solution can move by three separate pathways and mechanisms: by runoff and erosion to the aquatic environment, by volatilization to the air, and by lateral or vertical movement (leaching) to groundwater. The transport component is critical in dealing with environmental contamination problems. Chemical spills would impact only the immediate spill site; through transport, spills can move over the land and through the soil to contaminate surface and groundwater supplies.

Unless a compound is very volatile, it is transported predominantly as a dissolved constituent of the water phase by bulk movement. At the pore scale, the solute moves through the porous medium by convection and diffusion. The total flux of dissolved chemical describing the solute movement through water phase is an impractical quantity because it is not measurable and describes the 3-D flow around solid phase and through gaseous phase of the soil matrix. Therefore, for a macroscopic scale representation of the system properties, the local quantities have to be volume-averaged. The dimension of the averaging

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volume is established so that the statistical distribution of geometric obstacles is about the same from place to place. As a consequence of this averaging, the resulted mean quantity is macroscopically homogenous over the new transport volume containing the averaged elements (Jury and Fluhler, 1992).

Convection refers to the transport of dissolved solute carried along with the flow of host water phase. Assuming soil to be macroscopically homogenous for porposes of modeling, the local dissolved chemical flux can be volume-averaged. In the conditions of incompressibility of soil water, the volumetric flux of water is given by (Charbeneau, 2000):

$$q = -K grad(h) = KI$$

where K is the hydraulic conductivity

        h is the hydraulic head

        I is the hydraulic gradient

The pore water velocity or seepage velocity v gives the average speed of the water movement. For unsaturated flow (Charbeneau, 2000):

$$v = \left(\frac{q}{\theta} \right)$$

where θ is the volumetric water content

For a chemical present at concentration c in an aqueous solution, the total mass of the chemical carried across a unit area normal to the bulk fluid motion is given by its convection mass flux vector (Charbeneau, 2000):

$$J_{convection} = qc$$

The convection flux equals KIc based on Darcy's law. This implies that bulk transport is proportional to the hydraulic conductivity of the medium, the energy gradient, and the local concentration.

Liquid diffusion refers to the net movement of dissolved solutes within a solution from regions of the higher solute density to lower solute density due to random molecular interactions (Bird et al., 1960; Crank, 1975). While

convection is associated with bulk macroscopic groundwater movement, diffusion is a molecular-based phenomenon. The diffusion flux is proportional to the concentration gradient; the coefficient of proportionality being called the soil liquid diffusion coefficient (Charbeneau, 2000). According to Fick's law of diffusion, the diffusive mass flux vector for a saturated porous medium is:

$$J_{diffusion} = -nD_s grad(c)$$

where D_s is the *apparent diffusion coefficient* in soil for chemical species

D_s is smaller than the molecular diffusion coefficient because the solute moves along a tortuous path through the pore space. For unsaturated flow, the tortuosity increases with decreasing water content and D_s is still smaller.

In the soil air spaces, a chemical's vapour molecules collide and spread out by vapour diffusion. Similar to liquid diffusion, gaseous diffusion is defined as the product of the vapour density or concentration gradient and a proportionality coefficient called the soil vapour diffusion coefficient (Charbeneau, 2000).

The volume-average solute flux is not the sum of the convection and diffusion fluxes as is the case at the pore scale. By the averaging process from the pore scale to a macroscopic framework, some of the solute motion is lost so that it must be reinserted into the flux equation. Local 3-D fluctuations from the average motion due to movements around air and solid phases are lost, not contributing to the mean water flow at the macroscopic scale. However, the dissolved chemical convected along tortuous paths does contribute to the solute transport and this contribution cannot be neglected. This process is known as hydrodynamic dispersion (Jury and Fluhler, 1992).

Hydrodynamic dispersion is associated both with bulk fluid movement and with the complexity of the porous medium. There are at least four physical mechanisms causing fluid particles once close together to move apart. First, the

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particles near the channel center move more rapidly than those near the walls of the pore channel. Second, the particles move at different relative speeds because of variability in pore dimensions along the pore axes. Third, initially adjacent particles can follow different streamlines leading later to different channels. These particles may continue to move apart or may come together. The fourth mechanism is associated with heterogeneities in the hydraulic conductivity field, allowing solute molecules to move at different speeds – even if the hydraulic gradient is uniform. Statistically, mechanical dispersion refers to the deviation from the mean and it is scale dependant while advection refers to the average rate of movement. Compared with diffusion which is an active process responding to the concentration gradient irrespective of flow, dispersion is a passive process responding to fluid flow. In practice, diffusion and mechanical dispersion coefficients are combined into a single *hydrodynamic dispersion coefficient* (Charbeneau, 2000). Freeze and Cherry (1979) defined hydrodynamic dispersion as the process in which solutes spread out and are diluted compared to simple advection. It is defined as the sum of molecular diffusion and mechanical dispersion, where much dispersion is caused by local variations in velocity from the average velocity of flow. Dispersion coefficients are empirical and strongly dependent on scale (Schnoor, 1996). In general, for non-aggregated soils, only hydrodynamic dispersion and axial diffusion are considered as significant sources of dispersion, intraparticle and film diffusion making insignificant contributions (Brusseau, 1993). However, Nielsen et al. (1986) noted that in practice the dispersion coefficient is used as a "fudge" factor incorporating all solute-spreading mechanisms not directly considered in the advection-dispersion formulation. The axial diffusion is on the order of 10^{-5} cm^2/s, but generally neglijible in field situations. Its importance depends on pore-water velocity, decreasing with the increase of water velocity. For long periods of non-infiltration such as for very arid regions, molecular diffusion is an important transport mechanism between rainfalls, otherwise is much less than hydrodynamic dispersion.

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For 1-D system, the hydrodynamic dispersion coefficient is defined as (Nielsen et al, 1986):

$$D = D_0 \tau + \lambda |v|^n$$

where D_0 is diffusion coefficient

  τ is a tortuosity factor that depends on the water content (Kemper and

  van Schaik, 1966) but not on the pore water velocity

  λ and n are empirical constants

For relatively homogenous, saturated systems, the exponent n is approximately unity (Saffman, 1959), and hence λ is known as the *dispersivity*. The value of λ typically ranges from about 0.005 m or less for laboratory scale experiments involving disturbed soils, to about 0.1 m or more for field scale experiments (Biggar and Nielsen, 1976; Jury and Sposito, 1985). Studies also suggest that λ depends on the spatial scale of the experiment, as well as on vertical and areal heterogeneities of field soils (Dagan, 1983).

Hydrodynamic dispersion is a second order symmetric tensor (Bear, 1972; 1979). Bear and Bachmat (1967) have shown that the hydrodynamic dispersion tensor is composed of *dispersivity coefficients* that contain implicit information on the porous media and the bulk fluid movement.

The literature contains little guidance on estimating dispersivities. Different values were suggested in the literature, with great differences between laboratory and field measurements. In laboratory experiments, the longitudinal dispersivity is usually found to be 5 to 20 times larger than the transverse dispersivity. Estimates of dispersivity from bench scale laboratory experiments are lower than field values. The literature contains even less information on dispersivity in unsaturated soils where dispersivity is a function of water content. Biggar and Nielsen (1976) recommended an average dispersivity of 3 cm in field soils, this larger value than that obtained by laboratory columns accounting for the vertical heterogeneity. Schnoor (1996) suggested a range of 0.1-1 cm at laboratory scale; 10-100 cm at small scale, and an average of 25m at large scales. Regarding transverse dispersivity, its value was suggested as being

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10-30% of that of longitudinal dispersivity (Bedient et al. 1999). Jury and Fluhler (1992) present some data suggesting that dispersivity in the unsaturated media increases with depth below the soil surface. In the laboratory, it has been found to vary from 0.1 to 10 mm that is on the order of pore size. In the field, the dispersivities are sometimes measured through single and multiple well tracer tests. More often, the measured field concentrations are simulated with mathematical models and the coefficients adjusted to get an adequate match. The values found this way are usually much larger than laboratory values. Recent literature has shown field values of dispersivity to vary from 1 to 100m or larger. These values are larger than laboratory values by a factor of up to 10^5, suggesting that dispersion plays a different role in the field than in the laboratory. Detailed laboratory and field experiments used to measure dispersivity are described by Pickens and Grisak (1981). The field experiments show that the measured dispersivities depend on the way in which measurements are made and on the scale, with the apparent dispersivity increasing linearly with transport distance.

FACTORS AFFECTING CHEMICAL TRANSPORT

Soil water content. Volumetric water content significantly influences the liquid and gaseous diffusion mechanisms. As the chemical mass moved per unit time between two points is inversely proportional to the distance between these points, the length of the path followed by a dissolved solute/vapour molecules is strongly affected by water content. Liquid diffusive transport increases with the increasing of water content because the cross-sectional area available for flow increases, and as liquid replaces air in the porous medium, the path length decreases. Conversely, vapour diffusive transport decreases with increasing water content because the air space decreases.

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The partitioning of chemicals between different phases of a porous medium can affect chemical transport by affecting the availability of the chemical in solution and gaseous phases. When soil water contents decrease below a few monolayers of water (in the top few millimeters of soil during intense drying) water molecules, which preferentially occupy soil adsorption sites, are displaced from the surface, thus increasing the adsorption capacity of the soil. In this dry region, liquid and gaseous concentrations will decrease dramatically and the transport mechanisms will also be reduced significantly since most of the chemical amount is sorbed. This effect should be considered only for a permanent, dry surface. However, this adsorption effect does not appear to be reversible when the soil surface rewets (Hern and Melancon, 1986).

Bulk density or porosity

Soil porosity is related to bulk density by a linear relation:

$$n = 1 - \frac{\rho_b}{\rho_m}$$

where ρ_m is soil mineral density ($\frac{g}{cm^3}$) which, for most soils, lies between

2.65 $\frac{g}{cm^3}$ (clays) and 2.75 $\frac{g}{cm^3}$ (sands)

Based on this relationship, it is sufficient to discuss only the influence of the soil porosity on chemical transport. Decreasing soil porosity (equivalent to increasing bulk density) will generally decrease chemical transport. For liquid/vapour diffusive processes, decreasing porosity generally implies that the cross-sectional area available for flow will decrease and the path length of diffusing molecules will increase as more solid obstacles per unit volume are placed in their way.

Mass flow is also indirectly affected by porosity since low porosity regions are likely less permeable to water transport. Pore sizes influence the permeability of different soil types, strongly decreasing as porosity decreases. However, finer-textured soils such as clays generally have a higher porosity and lower

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permeability than sandy soils. Hydrodynamic dispersion has not been quantitatively related to porosity, but it could be linked given its proportionality to water flux which in most conditions decreases as porosity decreases. Porosity can also affect the transport since the density of mineral and organic adsorption sites will increase as porosity decreases. Hence, more chemical will be adsorbed with a corresponding decrease in solute and gaseous concentrations (Hern and Melancon, 1986).

Adsorption site density. The density of adsorption sites for chemicals may be represented by two soil specific indices: surface area (surface area per soil volume or mass) and soil organic content. Organic matter content has been found to be positively correlated with organic chemical adsorption. Therefore, an immediate effect of increasing organic matter content would be an increase of chemical adsorption and hence a decrease of liquid and gaseous concentrations with strong impacts on the extent of transport mechanisms (Hern and Melancon, 1986).

2.2.2 SORPTION

2.2.2.1 SOLUTE PARTITIONING

The partitioning of the chemicals between the sorbed and dissolved phases is a critical factor in determining how rapidly the chemicals will leach. *Sorption* is defined as the association of a dissolved contaminant with a solid material. The term sorption encompasses two more specific processes: *adsorption* and *absorption*. Adsorption refers to the association of a substance with the solid surface while absorption refers to the association within a solid particle (Bedient et al., 1999). Since both phenomena could occur simultaneously, it is difficult to distinguish between them and the term sorption is used to describe the overall process.

Highly-sorbed chemicals will not significantly migrate away from the region of the soil where they were initially applied; so that they will usually

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remain on or near the land surface unless extensive soil cracks, macropores, and other preferential flow paths exist to facilitate the rapid movement of soil particles and associated chemicals through soil columns. For these chemicals, transport by surface runoff and erosion will be more environmentally significant than chemical leaching. At the same time, non-sorbed chemicals will exist primarily in the dissolved phase, and their movement to groundwater will be controlled by soil characteristics, the amount of water applications (precipitation or irrigation), and fate processes. But most of the chemicals of environmental interest are moderately sorbed so that they exist in both dissolved and sorbed phases. For these chemicals in the mid-range of sorption properties, both runoff and leaching may be important, depending on the specific chemical, environmental, soil, and management conditions (Hern and Melancon, 1986).

Each chemical has a unique manner of moving in soil due to its different sorption affinity for solid surfaces in response to driving forces. Therefore, the descriptive models for chemical transport in soil have to include a quantitative description of sorption processes. At the same time, the diversity and complexity of the sorption surfaces and of nature of bonding mechanisms to the accessible adsorption sites make these phenomena difficult to be described in microscopic detail (Weber and DiGiano, 1996).

2.2.2.2 SORPTION ON SOIL ORGANIC CARBON

Soluble organic chemicals sorb onto solid particulate matter by different mechanisms: physical adsorption due to van der Waals forces, chemisorption due to chemical bonding, and partitioning of the chemical into an organic carbon phase. Physical adsorption is essentially a surface electrostatic phenomenon; for chemisorption the dissolved chemical molecules are bound to the binding sites of solid particles; and partitioning refers to the dissolution of hydrophobic organics into the organic phase of the solid matter (Schnoor, 1996). Because of the heterogeneity in adsorption sites of soil particles and of the complexity of the soil solution, it is extremely difficult to develop a general

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relationship describing in detail the sorption dependence on the variety of physical and chemical properties. Therefore, the complications of sorption are neglected in favour of linear sorption models (Bedient et al, 1999).

The most common approach to model sorption is the linear sorption isotherm. This refers to the equilibrium relationship between sorbed and solute concentrations at constant temperatures. When the organic compounds are present in trace concentrations, linear partitioning relationships are often observed. A linear isotherm plots as a straight line with a slope equal to the *distribution coefficient K_d* which is a measure of the actual partitioning in soil water:

$$k_d = \frac{mgchemical \ / \ kgsolids}{mgchemical \ / \ Lwater}$$

where units for k_d are [L.kg^{-1}]

The linear portion of sorption isotherm can be expressed as:

$$r = k_d c$$

where r is the mass of chemical sorbed per mass of particulate matter [mg.kg^{-1}]

c is the mass of dissolved chemical in soil water [mg.L^{-1}]

k_d is a function of the hydrophobic character of the organic compound and the amount of organic matter present in the soil (Karickhoff et al, 1979; Schwarzenbach and Westall, 1981). A plot of k_d versus organic content phase for a variety of soils proved to be near-linear and passing close to the origin:

$$K_d = K_{oc} f_{oc}$$

where K_{oc} is the organic carbon partition coefficient defined as:

$$k_{oc} = \frac{[mg]chemical \ / [kg]organiccarbon}{[mg]chemical \ / [L]water} \ [L/kg]$$

f_{oc} is the fraction of organic carbon within the soil matrix (mass/mass) and must be measured for a particular soil

This formulation provides a means of characterizing adsorption of organic compounds independently under site-specific soil conditions. For a given compound, it also reduces the coefficient of variation of K_{oc} significantly between soils compared to the variation of K_d.

Sorption partition coefficients are relatively invariant for natural sorbents, and K_{oc} can be estimated from other physical properties of pollutants such as aqueous solubility or octanol/water partition coefficients. Because data on octanol-water partitioning coefficients are more readily available, several investigators (reviewed by Lyman et al, 1982) correlated K_{oc} to K_{ow} defined as:

$$k_{ow} = \frac{[mg] \, chemical / [L] \, octanol}{[mg] \, chemical / [L] \, water} \quad \text{dimensionless}$$

Many relations are available in the literature for different classes of organic compounds to predict k_{oc} function of k_{ow} (Schwarzenbach and Westall, 1981; Lyman et al., 1982).

Karickhoff, 1981 suggested the following relationship for various organics:

$$k_{oc} = 0.411 f_{oc}$$

where 0.411 has the dimension of [L/kg]

This relation must be used with caution when f_{oc} is less than 0.01 and especially less than 0.001. Otherwise, sorption of organic compounds on non-organic solids (clay and mineral surfaces) can become significant. Also, the linear isotherm model is valid only if the solute concentration remains below one half of the solubility limit of the compound (Mackay, 1991).

2.2.2.3 FACTORS AFFECTING SORPTION

Soil properties

Clay composition and exchange capacity. In practical terms, for all chemicals the adsorption reaction will be influenced since clays usually carry a net negative charge on their surfaces. Therefore, the strongest influence is exerted on compounds carrying a permanent positive charge, and also on chemicals ionizing in water. In soils with a high cation-exchange capacity, inorganic cations such as calcium, magnesium, and potassium, as well as positively charged trace metals such as cadmium are strongly adsorbed. However, because of the non-polar nature of many organic chemicals and of the large preponderance of organic matter surfaces, there is usually no correlation observed between adsorption and percentage clay unless the compound is permanently charged (Hern and Melancon, 1986).

Organic matter content. A positive linear relationship between soil organic matter content and adsorption of organic chemicals has been observed by Hamaker and Thompson, 1972. However, as the soil organic matter is poorly characterized, no exact relationship had been established between its structure and its adsorbing properties. As the adsorption of organic chemicals varies greatly according to the nature of organic matter, it is likely that the adsorption capacity for a certain surface layer of soil will vary for a given total organic matter content depending on the state of residue decomposition. The correlation coefficient is likely to be highest when the organic matter content is large, but the correlation coefficient may still be significant even in soils with an organic carbon content as low as 0.1 percent (Lyman, 1982).

Soil water content. The adsorption is influenced by the soil water content in the two following ways: first, changes in water contents involve changes in solute pathways, and the accessibility of the solute to the adsorption sites is increased /

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decreased. Second, variations in water content produce modifications in the hydrolysis of the clay lattice, affecting, in this way, physical-chemical properties of the adsorbent. However, the influence of soil water content on adsorption becomes significant only in extremely dry soils when solute adsorption increases dramatically due to the removal of water molecules from soil sorbent surfaces. There is evidence that this effect is reversible when the soil rewets (Hern and Melancon, 1986).

Bulk density. By increasing soil bulk density, the density of adsorption sites per unit volume will increase, with direct influence on increasing the adsorption capacity of soil. However, the effect of increasing bulk density on adsorption refers to compressing a given soil volume. The correlation between adsorption and bulk density will be small because clay and organic soils have lower bulk density than coarser soils which are low in organic matter (Hern and Melancon, 1986).

Chemical properties

The electronic structure of solute molecules is extremely important in adsorption, because the mechanisms of binding to solid surfaces are strongly influenced. For example, between permanently − charged molecules and negatively - charged mineral surfaces, a strong ion exchange mechanism will be involved. On the other hand, neutral non-polar molecules may bind to solid surfaces only by the van der Waals interactions.

Water solubility. It is straightforward to think of a relationship between adsorption and solubility since the solute molecules compete with water for the adsorption sites. Although this kind of relationship has not been established for all chemicals, for certain classes of compounds the correlation appears to be strong enough to provide useful regression equations between solubility and adsorption. In this sense, Kenaga and Goring (1980) studied experimental data

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from 170 chemicals and obtained regression coefficients between water solubility and organic carbon partition coefficients with a significance below the 1% level.

Environmental properties

Soil temperature variations influence solute-surface and water-solute interactions, and the balance between these processes determines the direction of temperature dependence. Although some compounds may increase their adsorption as temperature increases, the majority decrease (Lyman, 1982). As a general rule, the effect of temperature on adsorption equilibrium is a direct indication of the strength of adsorption so that the weaker the bond, the less the influence of temperature (Hamaker and Thompson, 1972).

2.3 MECHANISMS OF CHEMICAL LOSS

Chemicals spilled on a soil profile may leave that area by one of the following pathways. The first pathway, known as *leaching,* refers to the downward movement of dissolved chemical principally by mass flow. *Volatilization* represents another pathway that refers to the loss of chemical vapour to the atmosphere through the soil surface. The final loss pathway is *degradation,* which comprises biological or chemical transformations of a substance into a form distinct from that of the chemical prior to transformation. While transport processes specify the vehicles for chemical movement, and sorption determines the relative importance of dissolved versus sorbed phase transport, transformation and degradation processes ultimately determine whether a chemical will persist long enough in the soil environment to be of concern.

2.3.1 TRANSFORMATION PROCESSES

The transformation processes represent those chemical and biological mechanisms that encompass the "fate" of a chemical and determine its persistence in the soil. They lead to structural changes in a chemical as a result of chemical reactions that transform a parent compound into various metabolites or daughter products, possibly with greater environmental concern because of their different mobility, persistence, or toxicity characteristics. Depending on the role of microorganisms, these processes can be categorized into *biological* and *non-biological transformations.*

Biological transformations are the result of the metabolic activity of microorganisms, which transform chemicals through the action of certain enzymes catalyzing chemical reactions. Generally, a certain group of chemicals is degraded only by a select group of organisms. Biodegradation refers to the complete conversion of a contaminant to mineralized end products through microbial metabolism.

Non-biological transformations can be classified into chemical and photochemical transformations depending on the role of light. In general, the transformation products of non-biological and biological processes may be similar and encompass a wide variety of specific characteristics of chemical reactions. In general, the rates of transformation processes are faster for surface processes than those that happen in the subsurface, and even they depend on the individual chemical, soil, and environmental characteristics. These rates are also changed when chemical leaching is superimposed. Therefore, a soil-incorporated or buried chemical would degrade at a slower rate than if it were surface applied, in this way posing a greater potential for leaching to groundwater. For non-persistent chemicals applied on the surface, the faster the chemical moves to the subsurface zones by soil-water movement, the greater the

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potential for reaching groundwater because of the slower decay in the subsurface soil.

2.3.1.1 FACTORS INFLUENCING TRANSFORMATION PROCESSES

The biodegradation of a chemical depends on factors affecting substrate availability, the nature of microbial population (size, composition, and activity), and those directly controlling the degradation rate (temperature). Most of these factors are highly interrelated. For example, pH may affect both the availability of a substrate and microbial composition. The overall effects on degradation depend on the extent of the inter-relationships among those factors. Even though some generalizations regarding the net effect of each factor can be made, the literature abounds in exceptions (Hern and Melancon, 1986).

The nonbiological transformations of a chemical depend on factors affecting the availability of reactants and the nature of the specific chemical in soil. Many of the factors affecting biological transformations may also affect nonbiological processes. Furthermore, factors affecting sorption can be expected to influence transformation processes.

Microbial and chemical concentrations are those parameters commonly incorporated into mathematical expressions describing transformation rates. It is axiomatic that an increase in the microbial population will increase the rate of biotransformation. The rate of chemical transformation should also increase with increasing chemical concentration unless the chemical is toxic.

Temperature. For nonbiological transformations, reaction's rates are increased with increases in temperature. For biotransformation, small increases in temperature cause increases in rates over the temperature range tolerated by microorganisms. Species composition and chemical availability are also affected by temperature. The temperature dependence of rate constants has been

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incorporated into empirical relationships or into some equations such as the Arrhenius equation.

Empirical factors were introduced to correlate temperature effects on rate constants for specific reactions (Grady and Lim, 1980):

$$k_2 = k_1 \theta^{(T_2 - T_1)}$$

where k_1 is the rate constant at temperature T_1

$\quad$ k_2 is the rate constant at T_2

$\quad$ θ is an empirical factor which depends on temperature

Rate data have also been correlated using Arrhenius equation:

$$k = A \exp\left(-E/_{RT}\right)$$

where k is the reaction rate constant

A is a pre-exponential constant

R is the gas constant

E is the activation energy (a constant)

T is absolute temperature

Even though the Arrhenius equation may be useful, it is applicable only to single rate chemical reactions and not to multi-steps reactions common in microbial systems.

Water content. As water is the vehicle carrying the chemical to the attached microorganisms and it is also essential for microbial growth, it is expected that moisture content would affect the rates of chemical transformation. At the same time, an oversupply of water can reduce gas exchange and limit oxygen whose diffusion rate is slow in water. If oxygen is depleted by microbial metabolism, an anaerobic environment will be created. An optimum level for aerobic organisms is about 50-75% of the soil moisture-holding capacity (Alexander, 1977). The moisture content affects chemical concentration since it affects

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sorption. Decreasing moisture causes increased sorption of chemicals which may then affect the degradation rate. Increased moisture could result in lower chemical concentrations in the aqueous phase and decreased biotransformation rates. Increased moisture could also dilute any potentially toxic chemical and thereby could possibly increase its biotransformation rate (Hern and Melancon, 1986).

Organic carbon content. Microbial concentrations are often correlated with soil organic carbon content. Organic carbon and associated nutrients represent the major part of microbial food. The population size of a microbial community has been directly related to organic matter content (Alexander, 1977). Additions of supplemental carbon resulted in both increased and decreased rates of biodegradation. An increased rate could be explained by increasing in microbial activity. The decreased rate may be the result of the more facile use of added carbon instead of the specific chemical.

2.3.1.2 MATHEMATICAL CONCEPTUALIZATION OF BIODEGRADATION

The mathematical conceptualization of biodegradation is frequently (Bedient et al, 1999) based on a simplified approach, which considers all processes together given the difficulty to distinguish between biological and non-biological transformations. Such models reduce the complexity of transformation of a chemical to a single first-order degradative process. Due to the concurrent abiotic and biological processes leading to chemical loss, separate biotransformation and non-biological transformation rate coefficients are hard to evaluate under field conditions.

It is common to express the biological breakdown of a mass of chemical as a first-order reaction (Jury and Fluhler, 1992; Bedient, 1999). This assumes that the disappearance of a compound occurs at a rate predicted by a first-order rate law. In soil systems, the treatment of biodegradation as a first-order

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degradation process leads to the simplification of data analysis since only chemical concentrations have to be measured. In principle, first-order rate constants can be obtained from batch experiments from the slope of the relationship:

$$\ln\left(\frac{S}{S_0}\right) = -K_1 t$$

where S is the substrate concentration at time t

S_0 is the initial substrate concentration

K_1 is the first-order rate constant

In addition, substrate half-life $t_{1/2}$ is easily related to the first order rate constant by (Hern and Melancon, 1986; Mackay, 1991):

$$k_1 = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}}$$

This approach is frequently taken even if the time dependence of chemical attenuation is more complex (Hern and Melancon, 1986).

LIMITATIONS OF THE DEGRADATION-RATE APPROACH

Measurement limitations

Abiotic vs. biotic processes

Dissemination between biological transformations and abiotic processes is difficult without carefully controlled experiments. In the absence of microorganisms or their enzymes, chemicals may undergo various transformations such as hydrolysis, oxidation, and reduction, their products being often identical to those of biological reactions.

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Microbial concentrations

Biomass and microbial numbers may be required in order to apply a certain degradation rate expression. Unfortunately, these parameters are not always well correlated with the observed degradation rates. The causes for this disagreement often go beyond imprecise or inappropriate methodology. Usually, the total microbial population does not degrade the chemical and just a fraction is responsible, meaning that only the "active" population should be measured. Furthermore, the metabolic microbial activity can be fundamentally modified as a result of environmental changes.

Model limitations

Specificity of constants

Experimental conditions (especially temperature, moisture content, soil properties, nutrient, oxygen, or chemical concentrations) have to be similar for field and laboratory measurements of rate constants to be comparable. In general, transformation rates under field conditions are greater than those determined by laboratory incubation due to the concurrent processes occurring in the field. In particular, first-order constants are more site-specific than second-order constants because microbial activity is not explicitly considered when first-order constants are determined (Boethling and Alexander, 1979).

Concentration dependence of constants

Degradation constants are assumed to be independent of concentration, an assumption that could be false. For example, Boethling and Alexander (1979) have shown that the constants determined at high concentrations may not be consistent with the observed degradation rates at low chemical concentrations.

Acclimation

Rate constants depend on the degree of acclimation of the microbial population exposed to a chemical, but in field conditions microbial populations may not be

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exposed long enough for acclimation to occur. Therefore, there may be a discrepancy between experimental degradation rates and those predicted from constants in acclimated conditions (Hern and Melancon, 1986).

2.3.2 VOLATILIZATION

Volatilization is generally defined as chemical loss in vapour form from soil and water surfaces to the atmosphere. It can be a significant loss mechanism resulting in reduced amounts of chemical in the soil otherwise susceptible to leaching and surface runoff. Chemical characteristics such as vapour pressure and Henry's law constant give clues about the significance of volatilization on the chemical distribution in the environment (Mackay, 1991). For buried and soil-incorporated chemicals, volatilization controls the extent to which the chemical will partition into a vapour phase, moving through the soil by vapour diffusion. Consequently, volatilization includes aspects of both chemical fate and transport. Even though the potential volatility of a chemical is related to its vapour pressure, the volatility rate from the soil depends on soil, atmospheric, and management factors.

As a general rule, chemicals with high Henry's constants are more volatile than those with low Henry's constant and are relatively independent of atmospheric conditions (Mackay, 1991). Those processes increasing vapour diffusion such as increased temperature and increased total concentration increase the amount of volatilization. Conversely, processes limiting vapour diffusion such as increased adsorption and water content will decrease the amount of volatilization.

The volatilization process from soil depends on the balance between two other processes: the flux of chemical from soil body to soil surface and the flux of chemical vapour from soil surface to atmosphere. Depending on the relative size of these phenomena, the chemical will accumulate or deplete at the surface layer. Soil and environmental parameters will influence volatility through their impact on these two processes.

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2.4 SPATIAL AND TEMPORAL VARIABILITY OF SOIL PROCESSES

A key aspect of the soil environment is its inherent variability in space and time. Spatial variability refers to changes in a measured value at a specified depth throughout the area of interest as well as changes with depth at a specific location. Temporal variability is the change in a value with time for any specific location in the field. In effect, we deal with a fully three-dimensional dynamic system resulting from the indigenous spatial variation of soil properties and impacted by the temporal variation of natural processes and human intervention. These variations are comprised of both intrinsic factors, such as natural variations in soil characteristics, and extrinsic factors, such as water and chemical applications. These variations have important implications for collection of field measurements, interpretation of field data, and modeling of soil system processes.

Spatial variations in chemical behaviour in soil systems are primarily a result of significant point-to-point changes in soil properties related to the origin structure, texture, composition, mineral content, and organic content. These properties have a direct impact on virtually all parameters that characterize chemical transport and on many of the parameters that characterize chemical fate processes.

Temporal variations

Temporal variations are also comprised of both intrinsic and extrinsic components. The major intrinsic factor is the natural variation of rainfall; although rainfall is also spatially variable, its temporal variation is the primary driving force behind the dynamic nature of the soil environment and the resulting movement of chemical. Other meteorological inputs, such as temperature, solar radiation, and wind are also highly time-variable and have significant impacts on chemical processes through their interdependent environmental conditions.

2.5 SOLUTE TRANSPORT MODELS. MATHEMATICAL FRAMEWORK

The movement of a contaminant in the vadose zone is an important hydrological problem. Physical, chemical, and biological phenomena in this zone often control the degree of contamination in the saturated zone. In reality, the vadose zone is much more complex and less understood compared to the saturated zone, and its measurement techniques are not as well developed. Due to the effect of capillary forces, nonlinear soil characteristics, and the numerous phases involved, flow and transport processes are very complex. A number of mathematical models have been developed to describe the multiphase flow and transport in the unsaturated zone, and the interrelationships between the vadose and saturated zones. These vary greatly in level of complexity and processes described. Several reviews of solute transport modeling have been written, such as those by Anderson and Woessner (1992), Zheng and Bennett (1995), Domenico and Schwartz (1998), offering a clear description of many transport mechanisms and deriving many of governing equations. However, regardless of the complexity of the model, there are some general concepts leading to theoretical formalisms based on which simpler or more complex models can be developed.

A model for chemical transport and transformation may be comprised of the following elements:

- mass conservation law for chemical species
- division of mass into appropriate phases with separate description
- flux law for each mobile phase
- interphase mass transfer laws to describe movement between phases
- reaction terms to describe the rate of appearance/disappearance of mass per unit volume from the system

Based on certain process assumptions, the above elements are described by model expressions combined into one or a system of chemical transport equations, which are used furthermore to calculate phase concentrations and fluxes as functions of space and time.

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2.5.1 GENERAL CONTINUITY EQUATION

Investigations of fate and transport of chemicals in unsaturated zones must inherently deal with a multiphase system consisting of water, air, and soil. The fundamental equation of pollutant transport is the conservation of mass equation. This law is applied to a chemical mass in an arbitrary volume of soil and summarizes in a mathematical expression all places where the considered chemical could move in the volume and all possible fates suffered. It states that *the rate of mass increase within a region is equal to the net mass flux into the region plus the increase in mass within the region due to biotic and abiotic processes:*

Rate of mass flow into volume considered
  - Rate of mass flow out of volume considered
    - Rate of increase of mass stored in volume considered
      - Rate of loss of mass in volume considered by reactions = 0

The mass increase term represents the total mass per bulk volume, including the mass in all of the separate phases. The most common phases into which a soil chemical is divided are: gaseous, dissolved, adsorbed, and nonaqueous phase liquid (NAPL). The space within a pore is filled by the sum of the fluids:

$$n = \theta_w + \theta_a + \theta_o$$

where n is porosity

θ_w is the volumetric water content

θ_a is the volumetric air content

θ_o is NAPL volumetric content

Individual chemical constituents partition themselves among the various phases according to thermodynamic equilibrium principles and mass transfer kinetic factors. The solute adsorbed to soil particles (*soil phase concentration*)

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is specified as the mass of chemical sorbed per mass of soil. For the general case, the constituent mass density or bulk concentration, m - the mass of constituent per bulk volume [mg/L] - may be represented as (Charbeneau, 2000):

$$m = \theta_w c_w + \theta_a c_a + \theta_o c_o + \rho_b c_s$$

where ρ_b is soil bulk density (mass of soil per unit bulk volume)

The general mass flux vector J is defined as the mass crossing a unit surface area per unit time in the direction normal to the surface. The symbol S^+ in the differential form of the continuity equation comprises different types of reactions such as radioactive decay, biodegradation of organic pollutants, precipitation and redox chemical reactions that may immobilize a pollutant, and others.

The differential form of the continuity equation is (Charbeneau, 2000):

$$\frac{\partial m}{\partial t} + div(J) = S^+$$

This is the most general form of the continuity equation and serves as a starting point for further investigations of the subsurface transport and fate of chemical constituents.

2.5.2 REPRESENTATIVE TYPES OF SOLUTE MOVEMENT IN A SOIL MATRIX

For classifying the kinds of solute behaviour and developing models valid at certain times, some representative types of solute movement through the soil are useful. Theoretical analysis of solute transport through media with random local water velocity variations conducted to two distinctive stages in the movement of the solute. In the first stage, the longitudinal dispersion coefficient will generally grow linearly with time or average distance from the source of solute injection. It follows the second stage when the longitudinal dispersion coefficient will reach a constant value in macroscopically homogenous media. These limiting cases are called the "near-field" and "far-field" dispersion behaviour or *zero-time* and *infinite-time models* (Butters and Jury, 1989).

2.5.2.1 ZERO-TIME MODEL OF SOLUTE DISPERSION

At time zero, as soon as a solute enters a porous medium, solute molecules move at different velocities in isolated water flow pathways called stream tubes through the wetted pore space. In this case, diffusion or small-scale transverse convection is neglected because the mixing has not begun yet (Jury and Fluhler, 1992).

Therefore, the solute convection along the mean direction of flow is described as parallel flow in different stream tubes. This approach is called the stochastic-convective model, all motion being convective but comprising a range of velocities along the direction of motion, and it is available when the convection time is much shorter than the mixing time (Jury and Fluhler, 1992). In such a framework, the solute flow is defined by averaging over the motion in different tubes, and the spreading along the flow direction reflects those parts of fluid body convected at slower or faster average velocities.

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2.5.2.2 INFINITE-TIME MODEL OF SOLUTE DISPERSION

The infinite-time model of solute dispersion is valid when the solute molecules spread by diffusion throughout zones of different water velocities. Therefore, the mean convective flow rate through the medium is the same for each molecule. When viewed in a reference frame moving at the mean convective velocity, the average motion of molecules is random or diffusion-like and the spreading of these molecules is due to the different amounts of time spent by a certain molecule in each stream tube. This approach is known as the convection-dispersion model where the overall solute movement is described as the sum of the mean drift motion and the random longitudinal spreading (Jury and Fluhler, 1992). It is approximately valid when the convective time is much greater than the mixing time.

2.5.3 PRINCIPAL CHEMICAL CHARACTERISTICS USED IN MODELING

An essential preliminary step in modeling the fate and transport of a chemical in the environment is to assign it to the appropriate category. The physicochemical properties generally used to determine chemicals persistence and transport are: aqueous solubility, air-water partition coefficient or Henry's Law coefficient, and octanol-water partition coefficient (Mackay, 1991; Pennington, 2001). These partition coefficients can be used to decide which media are relevant for the fate of chemicals with significant simplification of the model and without compromising the complexity of the problem. At the same time, the cut-off criteria established for these coefficients are essential to assign a chemical to the appropriate category for modeling porposes.

The aqueous solubility of a compound is defined as the solute concentration in equilibrium with the pure chemical phase. At environmental temperatures, the solubility of organic chemicals ranges from completely miscible to less than

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10^{-12} mol/L for hydrophobic chemicals. A number of databases are available and reviewed by Mackay et al. (1992-1997), Schwarzenbach et al. (1993), Howard and Meylan (1997). Aqueous solubilities depend strongly on temperature, generally increasing by a factor of 2 for each 25C increase in temperature; but they show weak temperature dependence for organic liquids. A solubility cut-off criterion of 10^{-6} (g/m^3) suggested by Mackay et al. (1996) is used to select soluble and miscible chemicals for modeling their fate once spilled into environment.

The air-water partition coefficient can be expressed as a dimensionless ratio of concentration or as Henry's constant defined as the ratio of vapour pressure and solubility. Each of these parameters is an indicator of chemical volatility from aqueous solution. These coefficients are determined both experimentally and by predictive methods that use molecular structure as input (Mackay et al., 1992-1997).

The model is applied only to almost environmentally involatile substances using the cut-off criterion of 10^{-5} for air-water partition coefficient based on substances classification diagram suggested by Mackay et al. (1996).

Octanol-water partition coefficient together with water solubility is essential in characterizing the behaviour of an organic chemical in the environment. Octanol was chosen because of its availability in pure form, spare solubility in water, and its carbon to oxygen ratio similar to lipids. It has widely been used as a model phase for living and non-living natural organic material. Octanol-water coefficient is a measure of the tendency of a chemical to partition out of water. It varies greatly from 0.1 to 10^7, this variation being primarily due to the variation in water solubility. Compilations of values of this coefficient and calculation methods have been prepared by Lyman et al. (1982). Howard and Meylan (1997) also reviewed the property estimation techniques and evaluated a number of computer programs now available to compute physico-chemical properties relevant to the environmental fate of a chemical.

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Partitioning of organic chemicals between water and solids in soils expressed in terms of *organic carbon partition coefficient* is well correlated with their partitioning to octanol. This could be explained because octanol is a good surrogate for the natural organic matter associated with soils. The Karickhoff relationship is used to determine the organic carbon partition coefficient based on the previous value of octanol-water partition coefficient. As this expression is validated for fraction of organic carbon $f_{OC} > 0.01$ and must be used with caution when f_{OC} less than this value and especially less than 0.001 (Mackay, 1991), values in the range [0.01; 0.05] are considered for f_{OC}. However, for some chemicals, there is information directly indicating the distribution coefficient, as it is the case of the chemical used to illustrate the algorithm.

Degradation half-lives

Persistence of a chemical in the environment is evaluated in terms of its susceptibility to degradation commonly expressed as a *degradation half-life*. The half-lives of chemicals in the environment depend not only on the chemical structure, but also on the nature of the environment, especially on the presence or absence of oxidising and reducing species, and the abundance of appropriate microorganisms. They differ from medium to medium and are dependent on temperature. An issue of debate in the scientific literature is whether it is preferable to assess chemicals on a single medium basis or on an overall persistence basis. Webster et al. (1998) who discussed in detail this aspect concluded that overall persistence is more appropriate.

Methods to assign half-lives to substances are on ongoing research. The methods try to relate structure to reactivity using sophisticated quantitative-structure activity relationships (QSARS). Even if all methods agree in deciding if a substance is rapidly degraded or persistent, the problems arise in assigning the half-lives from different environmental media because the variability and sometimes lack of measured environmental half-lives (Mackay et al., 2001). Furthermore, it is essential to decide on the relevance of the half-life in each individual medium on the overall persistence of the chemical in the

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environment. Many authors (Muller-Herold, 1996; Pennington, 2001) suggested that the overall persistence of a chemical is found between the highest and lowest medium-specific half-lives. Hence, the maximum feasible overall persistence corresponds to the maximum degradation half-life. The relevance of each degradation half-life is dependent on the relative magnitude of the half-lives across the environmental media, as well as on a chemical's mass distribution. Based on correlation studies (Boethling et al., 1995) and the analysis of available databases (Howard et al., 1991; Mackay et al., 1992-1997), the following cross-media trends in degradation half-lives are typical for many organic chemicals: h-l (air) < h-l (water) < h-l (soil). Since chemicals in soils are less bioavailable and shielded from photocatalytic degradation process, their degradation in soil is slower, so that their rates of removal from soils are controlled by intermedia transport to air and/or water. As this model applies to almost involatile substances, only h-l in soil and water are required.

When performing model calculations, internally consistent substance data are needed while taking advantage of all measured properties and exploiting the fundamental thermodynamic constraints to which they are subject. Therefore, values gathered from different databases and software to predict physical-chemical properties have to be confronted.

2.5.4 SPECIFIC MODELS FOR SOLUTE FLUX IN SOIL

Many models developed to simulate solute transport in the vadose zone are limited to simple 1-D conditions (Bresler, 1973; Biggar and Nielsen, 1976; van Genuchten, 1981; Amoozegar-Fard et al, 1982; Jury and Sposito, 1985; Gierke et al, 1990). Moreover, most of the models have been applied at the laboratory scale, so that translating information on chemical transport from lab to field scale is highly suspect. At the same time, the recent efforts to comprise spatial-temporal heterogeneity of parameters mostly influent on the mechanisms undergone by chemicals at field scale recognized the discouraging dimension of the problem.

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At the present time, there is a growing awareness that the nature of solute transport in the unsaturated zone should be analyzed from a 3-D perspective but, at the same time, these kinds of studies, which should supply the base from which theory may be developed, are very scarce. This makes it difficult to develop and validate model assumptions.

In general, the modeling approaches used for solute transport in the vadose zone may be divided in two categories: application of the convection-dispersion equation with either constant coefficients (deterministic) or random variable coefficients (stochastic) and transfer functions (Butters and Jury, 1989).

2.5.4.1 CONVECTION-DISPERSION REPRESENTATION

Convection-dispersion representation uses a constant average pore-water velocity and a constant dispersion coefficient to describe the area-averaged solute movement. These assumptions are justified when long-term impact effects are envisaged as suggested by some authors in the literature (Wierenga, 1977; Bresler and Dagan, 1981; Marshall, 2000).

Diffusion

Fick's laws describe mass transport by diffusion (Bedient et al, 1999; Charbeneau, 2000).

Fick's first law states that the diffusion mass flux is proportional to the concentration gradient:

$$J_{diff} = -D_m grad(c)$$

where J_{diff} is mass flux [ML^{-2}T^{-1}]

D_m is the molecular diffusion coefficient [L^{2}T^{-1}]

Fick's second law is the equation of conservation of mass for a fluid phase:

$$\frac{\partial c}{\partial t} = -\nabla J_{diff} = D_m \nabla^2 c$$

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The molecular diffusion coefficient is much larger for gases than for liquids. The water phase molecular diffusion coefficient for gases that dissolve is about 10^{-4} smaller than the air phase molecular diffusion coefficient (Lyman et al., 1982). Jury et al. (1983) recommend an average value of about $5x10^{-6} \frac{cm^2}{s}$ for the water phase molecular diffusion coefficient and a value of about $0.05 \frac{cm^2}{s}$ for the air phase molecular diffusion.

Diffusion in porous media

Fick's laws also describe diffusion through porous media. The difficulty in describing diffusion in porous media comes from the phenomenological relationship for an effective diffusive coefficient that depends on the pore structure and the saturation of the various existent phases.

Fick's first law for an unsaturated porous medium (Charbeneau, 2000):

$$J_{diff} = -\theta D_s grad(c)$$

where θ is the volumetric water content

D_s is the *effective diffusion coefficient in soil*

The diffusion coefficient in soil is smaller than the molecular diffusion coefficient of a fluid because the diffusing substance must follow a tortuous path through the porous medium.

The ratio $\frac{D_s}{D_m} = \tau$ is the tortuosity of the medium.

Substitution of Fick's first law with the expression of tortuosity gives:

$$\frac{\partial m}{\partial t} + \nabla(-\theta \tau D_m \nabla c) = 0$$

If θ, τ, and ρ_b are constant and if a local equilibrium is assumed, then:

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$$\frac{\partial c}{\partial t} = D_s \nabla^2 c$$ - Fick's second law written for diffusion in a porous medium

Convection-dispersion transport

Convection and diffusion describe the mass transport of solutes by bulk fluid movement due to fluid energy gradients and by mixing of chemical constituents due to concentration gradients and molecular collisions. It has been assumed that the porous medium is homogenous and isotropic and that the flow is steady-state. The flow is described by the average pore water velocity transporting the dissolved chemical by convection. Velocity variations within each pore channel and from one channel to another cause an additional mixing process – hydrodynamic dispersion. This phenomenon accounts for additional transport (spreading) caused by fluctuations in the velocity field.

For a conservative species, the process of convection and hydrodynamic dispersion (mechanical dispersion and diffusion) are modeled by the convection-dispersion equation (Bedient et al, 1999; Charbeneau, 2000):

$$\frac{\partial c}{\partial t} + v.grad(c) = div(D.grad(c))$$

where c is solute concentration[ML^{-3}]

      t is time [T]

      D is the combined mechanical dispersion and diffusion coefficient

        [$L^2 T^{-1}$]

      v is the average pore water velocity [LT^{-1}]

Solute transport and reactions can be modeled using a modified form of advection-dispersion equation including different terms for different reactions (physical, chemical, biological) considered for a certain simulation (Schnoor, 1996):

$$\frac{\partial c}{\partial t} + v.grad(c) = div(D.grad(c)) \pm \sum_{m=1}^{n} r_m$$

where r_m is reaction rate $[ML^{-3}T^{-1}]$

Different processes can be considered under the term for reactions, but usually only sorption and biodegradation processes are seen as the dominant mechanisms that alter contaminant concentrations.

Change in concentration = Advection + Dispersion − Sorption − Biodegradation

The sorption reactions in the vadose zone are most commonly modeled using the linear isotherm (Bedient et al, 1999):

$$S = k_d c$$

where S is the amount sorbed onto porous medium [M/M]

k_d is distribution coefficient $[L^3 M^{-1}]$

Biodegradation is usually modeled using the first-order decay of a solute (Jury and Fluhler, 1992; Bedient et al, 1999) and is generally represented in the transport equation by adding the term kc where:

k is the first-order degradation rate constant $[T^{-1}]$

Based on these assumptions, the equation for solute transport can be extended to:

$$\frac{\partial c}{\partial t} + v.grad(c) = div(D.grad(c)) - \frac{\partial S}{\partial t} \frac{\rho_s (1-\theta)}{\theta} - kc$$

where ρ_s is the solid density of the particles $[ML^{-3}]$

θ is the volumetric water content, dimensionless

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Taking time-derivative of both sides of the expression of S and using the bulk density of the porous medium instead of solid particle density, the transport equation will become:

$$\frac{\partial c}{\partial t} + v.grad(c) = div(D.grad(c)) - K_d \frac{\rho_b}{\theta} \frac{\partial c}{\partial t} - kc$$

Rearranging terms and defining the dimensionless retardation factor as:

$$R = 1 + \frac{K_d \rho_b}{\theta} = 1 + \frac{K_d \rho_s (1 - \theta)}{\theta}$$

which expresses the retardation of contaminant transport relative to the rate of non-sorbing species

Because this relation is based on the instantaneous equilibrium assumption, it may be interpreted that the sorbed solute spends 1/R as much time in the dissolved phase as an identical non-sorbing solute. This implies that it takes R times as long to travel a given distance as the non-sorbing one (Schnoor, 1996).

The following form for the transport equation is obtained:

$$\frac{\partial c}{\partial t} = -\frac{v}{R} grad(c) + \frac{1}{R} div(D.grad(c)) - \frac{k}{R} c$$

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2.5.4.2 MATHEMATICAL APPROACH FOR SPILLS

Mathematically, spills are represented as initial value problems. The initial distribution of chemical concentrations is specified, and the model determines how the concentration changes through time and space (Bedient et al, 1999; Charbeneau, 2000).

Consider the release of a mass M of volume V_0 centered at point $\bar{r}_0 = (x_0, y_0, z_0)$ at time t = 0, and containing a contaminant at concentration c_0. If the time period of the release is short compared to the time period of interest for transport, then the chemical release may be considered instantaneous (Charbeneau, 2000).

The bulk concentration of the chemical spilled is given by (Charbeneau, 2000):

$$m(\bar{r}, t) = M(t)\delta(\bar{r} - r_0)$$

where $\delta()$ is the Dirac delta function

The characteristic of this function is that for any function f(r):

$$\int f(r)\delta(r - r_0)dV = f(r_0)$$

so that in particular, $\int \delta(r - r_0)dV = 1$

One of the methods used to solve the transport equation in the case of spills is to use the Fourier method. The basic idea in Fourier analysis is to develop the solution in terms of waves of various frequencies and wave numbers (Charbeneau, 2000).

The general Fourier component is:

$$c \approx Ae^{i(\tilde{k}.\tilde{r} - \omega t)}$$

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where A is wave amplitude and $i = \sqrt{-1}$

k is the wave number vector: $\tilde{k} = (k_x, k_y, k_z)$

$\tilde{r}$ is position vector: $\tilde{r} = (x, y, z)$

ω is wave frequency

The dependency of ω on k called dispersion relation is obtained by substituting the general Fourier component into solute transport equation.

2.5.4.3 STOCHASTIC CONTINUUM MODEL

The modeling of solute transport is possible only if both local water flows and lateral mixing mechanisms are described in terms of measurable parameters. This kind of description is impossible at the pore scale because of its dependency on the unobservable soil structural features and local pore geometry. However, at larger scales, the local water flux can be calculated with a transport equation containing measurable parameters using a volume-averaged approach. With this approach, it is assumed that the solute has sufficient time to mix within the regions of different velocities comprised by the averaging volume. At field scales, local concentrations and transport parameters are assumed to be random functions oscillating around their mean values. Hence, the solute transport is described by statistically averaging the stochastic local transport model, so that the macroscopic model depends on the statistical properties of the random transport properties (Gelhar, 1986). However, in the unsaturated zone the water flux is much more difficult to measure than in saturated soil and also the mean soil properties can change significantly over short vertical distances. For these reasons, the formulation of stochastic continuum model is more difficult for unsaturated soil. Transport properties being strongly non-linear functions of the water content, stochastic model development has been restricted to limiting cases, which neglect most of the

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complexity of three-dimensional solute flow (Butters and Jury, 1989). Examples of near-field stochastic models for the vadose zone include the parallel soil column models of Dagan and Bresler (1979), Bresler and Dagan (1983), and the Monte Carlo simulation model of Amoozegar-Fard et al. (1982). The common feature of these models is the requirement for the lateral distribution of the vertical solute velocities determined experimentally. The main problem with these models using an inferred velocity distribution which needs clarification is to establish which measurements and model approximations best represent the spatial structure of unsaturated flow solute velocity over a wide range of soil moisture conditions (Butter and Jury, 1989).

2.5.4.4 TRANSFER FUNCTION MODEL REPRESENTATION

An alternative approach to estimate the solute velocity distribution via hydraulic properties of the soil and associated model approximations is to measure it directly as suggested by Jury, 1982 using the proposed transfer function model. The transfer function model is an application of superposition and mass balance principles to a finite soil volume bounded by an entry and an exit surfaces (Jury et al., 1986). Inside the considered volume, the transport mechanisms are characterized by a preliminary experiment in which a pulse of solute of a certain mass is added at zero-time and the mass leaving the exit surface is recorded as a function of time. The travel time for the solute to reach a certain depth is treated as a random variable and the normalized area-averaged concentration distribution defines a probability distribution function (pdf) whose shape may often be parameterized with a lognormal distribution (Jury, 1982; White et al., 1986).

This approach has some advantages and disadvantages over the differential equation models. Its advantage consists of not requiring a process model assumption due to the fact that transfer characteristics of the medium are completely described by travel time pdf that is valid for all linear transport models. However, this representation predicts the outflow concentrations only at

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steady-state conditions, so that it cannot be used in transitory situations and also it cannot predict the concentrations at any other distance within or beyond the transport volume without incorporating some hypotheses about transport process characteristics (Jury and Fluhler, 1992).

2.5.5 FIELD STUDIES OF SOLUTE TRANSPORT IN VADOSE ZONE

There have been a limited number of experiments conducted in unsaturated field soils under natural field conditions even for inert, non-reactive solutes. In one large-scale field study, Biggar and Nielsen (1976) monitored solute movement with solution samplers and found that the apparent velocity of the solute peak was distributed lognormally. They also reported a good correspondence between the monitored velocity of the solute peak and the pore water velocity calculated as the ratio between water flux rate and the porosity. Van de Pol et al. (1977) reported the same lognormal distributions of local solute velocity and dispersion coefficients during a field study of chloride movement also monitored by solution samplers. In a field study monitoring the movement of a chloride pulse with vacuum solution samplers during a winter of erratic rainfall, Jury et al. (1982) found a high degree of skewness in solute breakthrough curves at individual sites and also reported a velocity coefficient of variation similar to that observed by Van de Pol (1977). Gelhar et al. (1985) presented a review of unsaturated zone solute transport studies stressing the importance of three-dimensional flow of water to interpret solute transport in heterogeneous field soils. The major limitations of most of the reported investigations consist of limitations in the scale of the field studies, which could lead to erroneous conclusions on the extent of the solute spreading when extrapolating to larger field scale and of limitations in the depths at which the solute is monitored. A study reported by Butters et al. (1989) was designed to expand the database for unsaturated zone solute transport and to model validation on a scale of practical interest for agricultural and waste management, expanding the solute transport monitoring to a depth of 25 m. In

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this one-dimensional experiment, they reported irregularities in the dispersion process.

However, an adequate understanding of solute transport and dispersion at large scale requires a three-dimensional examination of transport processes during transit through heterogeneous soil. At the same time, because of the complex relationship between solute velocity and soil properties in unsaturated soil, even in homogenous soil, the number of local property measurements to evaluate variations in solute velocity is extensive. This explains why this kind of field study is very scarce.

Considerable lateral and vertical variability observed in a tracer movement prompted McCord et al. (1988) to conclude that considerable anisotropy in hydraulic conductivity exists for unsaturated conditions. Stephens et al. (1988) observed significant variations in vertical solute velocities and significant lateral spreading. Kung (1990) also observed extreme variability in transport of a dye tracer through an unsaturated sandy soil. Vertical heterogeneity also introduces significant problems in understanding solute transport. A large range of solute velocities is encountered in the literature from an order of units to some tens of units (Bigger and Nielsen, 1976; Van de Pol et al., 1977; Gierke et al., 1990; Ellsworth and Jury, 1991; Worch, 2003). An underestimation or overestimation of the solute velocity could be explained by the fact that not all wetted pore space is active in transport or by preferential flow channels which are not observed by shallow solution samplers (Butters et al. 1989; Ellsworth et al. 1991).

Besides the increased number of required measurements, solute behaviour at the interface between layers could have a significant effect on large-scale behaviour by increasing lateral mixing or terminating preferential flow channels, both substantially affecting large-scale longitudinal dispersion (Ellsworth and Jury, 1991). In an attempt to monitor transverse and longitudinal dispersion during transport, a three-dimensional study was performed by Ellsworth et al. (1991) at the same field site used for the one-dimensional study by Butters et al. (1989). Results of this study revealed the erratic behaviour of

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the vertical plume clearly related to vertical heterogeneity since the lateral spreading was small and seemingly unaffected by depth (Ellsworth et al., 1991).

The reported observations of the field studies imply the necessity of studying the nature of solute transport in the unsaturated zone using a three-dimensional approach, which has to incorporate not only a horizontal distribution of local velocities, but also the influence of vertical variability in soil hydraulic properties on solute transport. However, the scarcity of three-dimensional field studies implies a lack of an experimental database, so that model assumptions and theory cannot be developed and validated.

This chapter was conceived as radiography of the concepts and frameworks conducive to the present understanding of the phenomena undergone by chemicals once spilled into soil environment. This step is considered as a prerequisite in developing an approach for chemical spills assessment given the complexity of interwoven phenomena and factors affecting them.

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CHAPTER 3 DEVELOPMENT OF AN ALGORITHM TO QUANTIFY THE CUMULATED IMPACT OF CHEMICAL SPILLS

In this chapter, an algorithm is proposed to assess the accumulated impact of chemical spills in an area of interest. The idea arose from the need to find a simple way of detecting the "hot spots" of chemical pollution in proximal conditions to real situations where many spills happen with different spatial-temporal patterns in a changing environment. The proposed algorithm has the advantage that it can be used with different models of increasing complexity to simulate the fate and transport of a single-spill event depending on the data available and the requirements of a given situation. Once a model is chosen for a spill, different scenarios can be developed with spills of different quantities and occurring with different frequencies in space and time. A scenario of pollution having been constructed, this algorithm can detect the level of pollution in any chosen point of a selected area, based on the spatial-temporal dynamics of the spills within and adjacent to this area. A plastic image could be that of numerous waves with different amplitudes and wave numbers propagating from different points in space and with certain temporal patterns and their overall effect at a distant point materializing in a new and different wave.

Furthermore, this algorithm has the power of prediction. As each scenario could correspond to a present real situation and each new simulated spill to a future event, a possible "alarming" level of pollution could be detected in advance, so that the time between "now" and that moment associated with potential serious pollution could be efficiently used to take action.

METHODOLOGY

This thesis sets up two distinct steps to accomplish its purpose. One step consists of the development of a model to simulate a single-spill event based on certain characteristics of the chemical and the environment where the spill occurs. Furthermore, this model is implemented into a general algorithm developed to assess the accumulated impact of multiple spills taking place with different spatial-temporal patterns in a chosen area and its vicinity.

The simulation of single-spill events is conceived to illustrate the utility of the proposed algorithm. Therefore, an idealized situation of a homogenous porous medium and steady-state conditions are considered. The advantage of the proposed algorithm is that it can be used with different models of varying complexities to simulate single-spill events and also the cumulative effects of spills of different chemicals with changing parameters under various environmental conditions can be assessed.

3.1 SPILL MODELING

3.1.1 INTRODUCTION AND GENERAL ASSUMPTIONS

In contamination episodes such as chemical spills, the understanding of how a chemical moves through unsaturated soil is essential. Many times in spill accidents, the only information available is the volume of fluid entering the soil. Without an understanding of the degree of lateral/vertical dispersion of the spill, it is impossible to make even a rough assessment of the potential impact of the spill on the system where the accident happened. Moreover, in the absence of a preliminary means for making this assessment, expensive and time-consuming soil concentration measurements have to be done over a dense grid in the soil to characterize the impact of the spill.

At the present time, there is an increasingly recognized problem of chemical spills and also of the need for an adequate description of chemical

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movement through the unsaturated soil as a requirement for a sound approach to chemical spill problem. However, there is not yet an approach that incorporates a validated 3-D model capable of accurate prediction of spill migration and also a procedure to take into account the spatial-temporal pattern of spill accidents into real-world proximity conditions.

In these circumstances, a rational framework would be one capable of incorporating models of increasing complexity once new advancements in the field are taken. Simultaneously, this framework should be capable of simulating real-world situations where spills occur in open environmental systems, which are "immersed" in a background "noise" of pollution and are affected by the spatial-temporal adjacency of other pollution events. Based on this, the algorithm proposed in this thesis 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 method used to develop the mathematical expression describing the spatial-temporal evolution of the concentration for any spill event consists of the following steps. First, the type of that chemical to which the model is applied was chosen together with the environmental and chemical parameters influencing the fate and transport of the chemical once spilled into porous medium. This was done by an extensive review of literature related to contaminant modeling. The category of chemicals chosen to be modelled was that of involatile chemicals, miscible with water. Once processes and parameters describing the fate and transport of this type of chemicals were established, the next step was to describe mathematically each of these processes based on the literature review. Finally, the equation comprising these processes was developed and it was solved based on the mathematics used in the literature for the problem of instantaneous poin-release.

The proposed model considers the case of involatile and soluble substances spilled into a homogenous soil profile lying in the horizontal (x, y) plane and beneath the surface considered with $z = 0$ and z positive downwards.

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Steady-state conditions are assumed with water and dissolved chemicals moving in a downward vertical direction at a constant pore-water velocity. Chemicals can be furthermore sorbed by the soil or biodegraded by microorganisms. The next sub-section describes in detail the mathematical approach used to conceptualize every spill event based on certain solute mechanisms and using the theory of initial value problems and Fourier analysis.

3.1.2 MATHEMATICAL FRAMEWORK AND EQUATIONS

In order to develop the concentration function describing the spatial-temporal evolution of any spill event, it was considered that a chemical mass M with volume V_0 and concentration c_0 was released at the initial time t = 0 at the point $\tilde{r_0} = (x_0, y_0, 0)$.

The general continuity equation was adapted for an involatile substance:

$$m = (\theta + \rho_b k_d)c$$

where   m is bulk concentration

c is the aqueous concentration

θ is the volumetric water content

ρ_b is soil bulk density

k_d is distribution coefficient

and written in terms of retardation factor R (defined in the literature review) becomes: $m = \theta R c$

Each of these parameters was described in details in the previous chapter.

Based on the mathematical expression of the bulk concentration used in general to describe an instantaneous point release (Charbeneau, 2000) and on the characteristic of Dirac function mentioned in literature review, it can be write:

$$M = c_0 V_0 = \iiint m(\tilde{r_0}, 0) dV = (\theta + \rho_b k_d) \iiint c(\tilde{r_0}, 0) dV = \theta R \iiint c(\tilde{r_0}, 0) dV$$

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Combining this equation with equation for the bulk concentration (Charbeneau, 2000):

$$m(\tilde{r}, t) = M(t)\delta(\tilde{r} - r_0)$$

the initial condition on c can be deduced:

$$c(\tilde{r}_0, 0) = \frac{M}{\theta R}\delta(\tilde{r}_0) \quad (1)$$

Based on literature review, the following processes were considered for modeling: advection, diffusion and dispersion, sorption on solids particles of soils, and biodegradation. The mathematical expressions of each of the considered processes were developed using the general approach described in the previous chapter.

This way, the process of advection for a substance partially sorbing on solid phases in an unsaturated porous medium is described as proportional to the concentration gradient and a retarded velocity. For diffusion and dispersion processes, the Fickian approach was used with an effective hydrodynamic dispersion coefficient, which lump together these two processes. Since, in the field, the effects of diffusion are negligible, diffusive term is neglected further in this model, and the effective hydrodynamic coefficient is considered as a symmetric tensor composed of dispersivity coefficients. The sorption is modelled based on the assumption of instantaneous adsorption or exchange and simple linearity between solute concentration and solid phases of soil. Biodegradation is described by first-order decay in liquid and adsorbed phases. Based on these assumptions, the general solute transport equation described in literature review becomes:

$$\frac{\partial c}{\partial t} + v'\frac{\partial c}{\partial z} + \lambda c = D_x'\frac{\partial^2 c}{\partial x^2} + D_y'\frac{\partial^2 c}{\partial y^2} + D_z'\frac{\partial^2 c}{\partial z^2}$$

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$v' = \dfrac{v}{R}$ is retarded velocity

v is the average pore-water velocity

λ is defined as: $\lambda = \dfrac{K}{R}$ where K is overall first-order degradation rate (T^{-1})

Since the model is applied to involatile chemicals, only degradations in soil and water are considered: $K = \dfrac{K_w + K_s \rho_b K_d / \theta}{R}$ (Bedient et al, 1999)

where K_w is first-order degradation rate in water (T^{-1})

K_s is first-order degradation rate in soil (T^{-1})

The mathematical expression of K, defined as $K = \dfrac{\ln 2}{t_{1/2}}$ with $t_{1/2}$ being half-lif

in the corresponding medium, was adopted from literature of biodegradation processes (Hern and Melancon, 1986).

ρ_b is soil bulk density (ML^{-3})

K_d is distribution coefficient $(L^3 M^{-1})$

θ is volumetric water content (L^3/L^3)

R is retardation factor (dimensionless) whose expression was reviewed in the previous chapter:

$R = 1 + \dfrac{k_d \rho_b}{\theta}$ equivalent to $\theta + \rho_b k_d = \theta . R$

D_i' is retarded i-dispersion coefficient:

$D_i' = \dfrac{D_i}{R}$ $(L^2 T^{-1})$ with i = x, y, z

$D_i = \alpha_i v$ is hydrodynamic coefficient

The expression of hydrodynamic coefficient was deduced from the general expression described in literature review and approximating the diffusion factor with zero based on the initial assumptions of this model.

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The solute transport equation was solved using the Fourier method. The general Fourier component described in previous chapter was substituted into transport equation. This way, the following expression for wave frequency as a function of wave number vector was obtained:

$$\omega = k_z v' + i\lambda + i(D_x' k_x^2 + D_y' k_y^2 + D_z' k_z^2)$$

where ω is wave frequency

k is the wave number vector: $\tilde{k} = (k_x, k_y, k_z)$

$i = \sqrt{-1}$

(x, y, z) are the components of position vector

The expression of ω is further substituted into the general Fourier component to eliminate wave frequency, so that the following expression for concentration was obtained:

$$c \approx A e^{i[k_z(z - v't) + k_y y + k_x x]} . e^{-[D_x' k_x^2 + D_y' k_y^2 + D_z' k_z^2 + \lambda]t}$$

where A is wave amplitude

Analysing this expression for the general Fourier component, it can be observed that the general component decays exponentially at a rate corresponding to λ, regardless of its other characteristics. One other observation is that physical dispersion results in a "decay" with the shorter wavelength (larger k) dissipating first. This process results in a smoothing of the concentration distribution over time, because the "lumps" made up of small waves decay rapidly, leaving the smoother distribution made up of longer waves.

The general solution comes from the superposition of waves with different wave numbers (wavelength). Considering the amplitude as a function of wavelength, the general solution for 1D case:

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$$c(z,t) = \int_{-\infty}^{\infty} A(k)e^{ik_z(z-v't)-(D_z'k_z^2+\lambda)t}dk$$

the integral being over all wave numb .s

The initial conditions must satisfy:

$$c(z,0) = \int_{-\infty}^{\infty} A(k)e^{ikz}dz$$

which shows that c(z,0) is the Fourier transform of A(k) called the spectrum of c(z,0)

The Fourier inversion theorem states that the function A(k) is given by:

$$A(k) = \frac{1}{2\pi}\int_{-\infty}^{\infty} c(\xi,0)e^{-ik\xi}d\xi$$

Substituting the expression for A into the general solution, it is obtained:

$$c(z,t) = \int_{-\infty}^{\infty}(\frac{1}{2\pi}\int_{-\infty}^{\infty} c(\xi,0)e^{-ik\xi}d\xi)e^{ik_z(z-v't)-(D_z'k_z^2+\lambda)t}dk$$

Changing the order of integration and completing the squares of the argument as a quadratic in k, this process ultimately gives:

$$c(z,t) = \int_{-\infty}^{\infty} c(\xi,0)G(z,t/\xi,0)d\xi .e^{-\lambda t}$$

where $G(z,t/\xi,0) = \dfrac{1}{\sqrt{4\pi D_z't}}\exp(-\dfrac{(z-\xi-v't)^2}{\sqrt{4D_z't}})$

is called Green's function and contribues to the solution at point z and time t due to the initial unit mass at point $z = \xi$

For 3D case, the general Fourier component can be written as the product of terms involving exponentials with x, y, and z separately.

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The general solution to 3D problem may be written:

$$c(x, y, z, t) = \iiint c(\zeta, \eta, \xi, 0) G_x G_y G_z d\xi d\eta d\zeta . e^{-\lambda t}$$

where G_x, G_y, G_z are the individual Green's functions, the y and x components being defined by analogy with z- component:

$$G(x, t / \zeta, 0) = \frac{1}{\sqrt{4\pi D_x' t}} \exp(-\frac{(x-\zeta)^2}{\sqrt{4 D_x' t}})$$

$$G_y(y, t / \eta, 0) = \frac{1}{\sqrt{4\pi D_y' t}} \exp(-\frac{(y-\eta)^2}{\sqrt{4 D_y' t}})$$

More concisely, with the notation

$$G(x, y, z, t / \zeta, \eta, \xi, 0) = G_x G_y G_z ,$$

the general solution can be written:

$$c(\tilde{r}, t) = \int_{-\infty}^{\infty} c(\tilde{r_0}, 0) G(\tilde{r}, t / \tilde{r_0}, 0) d\,\tilde{r_0} . e^{-\lambda t} \qquad (2)$$

Combining equations (1) and (2), the general solution for solute transport equation is obtained:

$$c(x, y, z, t) = \frac{M/(\theta R) \exp[-\frac{(z-v't)^2}{4 D_z' t} - \frac{(x-x_0)^2}{4 D_x' t} - \frac{(y-y_0)^2}{4 D_y' t}]}{\left(64\pi^3 D_x' D_y' D_z' t^3\right)^{1/2}} . e^{-\lambda t}$$

with initial condition that a mass M is released at t=0 at the point $\tilde{r_0} = (x_0, y_0, 0)$

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This way, the concentration of a chemical spilled initially with a mass M on the soil surface at the point (x_0, y_0) in the horizontal plan, can be described as a 4D (3D-space plus time dimension) function 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

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

3.1.3 MODEL PARAMETERS

Soil parameters

Although a substantial amount of research was conducted to describe the transport and transformations of chemicals in soil using measurable parameters, the majority of these studies have been performed in the laboratory. At the same time, there are significant differences between laboratory and field environments and the extension from the laboratory scale to the field should consider the degree of heterogeneity in field environments. In contrast with the abundance of data from laboratory studies, there is little quantitative information available for deciphering the mechanisms undergone by chemicals at the field scale. However, based on these few studies it can be seen that there are fundamental differences between transport characteristics at laboratory and field scales (Jury and Fluhler, 1992). Furthermore, water and solute transport and retention properties can vary significantly under field conditions both in lateral and vertical directions due to pronounced spatial heterogeneity (Jury, 1985). Because of the scarcity of field studies examining the three-dimensional nature of solute transport in an unsaturated zone, there is a lack of experimental

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database from which model assumptions and theory may be developed or validated.

The proposed model was conceived to illustrate how the algorithm can be used to assess the cumulative effects of different spatial-temporal patterns of spills. Any kind of models with varying degrees of complexity can be implemented into this algorithm. Hence, the simplified assumption of a homogenous porous medium under quasi-steady-state conditions is the straightforward consequence of the objectives of this thesis. Based on this assumption, the *flow variables* (v, θ) are approximately constant. This implies that the retardation factor and hydrodynamic coefficients could be considered constant.

There are two situations which are best described by quasi-steady-state conditions. By analogy to heat propagation into a semi-infinite medium, with the surface temperature varying sinusoidally around a mean, for rainfall rates changing rapidly around the mean, the variations will damp out quickly along the soil profile, implying that velocity will be constant at most of the depths. The second situation is that of rainfall rates changing slowly, each rainfall rate persisting long enough so that the velocity of the front propagates deeply into the soil profile. For both cases there is no difference between variable- rainfall case and constant-flux case. Thus, the use of a constant average pore water velocity will not result in significant error in estimating the transport of chemical spilled (Marshall et al., 2000).

This model uses for *pore-water velocity* an average value of 7.5 cm/d suggested by Ellsworth and Jury (1991) in their three-dimensional field study.

The range for *volumetric water content* is usually [0.2; 0.6] (cm^3/cm^3), guided by the range of porosity values for different types of soils (Hern and Melancon, 1986). An average value of 0.5 is considered and the effects of other possible values are tested in the sensitivity analysis.

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The range for *soil bulk density* is taken as [1.2; 1.6] (g/cm^3) based on the relationship between porosity, bulk and soil particle density; and on the values recommended by literature for soil particle density between 2.65 (g/cm^3) for clays to 2.75 g/cm^3) for sands (Hern and Melancon, 1986). In general, an average value of 1.5 (g/cm^3) is considered (Mackay, 1991).

Hydrodynamic dispersion is considered the predominant source of dispersion. Based on this assumption, dispersivity is velocity-invariant and independent on solute size. Thus, for a given system the same values of dispersivity and D should apply to all solutes and dispersivity measured for a tracer can be used for other solutes (Brusseau, 1993).

Dispersivity

The value of the average dispersivity was chosen as 10 cm based on the previously mentioned 3-D study of Ellsworth and Jury (1991). In (x,y) plane, dispersivity was taken as 10% of that on the z-axis (Bedient et al., 1999).

Chemical parameters

The simulation is illustrated for LAS (Linear Alkylbenzene Sulfonates). LAS are an involatile mixture of anionic surfactants widely used in laundry and cleaning products and with high impact on soils. It is estimated that for southern Ontario LAS emissions to soil are approximately 94% of total (Mackay et al, 1996). This chemical fits into the category of chemicals for which this model was conceived and also its impact on soil is of great interest because of its large use and great potential emissions to soil. To assign the chemical to a certain category, the cut-off criteria presented in literature review as the main chemical characteristics used in modeling were used.

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Degradation half-lives and distribution coefficient

For LAS, being a mixture, average values for half-lives in soil and water, and an average values for distribution coefficient were chosen based on different literature sources (Hoiysh et al., 1986; Larson, 1990; Larson et al., 1993). The selected input data are displayed in the developed algorithm, which is described ulterior.

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3.1.4 IMPLEMENTATION OF CONCENTRATION FUNCTION

The function of concentration was conceived as a four-dimensional object, having as input data the soil and chemical parameters described in the previous section. This four-dimensional representation has the advantage that it facilitates the development of spatial-temporal analysis models, which concentrates the relevant information in a single object.

Figure 6 represents the spatial distribution (3D) of the concentration function for single-spill event. For each spill simulated, the maximum area and depth impacted by a certain amount of chemical are calculated and displayed. The implementation of concentration function in Matlab is included in Appendix 1.
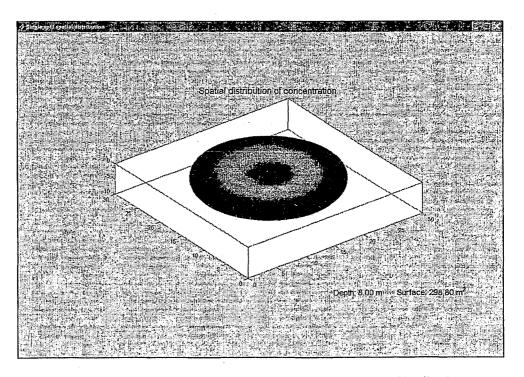

Figure 6 Concentration function: single-spill spatial distribution

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Figure 7 presents the spatial-temporal evolution of a single spill. This 4D representation offers the possibility of following and visualizing the history of a spill event simultaneously in time and space.
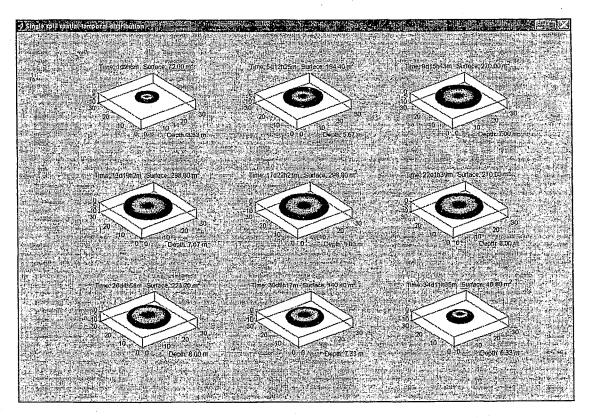

Figure 7 Concentration function: single-spill spatial-temporal evolution

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3.2 ALGORITHM DEVELOPMENT

To assess the accumulated effects of chemical spills based on their spatial-temporal dynamics, an algorithm is proposed consisting of the following steps.

3.2.1 DATABASE

DATA SOURCE

Chemical spill data from 1988 to 2000 are compiled from the Ontario Spill Action Centre (SAC) spill database. 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. Reported occurrences are recorded on a computerized database management system called Occurrence Report Information System (ORIS), which facilitates tracking of occurrence status and preparation of data summaries. Furthermore, the locations of spills are identified by geocoding the addresses where spills were reported to have occurred. A spatial analysis of chemical spills in southern Ontario has been undertaken based on this information (Li, 2003).
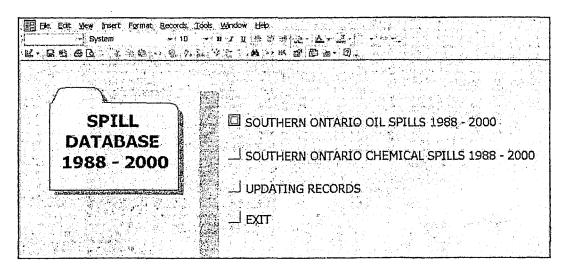

Figure 3 Data source: Spills Database based on Ontario Spill Action Centre data

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However, the database used for the above-mentioned analysis does not contain specific information on the chemicals spilled, most of the recorded chemicals being assigned a general description such as: wax, liquid, paint. This represents a serious impediment for a more realistic assessment of spill effects incorporating both chemical and environmental characteristics and also a temporal component.

DATABASE DESIGN

A new database is designed as a starting point to achieve the spatial-temporal dynamics of chemical spills in this study. It keeps the structure of the previous database, but it uses a set of specific events to simulate the cumulated impact of spills in a certain area.

The database consists of three related tables. One defines the chemical and soil parameters, another one defines the regions in Ontario with their geographical coordinates and holds the maps and the third one records the chemical spills characteristics. Figure 9, Figure 10, and Figure 11 present the data definitions and relations.

Field Name	Data Type	
ID Chemical	AutoNumber	
Name	Text	
Water_fraction_volume	Number	
distribution_coefficient	Number	l/kg
soil_bulk_density	Number	Kg/l
water_pore_velocity	Number	m/d
longitudinal_dispersivity	Number	m
FODRW	Number	d^(-1)
FODRS	Number	d^(-1)

Figure 9 Database: Chemical and soil parameters table

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The chemical and soil parameters were presented in detail in chapter 3.1.3. The values stored in this table were selected from the literature, but given the wide range of variability, the algorithm using this data must have the possibility to interactively modify them.
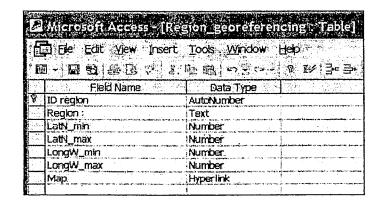

Figure 10 Database: Region table

The Region table uses the territorial-administrative regions of Ontario to store the maps along with the geographical coordinates of the maps. This table could be easily linked with a GIS to retrieve more accurate maps, soil maps, and local topographic characteristics that could be used by the model.

Figure 11 Database: Chemical spills table

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The Chemical spills table stored the type and quantity of spill, the date of occurrence and the location of the spill in geographical coordinates and, where available, in postal address and code.

Figure 12 Database: Relationships

This relational database has the three tables linked through the Chemical ID and Region ID and data could be retrieved or modified (for the chemical and soil parameters) through the interface designed in Matlab.

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3.2.2 CHEMICAL AND SPACE SELECTION INTERACTIVE INTERFACE .

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 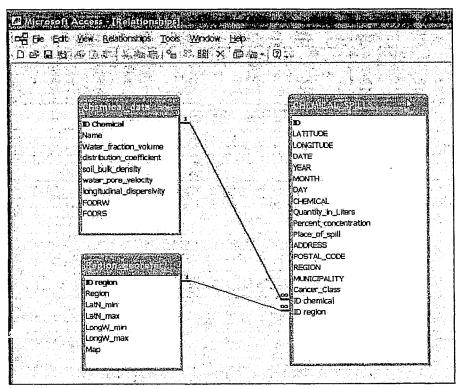accumulated effects of those spills of the selected chemical follow to be assessed. In order to fulfill this step of the algorithm, the following sub-steps are set up:

Region selection

An area of study has to be extracted from the region including that area. 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.

Figure 13 Interactive interface: Region selection

The region maps are not scale-restricted since the analysis algorithm is scale-independent.

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Chemical selection

The next sub-step is to retrieve from the 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 on Figure 14).

Figure 14 Interactive interface: Chemical selection

Chemical/environmental parameters selection

For each selected chemical, an interface was designed to interactively modify different chemical and environmental parameters considered i.. the single-event modeling. This option is essential since most of the parameters have a large range of variability. Figure 15 shows the values for LAS, the chemical considered for the simulation.

Figure 15 Interactive interface: Chemical parameters

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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 interval are selected from the database and displayed on the map of previously selected region.

Area selection

Within the borders of 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. For a better sense of the area size, the metric dimensions of the considered area are also displayed.

Figure 16 Interactive interface: Area selection

The selection algorithm also considers for analysis all spills that could potentially affect the area of study. One example is the case of the spills in the selected area that have occurred earlier but are still present at the moment the analysis. Another example is the case of the spills occurring in the specified

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time interval but located in the vicinity of the area borders and that could affect this particular area. To do so, the maximum persistence and impact area of a single spill event must be assessed and ext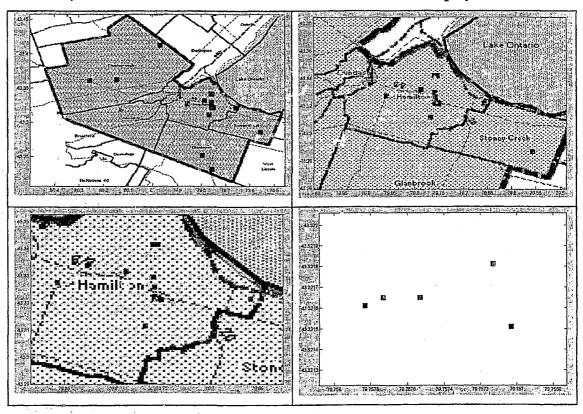end the analysis space with maximum impact radius and consider all those spills occurred before the initial time of analysis within maximum persistence time.

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.

3.2.3 SIMULATION OF SPATIAL-TEMPORAL DYNAMICS OF MAXIMUM-QUANTITY SPILL

An essential step of the algorithm is to simulate the spatial-temporal dynamics of the maximum-quantity spill. This assures that the potential effects of those spills occurring in the spatial-temporal vicinity of the selected area were taken into account. In practical terms, the maximum persistence and maximum radius of impact for the maximum-quantity spill are assessed and the spatial-temporal unit of study is extended with these two parameters. One of the reasons for using Matlab was that it allows easy computation in N-dimensional spaces, thus incorporating all spatial-temporal information in one 4D concentration variable.

The database is queried to retrieve the maximum-quantity spill for which the simulation will be done. The formula used for concentration, described in chapter 3.1.2 was implemented as a Matlab function (see Appendix 1) to be called with the selected chemical and soil parameters. This function returns a 4D-object that is dynamically displayed while calculating the impact area and depth for every moment of time. The (x,y) scale, the depth scale and maximum time (persistence) could be changed in order to capture the entire phenomenon.

The spatial distribution of concentration is eventually plotted for the moment in time when the maximum impact occurred and the maximum impact distance and depth are displayed.

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Figure 17 Simulation of spatial-temporal dynamics of highest-quantity spill

This simulation is used to search for all adjacent spills that could potentially have an effect in the selected area & time interval. The selected area will be extended in all directions with maximum impact radius and the time interval will be extended before the start time with maximum persistence. The database is queried with these new spatial-temporal limits and the detected spills will be included in the analysis. The number of spills in the selected area and the number of adjacent spills is displayed.

These values are then used to define the 4D-object dimensions (spatial and temporal scale) to be used in computing of the concentration for all selected spills. This 4D-object, whose dimensions are defined by the two parameters of the maximum-quantity spill, is assigned to each spill. This way, the whole spatial-temporal evolution of the concentration function is captured within the 4D-object.

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3.2.4 SPATIAL-TEMPORAL DYNAMICS OF CUMULATED EFFECTS OF CHEMICAL SPILLS

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 dimensions given by the maximum impact depth and maximum persistence of the maximum-quantity spill. For each spill, 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 "pieces" of their assigned 4D-objects included in the area of study are taken into account in the calculation of the accumulated effects. This way, the spatial-temporal dynamics of all those 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 object is used furthermore to assess the cumulative effects of a certain scenario of pollution.

The algorithm allows the user to select one point in the 4-D space by entering the values of time (days from the start time of analysis), depth (Z) and the (X,Y) coordinates on the selected layer. For better positioning, the (X,Y) coordinates could be selected graphically with a cursor 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 this is assigned to the selected chemical.

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Calculations

The values calculated based on this algorithm are divided into two categories: values describing the overall impact of a scenario of pollution and values describing the level of pollution at a selected point of the area of study.

In the first category, the following values are calculated to describe the accumulated effects of a certain scenario of pollution:

- Maximum impact area

- Maximum concentration

- Maximum depth

For each moment of time within the period of analysis, the current values of impact area, concentration, and depth where accumulated effects propagate are calculated. Furthermore, the three parameters mentioned above as characterising a scenario of pollution within a specified time-interval are calculated as the maximal values of the current values.

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

- Maximum concentration

- Current concentration

- Concentration ratio (C / C limit) if the chemical of interest has been assigned a maximum admissible limit

- The time period when the concentration exceeds this limit

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

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3.3 CASE STUDY

3.3.1 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 occur in different quantities and at different times and locations.

The data set containing the spill quantities and dates when each spill happens is shown in the table below.

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

Table 1 Case Study data set

The environmental specialist wants to analyse what happened in that particular area between March 8th and April 30th searching for answers to the following questions:

1. What is the maximum concentration of LAS in soil and when did it occur?
2. Is the concentration exceeding 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 are the effects in the near future?

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The spatial-temporal analysis model calculates the parameters shown in Figure 18. To get the 2D and temporal concentration dynamics, one could enter the time and select the position corresponding to the maximum value.

Figure 18 Spatial-temporal dynamics: The maximum concentration

The instance of maximum concentration usually corresponds with the moment of the maximum-quantity spill in the selected area. For the example above, the maximum concentration is reached on the 18th day of the analysis period.

Furthermore, it could be easily estimated what time period was when the concentration exceeded a maximum acceptable limit, in this case being 38 days.

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The algorithm calculates the maximum depth where the chemical can still be found. Figure 19 shows the moment when the maximum depth is reached.

This also illustrates an instance where two spills occurring at different moments and places, however adjacent, have a cumulative effect in the selected point.

Figure 19 Spatial-temporal dynamics: The maximum depth

Another model output essential to the spills assessment is the maximum impact area.   Figure 20 shows the moment when the spills spread to the maximum extent in the selected area and time interval. It can be noticed that an adjacent spill (in the lower left corner), which drops outside of the selected area, brings its influence to the total concentration in the selected point.

Figure 20 Spatial-temporal dynamics: The maximum impact area

Further, this algorithm permits the prediction of contamination given the current distribution of concentration and the quantity and place of a new spill. Figure 21 illustrates how the algorithm could be used for prediction. Figure 21 a represents the concentration distribution before a new spills event. Once a new spill is reported, the algorithm could be used to estimate the concentration profile in the future. Figure 21 b shows the predicted distribution for five days after the event. This prediction capability of the model can bring clues guiding the response strategy.

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Figure 21 Spatial-temporal dynamics: Prediction

a) Concentration distribution before the new spill event

b) Concentration distribution predicted for five days after the event

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3.3.2 Sensitivity analysis

Sensitivity analysis was conducted to prioritize those factors mostly affecting the reliability of analysis. The following procedure was followed to achieve it. Firstly, one-at-a-time sensitivity analysis was done by modifying each of the chemical and soil parameters in a range of +/- 50% of the initial values. Secondly, based on the previous analysis, the parameters with maximum and minimum outputs were detected and a maximum envelope analysis was performed to outline the potential range of variability for concentration.

3.3.2.1 Single- parameter sensitivity analysis

At this step, the parameters of the model were categorized as chemical and soil parameters. Within each category, every parameter was changed with a 10% step to assess the 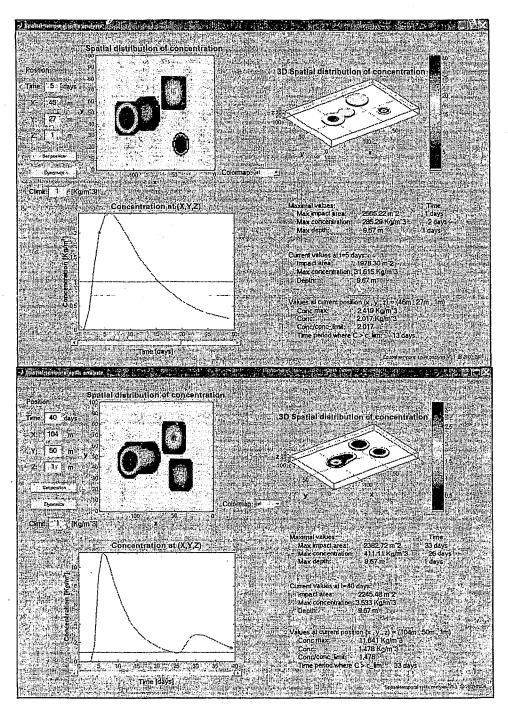sensitivity of the model to each of these parameters. Some model outputs were chosen as relevant to the impact analysis – maximum concentration, maximum concentration in a selected point, maximum area, maximum depth, and time period when maximum concentration is exceeded – and the influence of each parameter was analyzed by plotting every considered output versus parameter values changing with 10% incremental step.

Table 2 synthesizes the changes in each of the chosen outputs as a consequence of modifying chemical parameters in the range of +/- 50% of their initial values.

The same approach was conducted to evaluate the model sensitivity to soil parameters. Table 3 summarizes the influences of every soil parameter on the model outputs considered as relevant to our analysis.

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		-50%	-40%	-30%	-20%	-10%	Initial value	10%	20%	30%	40%	50%
Sensitivity analysis for the chemical spills model												
Parameter	Model Output											
		-50%	-40%	-30%	-20%	-10%	Initial value	10%	20%	30%	40%	50%
Chemical parameters												
Distribution coefficient (l/kg)		5	6	7	8	9	10	11	12	13	14	15
	Maximum impact area (m^2)	3124.4	3019.28	2899.56	2730.2	2540.4	2382.72	2235.26	2121.38	2008.96	1911.14	1841.06
	Maximum depth (m)	11.5	10.5	10	9.5	9	8.5	8.5	8	7.5	7.5	7.5
	Maximum concentration (Kg/m^3)	295.69	323.2	348.04	370.74	391.67	411.11	429.26	446.3	462.34	477.49	491.85
	Max Concentration at (x,y) (Kg/m^3)	23.419	19.928	16.67	14.576	13.078	11.642	10.977	9.56	8.774	8.019	7.432
	Time where C exceedes C_lim (days)	30	32	34	35	37	36	37	36	37	38	38
first order degradation rate in water (d^-1)		0.34657	0.41589	0.4852	0.55452	0.62383	**0.6931472**	0.76246	0.83178	0.90109	0.97041	1.03972
	Maximum impact area (m^2)	2604.64	2571.06	2517.04	2477.62	2427.98	2382.72	2331.62	2292.2	2244.02	2216.28	2169.56
	Maximum depth (m)	9	9	9	9	8.5	8.5	8.5	8.5	8.5	8.5	8.5
	Maximum concentration (Kg/m^3)	415.81	414.86	413.92	412.98	412.04	411.11	410.18	409.25	408.32	407.4	406.48
	Concentration at (x,y) (Kg/m^3)	12.039	11.958	11.878	11.799	11.72	11.642	11.564	11.486	11.41	11.333	11.258
	Time where C exceedes C_lim (days)	40	40	39	38	37	36	36	35	34	34	33
first order degradation rate in soil (d^-1)		0.01733	0.02079	0.02426	0.02773	0.03119	**0.0346574**	0.03812	0.04159	0.04505	0.04852	0.05199
	Maximum impact area (m^2)	2743.34	2670.34	2584.42	2517.04	2457.18	2382.72	2306.8	2244.02	2188.54	2138.9	2086.34
	Maximum depth (m)	9.5	9	9	9	9	8.5	8.5	8.5	8.5	8	8
	Maximum concentration (Kg/m^3)	418.81	416.75	415.33	413.92	412.51	411.11	409.71	408.32	406.94	405.56	404.19
	Concentration at (x,y) (Kg/m^3)	12.242	12.119	11.998	11.878	11.759	11.642	11.525	11.409	11.295	11.182	11.07
	Time where C exceedes C_lim (days)	41	41	40	39	38	36	36	34	33	32	31

Table 2 Sensitivity analysis: Chemical parameters

Parameter	Model Output	-50%	-40%	-30%	-20%	-10%	Initial value	10%	20%	30%	40%	50%
Model parameters												
Water fraction volume		0.25	0.3	0.35	0.4	0.45	0.5	0.55	0.6	0.65	0.7	0.75
	Maximum impact area (m^2)	1495.04	1711.12	1893.62	2064.44	2222.12	2382.72	2524.34	2652.82	2790.06	2874.74	2953.58
	Maximum depth (m)	6.5	7	7.5	8	8.5	8.5	9	9.5	9.5	10	10.5
	Maximum concentration (Kg/m^3)	1107.76	856.99	688.1	568.04	479.12	411.11	357.72	314.91	279.97	251	226.68
	Concentration at (x,y) (Kg/m^3)	10.702	11.036	11.158	11.456	11.429	11.642	11.767	11.727	11.57	11.594	11.813
	Time where C exceedes C_lim (days)	46	43	41	40	39	36	34	32	30	29	27
soil bulk density (kg/l)		0.75	0.9	1.05	1.2	1.35	1.5	1.65	1.8	1.95	2.1	2.25
	Maximum impact area (m^2)	3124.4	3019.28	2899.56	2730.2	2540.4	2382.72	2235.26	2121.98	2008.96	1911.14	1838.14
	Maximum depth (m)	11.5	10.5	10	9.5	9	8.5	8.5	8	7.5	7.5	7.5
	Maximum concentration (Kg/m^3)	295.69	323.2	348.04	370.74	391.67	411.11	429.26	446.29	462.33	477.49	491.84
	Concentration at (x,y) (Kg/m^3)	23.418	19.928	16.669	14.576	13.078	11.642	10.377	9.563	8.774	8.019	7.431
	Time where C exceedes C_lim (days)	30	32	34	35	37	36	37	36	37	38	38
pore water velocity (cm/d)		3.75	4.5	5.25	6	6.75	7.5	8.25	9	9.75	10.5	11.25
	Maximum impact area (m^2)	1359.42	1563.66	1768.06	1979.76	2179.78	2382.72	2585.66	2800.28	2959.42	3141.92	3274.78
	Maximum depth (m)	6	6.5	7	7.5	8	8.5	9	9.5	10	10.5	11
	Maximum concentration (Kg/m^3)	1103.22	854.38	686.62	567.26	478.8	411.11	357.94	315.29	280.46	251.57	227.31
	Concentration at (x,y) (Kg/m^3)	9.844	10.41	10.734	11.182	11.298	11.642	11.883	11.948	11.885	12.004	12.311
	Time where C exceedes C_lim (days)	42	41	40	39	38	36	34	34	32	31	29
longitudinal dispersivity (cm)		5	6	7	8	9	10	11	12	13	14	15
	Maximum impact area (m^2)	1248.3	1476.06	1715.5	1938.88	2160.8	2382.72	2620.7	2845.54	3039.72	3236.82	3400.34
	Maximum depth (m)	7	7.5	8	8	8.5	8.5	9	9	9.5	9.5	10
	Maximum concentration (Kg/m^3)	1093.22	848.85	683.57	565.7	478.18	411.11	358.36	316	281.38	252.64	228.48
	Concentration at (x,y) (Kg/m^3)	9.322	10.08	10.547	11.061	11.241	11.642	11.924	12.028	12	12.104	12.435
	Time where C exceedes C_lim (days)	39	39	39	38	37	36	35	35	33	32	31

Table 3 Sensitivity analysis: Soil parameters

The variability profile of every output when chemical and soil parameters are individually changed is plotted on the same graph for a better grasp of the most influential factors. As a general observation for all outputs, it is stated that the distribution coefficient from the chemical parameter category and soil density from soil parameter category have very similar influences on each output. This could be expected since bulk density has a direct influence on the sorption process described by the distribution coefficient. By increasing soil bulk density, the soil capacity for adsorption is increased because the density of adsorption sites will also increased. In other words, between the two parameters a direct proportionality exists.

The variation of each output as a function of each model parameter is shown in Figure 22 - Figure 27.

Figure 22 Sensitivity analysis: Maximum concentration

One output of interest was maximum concentration. As can be seen in Figure 22, the concentration is the most sensitive to water fraction, pore water velocity and dispersivity, and, more than this, this influence is equally distributed among these parameters.

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At the same time, the concentration is almost insensitive to chemical degradation rates in water and soil. This could be a positive aspect since chemical half-lives in different media - based on which degradation rates are calculated - are generally scarce and difficult to be determined experimentally.

Compared to maximum concentration of a certain scenario of pollution, the maximum concentration at a selected point of this scenario is mostly influenced by soil density and distribution coefficient; the other parameters having a negligible effect. This is a very interesting aspect which shows that the perspective on the contamination problem could be significantly changed once cumulative effects are taken into account.

Figure 23 Sensitivity analysis: Maximum concentration in a selected point

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Figure 24 shows how the profile of concentration at a point changes with different distribution coefficients considered as the most influential parameter for this output.

Figure 24 Sensitivity analysis: temporal variation of concentration in a selected point vs. distribution coefficient

While the distribution coefficient is decreasing, the concentration curve is depleting and the maximum is shifted later in time. This was expected since a lower distribution coefficient will lead to a higher persistence at other locations away from that point.

Another model output considered in the sensitivity analysis is the maximum impact area. Unfortunately, as can be noticed from Figure 25, this output is highly influenced by all parameters. This could be partially explained by the fact that this is a "global" output, characterising the overall effects of pollution, meaning that it is affected by the summed influences from all events, so that its sensitivity is increased.

Figure 25 Sensitivity analysis: maximum impact area

The maximum depth is also influenced by all parameters, but to a lesser extent than the maximum impact area. Figure below suggests that, if the values of parameters are kept in +/- 20% range, then the output would stay in +/-10% of its initial value. However, if model parameters are significantly changed, high variations in the estimated values for maximum depth can be observed.

Figure 26 Sensitivity analysis: maximum depth

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Figure 27 Sensitivity analysis: Number of days when C > C limit

The time interval when the concentration exceeded the maximum acceptable value is an important output of the model and is slightly affected by changes in parameters values.

3.3.2.2 Maximum envelope analysis

Figure 22 shows that the model is most sensitive to the water fraction volume, pore water velocity and longitudinal dispersivity. The variation of these parameters in +/- 50% range leads to the extreme values for concentration. Therefore, the envelope analysis uses these three model parameters to describe the extreme conditions.

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Figure 28 Maximum envelope analysis

Model output for extreme values of water fraction volume, pore water velocity and
longitudinal dispersivity. a) variation with -50% from the initial value;
b) variation with +50% from the initial value

As clearly shown in Figure 28, the shape of the concentration plume is changing radically when the model parameters vary with +/- 50%. These two cases are extreme and any other situations lies within the two envelopes.

For a better understanding of the magnitude of change, an analysis of temporal variation of concentration was performed (Figure 29). This not only shows that the concentration amplitude decreases with the decrease of parameters values but also the persistence of the chemical is increased leading to a different shape of plume in the 3D model. This suggests that the model parameters should be calibrated carefully for reliability of analysis.

Figure 29 Concentration envelope in one selected point.

Concentration for the +50% variation to -50% variation of the set of parameters.

3.4 LIMITATIONS OF THE ALGORITHM

Even though the proposed algorithm brings contributions to a better assessment of the impact of chemical spills on the environment in real-world conditions, it certainly has its limitations. In general, the model used to simulate the fate and transport of any single-spill event dictates the complexity and accuracy of the algorithm. 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 spills and chemical data availability and accuracy. This algorithm is useful for those situations when spills are persistent and frequent enough, so that cumulated effects emerge.

Being conceived for a daily temporal scale, the algorithm can analyze spills of short persistence in the range of hours only after certain modifications, which are not addressed at this moment.

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CHAPTER 4 CONCLUSIONS AND RECOMMENDATIONS

4.1 CONCLUSIONS

In spite of a complex set of policies in place to regulate emissions from industry with the intent of minimizing the potential for adverse environmental and human health effects, chemical accidents do happen. Depending on the nature of release, industrial accidents can pose serious threats and also become a salient issue from the public point of view.

It is clear that industry spill prevention/accident reduction efforts, whether initiated in response to regulation or through voluntary initiatives, can reduce significantly the contribution of chemical spills to environmental and human exposures. However, as accidents do occur, it is essential to undertake an evaluation of these events to determine their potential long-term implications on environment, human health or both. In these circumstances, the actual spill management is challenged to figure out the best approach not only to respond efficiently to emergency events, but also to provide both a sound estimation of environmental/human health impacts and consistent measures to reduce the probability and severity of spill accidents.

This thesis responds to the present challenges of spill management 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 a o on groundwater vulnerability.

Furthermore, this thesis 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, the "alarming" levels of pollution can be predicted and localized in space and time. More than this, the

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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. Different models of certain 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.

4.2 RECOMMENDATIONS

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 present spill management.

A matrix of standardized responses appropriate to certain real 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. More specific information about the environment can be retrieved from GIS layers.

This way, the algorithm is corroborated by other information provided by GIS, such as soil maps, information on terrain slopes, location of environmentally sensitive areas, detailed land use, biota or demographic data that could lead to a better 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. The applicability of this new tool varies depending on the complexity of the fate and transport model incorporated into the algorithm, on the variety of receptors and exposure routes considered.

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.

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APPENDIX 1 Single spill modelling function

function c=conc4D(M,theta,kd,rob,v,alfaL,kw,ks,X,X0,Y,Y0,Z,Z0,T,T0);

```
% Concentration function
% Parameters
% M                      mass released at t=0 [Kg]
% theta = 0.2 .. 0.6;    water fraction volume
% kd = 20 ( ex for LAS)  distribution coefficient [l/kg]
% rob = 1.2 .. 1.6;      soil bulk density [kg/l]
% v = 7.5;               water pore velocity [cm/d]
% alfaL = 10             longitudinal dispersivity [cm]
% kw = log(2)/1 (for LAS) first order degradation rate in water [d^-1]
% ks = log(2)/20 (for LAS) first order degradation rate in sol [d]


Dz=v*alfaL;          % longitudinal diffusion coefficient
alfaT=0.3*alfaL;     % transversal dispersivity
Dx=v*alfaT;          % transversal diffusion coefficient
Dy=Dx;
R=1+(kd*rob)/theta;    % retardation factor
lambda=(kw+ks*rob*kd/theta)/R;    % first-order degradation rate constant


% Concentration

c = M / (theta*R*(64*pi^3*Dx/R*Dy/R*Dz/R).*(T.^3)).^(1/2).*
        exp(-(X-X0).^2./(4*Dx/R.*T) - (Y-Y0).^2./(4*Dy/R.*T) - (Z-
v/R.*T).^2)./(4*Dz/R.*T).*
        exp(-lambda.*T);
```

APPENDIX 2 Analysis software code

```
function chem_spills(action);

% MIHAELA DINCA-PANAITESCU
% MASTER THESIS - RYERSON UNIVERSITY
% @2003-2004
%
% VERSION V1.3    Updated: 01 JUNE 2004


if nargin<1,
    action='start';
end;

global Spills_data Spills_data_m;
global lat_start long_start lat_stop long_stop;
global lat_start_m long_start_m lat_stop_m long_stop_m t_start_m;
global lat_start_field long_start_field lat_stop_field long_stop_field;
global region harta;
global chem reg;
global t_start t_end;
global t_start_field t_end_field;
global H_plot H_axes;
global WFV DC SBD WPV LD FODRW FODRS;
global WFV_field DC_field SBD_field WPV_field LD_field FODRW_field FODRS_field;
global sf st zsf sf_field st_field zsf_field;
global SQLT;
global zmax;
global Ts;

global cc;
global tmax xmax ymax;
global xcc ycc zcc tcc;
global scalare scalare_cc;
global x_field y_field z_field t_field c_field;
global x_current y_current z_current t_current;
global H_subplot;
global culoare;
global t_slide;
global c_lim;
global NF;
global map_g

if strcmp(action,'start'),

    t_start=datestr('03/01/2004',23);
    t_end=datestr('04/25/2004',23); %datestr(date,23);
    reg='HAMILTON-WENTWORTH';
    chem='LAS';
    sf=30;
    st=40;
    zsf=10;

    close all;
    figure(1)

    set(gcf,'backingstore','off','NumberTitle','off',...
        'Resize','off','Position',[2 2 1398 1018],'color', [0.8 0.8 0.8],...
        'Name','Spatial-temporal spills analysis V1.1 - selection of spills, time, region and area of
analysis','Menubar','none','Pointer','crosshair');
    tip_text1=uicontrol('Style','text','Position',[1080 10 300 30],...
        'BackgroundColor',[0.8 0.8 0.8],...
        'ForegroundColor','blue','String','Spatial-temporal spills analysis V1.1  @ 2003-2004 ');
    pause(0.01);

    uicontrol('style','text','pos',[350 780 700 140], 'BackGroundColor',[0.2 0.2 0.6],'ForeGroundColor',[1 0.1
0.1],'FontWeight','bold',...
```

```
'string',[ {'Spatial-temporal chemical spills analysis software'}; {'Author: Mihaela Dinca-Panaitescu'};{'Ryerson
University, 2004'}; {'Master Thesis'}],'FontSize',18);

    uicontrol('style','text','pos',[20 680 200 40], 'BackGroundColor',[0.8 0.8 0.8],...
        'string','Select Region:','FontSize',12);
    region=uicontrol('style','popup',...
        'string','HAMILTON-WENTWORTH|DURHAM|WATERLOO-WELLINGTON|TORONTO|SARNIA-
LAMBTON|NIAGARA|PEEL-HALTON-DUFFERIN|YORK',...
        'Position',[100 650 300 30],...
        'callback','chem_spills("sel_region")','ToolTipString','Region selection');

    uicontrol('style','text','pos',[30 580 200 40], 'BackGroundColor',[0.8 0.8 0.8],...
        'string','Select Chemical:','FontSize',12);
    culoare=uicontrol('style','popup',...
        'string','LAS|ETHYLENE GLYCOL (ANTIFREEZE)|HYDROCHLORIC ACID (MURIATIC ACID)|USED
MOTOR OIL|SULPHURIC ACID|AMMONIA GAS (ANHYDROUS)|FREON R-22 (CFC)|SODIUM HYDROXIDE
(SOL) (CAUSTIC SODA)|INK|METHYL CHLORIDE|TOLUENE|BENZENE',...
        'Position',[100 550 300 30],...
        'callback','chem_spills("sel_chemical")','ToolTipString','Chemical selection');

    uicontrol('style','text','pos',[44 480 200 40], 'BackGroundColor',[0.8 0.8 0.8],...
        'string','Select Time Interval:','FontSize',12);

    uicontrol('style','text','pos',[234 455 200 40], 'BackGroundColor',[0.8 0.8 0.8],...
        'string',' mm/dd/yyyy','FontSize',12);


    uicontrol('style','text','pos',[44 430 200 40], 'BackGroundColor',[0.8 0.8 0.8],...
        'string','Start Time:','FontSize',12);
    t_start_field=uicontrol('Style','edit','Position',[250 440 170 30],'FontSize',10,...
        'Callback','chem_spills("set_t_start")','String',t_start);

    uicontrol('style','text','pos',[44 380 200 40], 'BackGroundColor',[0.8 0.8 0.8],...
        'string','End Time: ','FontSize',12);
    t_end_field=uicontrol('Style','edit','Position',[250 390 170 30],'FontSize',10,...
        'Callback','chem_spills("set_t_end")','String',t_end);

    uicontrol('style','text','pos',[18 330 300 40], 'BackGroundColor',[0.8 0.8 0.8],...
        'string','Select Geographical area:','FontSize',12);

    uicontrol('style','text','pos',[185 305 50 40], 'BackGroundColor',[0.8 0.8 0.8],...
        'string','Min','FontSize',12);

    uicontrol('style','text','pos',[305 305 50 40], 'BackGroundColor',[0.8 0.8 0.8],...
        'string','Max','FontSize',12);

    uicontrol('style','text','pos',[5 280 150 40], 'BackGroundColor',[0.8 0.8 0.8],...
        'string','Latitude N:','FontSize',12);
    lat_start_field=uicontrol('Style','edit','Position',[150 290 120 30],'FontSize',10,...
        'Callback','chem_spills("set_area")','String',num2str(lat_start,9));
    lat_stop_field=uicontrol('Style','edit','Position',[270 290 120 30],'FontSize',10,...
        'Callback','chem_spills("set_area")','String',num2str(lat_stop,9));


    uicontrol('style','text','pos',[15 230 150 40], 'BackGroundColor',[0.8 0.8 0.8],...
        'string','Longitude W:','FontSize',12);
    long_start_field=uicontrol('Style','edit','Position',[150 240 120 30],'FontSize',10,...
        'Callback','chem_spills("set_area")','String',num2str(long_start,9));
    long_stop_field=uicontrol('Style','edit','Position',[270 240 120 30],'FontSize',10,...
        'Callback','chem_spills("set_area")','String',num2str(long_stop,9));

    buton1=uicontrol('Style','Pushbutton','Position',[80 150 140 30],...
        'Callback','chem_spills("set_coordinates")','String','Set coordinates',...
        'ToolTipString','Set coordinates for analysis and freeze image');

    buton2=uicontrol('Style','Pushbutton','Position',[250 150 140 30],...
        'Callback','chem_spills("analysis")','String','Analysis',...
        'ToolTipString','Start spatial-temporal analysis');
```

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```
buton3=uicontrol('Style','Pushbutton','Position',[260 590 140 30],...
    'Callback','chem_spills("set_chem_data")','String','Set parameters',...
    'ToolTipString','Set chemical and soil parameters');

chem_spills('sel_region');
imzoom

elseif strcmp(action,'get_data'),
    % Imports data into Matlab from spills database.
    % Set maximum time allowed for establishing a connection.
    timeoutA=logintimeout(5);
    % Connect to spills database.
    connA=database('Spills','','');
    % Check the database status.
    ping(connA);
    % Open cursor and execute SQL statement.
    SQL=sprintf('SELECT ALL
ID,LATITUDE,LONGITUDE,DATE,CHEMICAL,Quantity_in_Liters,Percent_concentration,REGION FROM
CHEMICAL_SPILLS WHERE CHEMICAL = "%s" AND REGION = "%s" AND DATE BETWEEN #%s# AND
#%s# AND LATITUDE BETWEEN %3.6d AND %3.6d AND LONGITUDE BETWEEN %3.6d AND
%3.6d',chem,reg,t_start,t_end,lat_start,lat_stop,long_start,long_stop);
    cursorA=exec(connA,SQL);
    % Fetch the first 10 rows of data.
    cursorA=fetch(cursorA,100);
    % Display the data.
    Spills_data=cursorA.Data;
    % Close the cursor and the connection.
    close(cursorA);
    close(connA);




elseif strcmp(action,'sel_region'),

    s_reg=get(region,'string');
    s_value=get(region,'value');

    if s_value==1
        reg='HAMILTON-WENTWORTH';
    elseif s_value==2
        reg='DURHAM';
    elseif s_value==3
        reg='WATERLOO-WELLINGTON';
    elseif s_value==4
        reg='TORONTO';
    elseif s_value==5
        reg='SARNIA-LAMBTON';
    elseif s_value==6
        reg='NIAGARA';
    elseif s_value==7
        reg='PEEL-HALTON-DUFFERIN';
    elseif s_value==8
        reg='YORK';
    end

    harta=sprintf('%s.jpg',reg);

    chem_spills('set_geo');

    H_plot=subplot(1,1,1);
    set(H_plot,'color',[ 0.7 0.7 0.7],'Box','on','Position',[0.35 0.11 0.615 0.615]);

    [map_current,map]=imread(harta,'jpeg');
    colormap(map);

    x_val=linspace(long_stop,long_start,size(map_current,2));
    y_val=linspace(lat_stop,lat_start,size(map_current,1));

    imagesc(x_val,y_val,map_current);
```

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```matlab
        chem_spills('get_data');
        % Plot retreived data
        set(gca,'Ydir','normal','XDir','reverse');
        for i=1:size(Spills_data,1)'
            set(H_plot,'NextPlot','add');
            H_line=plot(Spills_data{i,3},Spills_data{i,2},'bo');
            set(H_line,'marker','square','MarkerFaceColor','red', 'MarkerSize',12)
        end
        set(H_plot,'NextPlot','replace');


    elseif strcmp(action,'set_area'),

        lat_start=str2num(get(lat_start_field,'String'));
        lat_stop=str2num(get(lat_stop_field,'String'));
        long_start=str2num(get(long_start_field,'String'));
        long_stop=str2num(get(long_stop_field,'String'));
        %figure(1)
        %imzoom
        set(H_plot,'Ylim',[lat_start lat_stop],'Xlim',[long_start long_stop]);


    elseif strcmp(action,'set_coordinates'),

        imzoom
        ccy=get(H_plot,'Xlim');
        long_start=ccy(1);
        long_stop=ccy(2);
        ccx=get(H_plot,'Ylim');
        lat_start=ccx(1);
        lat_stop=ccx(2);
        set(lat_start_field,'String',num2str(lat_start,9));
        set(lat_stop_field,'String',num2str(lat_stop,9));
        set(long_start_field,'String',num2str(long_start,9));
        set(long_stop_field,'String',num2str(long_stop,9));

        uicontrol('style','text','pos',[70 100 250 40], 'BackGroundColor',[0.8 0.8 0.8],...
            'string',sprintf('Xmax = %7.2f m',deg2km(distance(lat_start,long_start,lat_start,long_stop)*1000)),'FontSize',12);

        uicontrol('style','text','pos',[70 60 250 40], 'BackGroundColor',[0.8 0.8 0.8],...
            'string',sprintf('Ymax = %7.2f m',deg2km(distance(lat_start,long_start,lat_stop,long_start)*1000)),'FontSize',12);

    elseif strcmp(action,'set_geo'),
        timeoutA=logintimeout(5);
        connA=database('Spills','','');
        ping(connA);
        SQL1=sprintf('SELECT ALL LatN_min,LatN_max,LongW_min,LongW_max FROM Region_georeferencing
WHERE Region = "%s"', reg) ;
        cursorA=exec(connA,SQL1);
        cursorA=fetch(cursorA,100);
        Geo_data=cursorA.Data;
        close(cursorA)
        close(connA)
        lat_start=Geo_data{1};
        lat_stop=Geo_data{2};
        long_start=Geo_data{3};
        long_stop=Geo_data{4};;
        set(lat_start_field,'string',num2str(lat_start,9));
        set(lat_stop_field,'string',num2str(lat_stop,9));
        set(long_start_field,'string',num2str(long_start,9));
        set(long_stop_field,'string',num2str(long_stop,9));

    elseif strcmp(action,'set_t_start'),

        t_start=get(t_start_field,'string');
        lat_start_t=lat_start;
        lat_stop_t=lat_stop;
        long_start_t=long_start;
        long_stop_t=long_stop;
```

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```
        chem_spills('sel_region');

        set(lat_start_field,'String',num2str(lat_start_t,9));
        set(lat_stop_field,'String',num2str(lat_stop_t,9));
        set(long_start_field,'String',num2str(long_start_t,9));
        set(long_stop_field,'String',num2str(long_stop_t,9));

        chem_spills('set_area');
        set(t_start_field,'string',t_start);

elseif strcmp(action,'set_t_end'),

        t_end=get(t_end_field,'string');

        lat_start_t=lat_start;
        lat_stop_t=lat_stop;
        long_start_t=long_start;
        long_stop_t=long_stop;

        chem_spills('sel_region');

        set(lat_start_field,'String',num2str(lat_start_t,9));
        set(lat_stop_field,'String',num2str(lat_stop_t,9));
        set(long_start_field,'String',num2str(long_start_t,9));
        set(long_stop_field,'String',num2str(long_stop_t,9));

        chem_spills('set_area');
        set(t_end_field,'string',t_end);


elseif strcmp(action,'set_chem_data');

        timeoutA=logintimeout(5);
        connA=database('Spills','','');
        ping(connA);
        SQL3=sprintf('SELECT ALL
Water_fraction_volume,distribution_coefficient,soil_bulk_density,water_pore_velocity,longitudinal_dispersivity,FODR
W,FODRS FROM Chemical_data WHERE Name = "%s"',chem);
        cursorA=exec(connA,SQL3);
        cursorA=fetch(cursorA,100);
        Chem_data=cursorA.Data;
        close(cursorA);
        close(connA);

        WFV=Chem_data{1};
        DC=Chem_data{2};
        SBD=Chem_data{3};
        WPV=Chem_data{4};
        LD=Chem_data{5};
        FODRW=Chem_data{6};
        FODRS=Chem_data{7};

        set(figure(2),'backingstore','off','NumberTitle','off',...
            'Resize','off','Position',[10 10 420 500],'color', [0.8 0.8 0.8],...
            'Name','Select chemical and soil parameters','Menubar','none','Pointer','crosshair');
        pause(0.0001);
        buton4=uicontrol('Style','Pushbutton','Position',[250 50 140 30],...
            'Callback','chem_spills("update_chem_data")','String','OK',...
            'ToolTipString','Validate');
        uicontrol('style','text','pos',[20 450 200 25], 'BackGroundColor',[0.8 0.8 0.8],...
            'string',sprintf('CHEMICAL :  %s',chem),'FontSize',12);

        uicontrol('style','text','pos',[10 400 260 25], 'BackGroundColor',[0.8 0.8 0.8],...
            'string',sprintf('Water fraction volume . . . . . . . . . . . . . . . .
'),'FontSize',9,'FontWeight','bold','HorizontalAlignment','left');
        WFV_field=uicontrol('Style','edit','Position',[280 410 70 20],'FontSize',9,...
            'Callback','chem_spills("modify_chem_data")','String',WFV);


        uicontrol('style','text','pos',[10 360 260 25], 'BackGroundColor',[0.8 0.8 0.8],...
```

```
            'string',sprintf('Distribution coefficient . . . . . . . . . . . . . . .
.'),'FontSize',9,'FontWeight','bold','HorizontalAlignment','left');
    DC_field=uicontrol('Style','edit','Position',[280 370 70 20],'FontSize',9,...
        'Callback','chem_spills("modify_chem_data")','String',DC);
    uicontrol('style','text','pos',[370 360 260 25], 'BackGroundColor',[0.8 0.8 0.8],...
        'string',sprintf('l/Kg'),'FontSize',9,'FontWeight','bold','HorizontalAlignment','left');

    uicontrol('style','text','pos',[10 320 260 25], 'BackGroundColor',[0.8 0.8 0.8],...
        'string',sprintf('Soil bulk density . . . . . . . . . . . . . . . . . . .
.'),'FontSize',9,'FontWeight','bold','HorizontalAlignment','left');
    SBD_field=uicontrol('Style','edit','Position',[280 330 70 20],'FontSize',9,...
        'Callback','chem_spills("modify_chem_data")','String',SBD);
    uicontrol('style','text','pos',[370 320 260 25], 'BackGroundColor',[0.8 0.8 0.8],...
        'string',sprintf('Kg/l'),'FontSize',9,'FontWeight','bold','HorizontalAlignment','left');

    uicontrol('style','text','pos',[10 280 260 25], 'BackGroundColor',[0.8 0.8 0.8],...
        'string',sprintf('Water pore velocity . . . . . . . . . . . . . . . . . .
.'),'FontSize',9,'FontWeight','bold','HorizontalAlignment','left');
    WPV_field=uicontrol('Style','edit','Position',[280 290 70 20],'FontSize',9,...
        'Callback','chem_spills("modify_chem_data")','String',WPV);
    uicontrol('style','text','pos',[370 280 260 25], 'BackGroundColor',[0.8 0.8 0.8],...
        'string',sprintf('cm/d'),'FontSize',9,'FontWeight','bold','HorizontalAlignment','left');

    uicontrol('style','text','pos',[10 240 260 25], 'BackGroundColor',[0.8 0.8 0.8],...
        'string',sprintf('Longitudinal dispersivity . . . . . . . . . . . . . . . . . . .
.'),'FontSize',9,'FontWeight','bold','HorizontalAlignment','left');
    LD_field=uicontrol('Style','edit','Position',[280 250 70 20],'FontSize',9,...
        'Callback','chem_spills("modify_chem_data")','String',LD);
    uicontrol('style','text','pos',[370 240 260 25], 'BackGroundColor',[0.8 0.8 0.8],...
        'string',sprintf('cm'),'FontSize',9,'FontWeight','bold','HorizontalAlignment','left');

    uicontrol('style','text','pos',[10 200 260 25], 'BackGroundColor',[0.8 0.8 0.8],...
        'string',sprintf('First order degradation rate in water . . . . .
.'),'FontSize',9,'FontWeight','bold','HorizontalAlignment','left');
    FODRW_field=uicontrol('Style','edit','Position',[280 210 70 20],'FontSize',9,...
        'Callback','chem_spills("modify_chem_data")','String',FODRW);
    uicontrol('style','text','pos',[370 200 260 25], 'BackGroundColor',[0.8 0.8 0.8],...
        'string',sprintf('d^-1'),'FontSize',9,'FontWeight','bold','HorizontalAlignment','left');

    HH=uicontrol('style','text','pos',[10 160 260 25], 'BackGroundColor',[0.8 0.8 0.8],...
        'string',sprintf('First order degradation rate in soil . . . . .
.'),'FontSize',9,'FontWeight','bold','HorizontalAlignment','left');
    FODRS_field=uicontrol('Style','edit','Position',[280 170 70 20],'FontSize',9,...
        'Callback','chem_spills("modify_chem_data")','String',FODRS);
    uicontrol('style','text','pos',[370 160 260 25], 'BackGroundColor',[0.8 0.8 0.8],...
        'string',sprintf('d^-1'),'FontSize',9,'FontWeight','bold','HorizontalAlignment','left');


elseif strcmp(action,'modify_chem_data');

    WFV=str2num(get(WFV_field,'string'));
    DC=str2num(get(DC_field,'string'));
    SBD=str2num(get(SBD_field,'string'));
    WPV=str2num(get(WPV_field,'string'));
    LD=str2num(get(LD_field,'string'));
    FODRW=str2num(get(FODRW_field,'string'));
    FODRS=str2num(get(FODRS_field,'string'));

elseif strcmp(action,'update_chem_data');

    timeoutA=logintimeout(5);
    connA=database('Spills','','');
    ping(connA);
```

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```matlab
%Define a cell array containing the column names to be updated.
colnames
=[{'Water_fraction_volume'},{'distribution_coefficient'},{'soil_bulk_density'},{'water_pore_velocity'},{'longitudinal_di
spersivity'},{'FODRW'},{'FODRS'}];

%Define a cell array containing the new data.

newdata = [{WFV},{DC},{SBD},{WPV},{LD},{FODRW},{FODRS}];

WhereClause=sprintf('where Name = "%s"',chem);
%Perform the update.

update(connA, 'Chemical_data', colnames, newdata, WhereClause)

close(connA);

close(figure(2))

elseif strcmp(action,'analysis'),


if isempty(WFV) | isempty(DC) | isempty(SBD) | isempty(WPV) | isempty(LD) | isempty(FODRW) |
isempty(FODRS)
    chem_spills('set_chem_data')
end

chem_spills('set_coordinates');
chem_spills('get_data');

%Retrieve from database the max qty spill
% timeoutA=logintimeout(5);
% connA=database('Spills','','');
% ping(connA);
% SQL2=sprintf('SELECT DISTINCT MaxOfQuantity_in_Liters,CHEMICAL,REGION FROM Q_Max_qty
WHERE REGION = "%s" AND CHEMICAL = "%s"',reg,chem);
% cursorA=exec(connA,SQL2);
% cursorA=fetch(cursorA,100);
% Maxconc_data=cursorA.Data;
% close(cursorA);
% close(connA);
% max_qty=Maxconc_data{1};


timeoutA=logintimeout(5);
connA=database('Spills','','');
ping(connA);
SQL2=sprintf('SELECT ALL
ID,LATITUDE,LONGITUDE,DATE,CHEMICAL,Quantity_in_Liters,Percent_concentration,REGION FROM
CHEMICAL_SPILLS WHERE CHEMICAL = "%s" AND REGION = "%s" AND DATE BETWEEN #%s# AND
#%s# AND LATITUDE BETWEEN %3.6d AND %3.6d AND LONGITUDE BETWEEN %3.6d AND
%3.6d',chem,reg,t_start,t_end,lat_start,lat_stop,long_start,long_stop);
cursorA=exec(connA,SQL2);
cursorA=fetch(cursorA,100);
Maxconc_data=cursorA.Data;
close(cursorA);
close(connA);
max_qty=max([Maxconc_data{:,6}]);



[MM,II]=max([Spills_data{:,6}]);
xx=Spills_data{II,4};
t_start_m=datenum(sprintf('%s/%s/%s',xx(6:7),xx(9:10),xx(1:4)));
t_end_m= t_start_m+st;

%Estimate the max impact distance to include the spills in the vecinity of the selected area
X0=sf*100/2;
Y0=sf*100/2;
Z0=0;
T0=0;
```

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```
Ts=30;

x = linspace(0,sf*100,Ts);
y = linspace(0,sf*100,Ts);
z = linspace(0,zsf*100,Ts);
t = linspace(0,t_end_m-t_start_m,Ts);
[X,Y,Z,T] = ndgrid(x,y,z,t);
t_current=15;

c=conc4D(max_qty,WFV,DC,SBD,WPV*100,LD*100,FODRW,FODRS,X,X0,Y,Y0,Z,Z0,T,T0);
scalare=max(max(max(max(c))))*10^-3;


set(figure(3),'backingstore','off','NumberTitle','off',...
    'Resize','off','Position',[430 50 950 680],'color', [0.8 0.8 0.8],...
    'Name','Simulate spatial-temporal distribution for the high quantity spill','Menubar','none','Pointer','crosshair');

opengl neverselect
clf;

for i=1:Ts
    figure(3);
    cla
    set(gca,'DrawMode','fast');
    [xc,yc,zc,cs(:,:,:,i)]=subvolume(x/100,y/100,z/100,c(:,:,:,i),[nan nan nan nan nan nan]);
    zc=-zc;
    p = patch(isosurface(xc,yc,zc,cs(:,:,:,i),scalare), 'FaceColor', 'blue', 'EdgeColor', 'none'); %,scalare
    p2 = patch(isocaps(xc,yc,zc,cs(:,:,:,i),scalare), 'FaceColor', 'interp', 'EdgeColor', 'none');
    isonormals(xc,yc,zc,cs(:,:,:,i),p);
    axis equal;
    axis([0 max(x)/100 0 max(y)/100 -max(z)/100 0]);
    daspect([1 1 2]);
    [xf,yf]=find(cs(:,:,1,i)>scalare);
    if ~isempty([xf,yf])
        xymax(i,1:2)=[max(xf)-min(xf),max(yf)-min(yf)];
    else
        xymax(i,1:2)=[0,0];
    end
    grid on;
    xlabel('x','FontSize',12,'FontWeight','bold');
    ylabel('y','FontSize',12,'FontWeight','bold');
    zlabel('z','Rotation',0,'FontSize',12,'FontWeight','bold');

    camva(10);
    box on;
    camlight(40, 40);
    camlight(-20,-10);
    lighting gouraud;
    clear xc yc zc p p2 cs
    pause(0.01);
end

[r_max,t_max]=max(xymax);

izmax=size(c,3);
for i=1:size(c,3)
    if isempty(find(c(:,:,i,:)>scalare))
        izmax=i;
        %tz_ccmax=
        break
    end
end

zmax=izmax*zsf/Ts;

figure(3);
H_sub=subplot(1,1,1);
set(H_sub,'Box','on','Position',[0.1 0.3 0.615 0.615]);
[xc,yc,zc,cs(:,:,:,max(t_max))]=subvolume(x/100,y/100,z/100,c(:,:,:,max(t_max)),[nan nan nan nan nan nan]);
zc=-zc;
```

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```
p = patch(isosurface(xc,yc,zc,cs(:,:,:,max(t_max)),scalare), 'FaceColor', 'blue', 'EdgeColor', 'none');
p2 = patch(isocaps(xc,yc,zc,cs(:,:,:,max(t_max)),scalare), 'FaceColor', 'interp', 'EdgeColor', 'none');
isonormals(xc,yc,zc,cs(:,:,:,max(t_max)),p);
axis equal;
axis([0 max(x)/100 0 max(y)/100 -max(z)/100 0]);
daspect([1 1 2]);
pause(0.0001);

title('Spatial distribution of concentration at highest impact area','FontSize',14,'FontWeight','bold');
uicontrol('style','text','pos',[620 490 200 25], 'BackGroundColor',[0.8 0.8 0.8],...
    'string',sprintf('CHEMICAL :  %s',chem),'FontSize',12,'HorizontalAlignment','left');

uicontrol('style','text','pos',[620 450 200 25], 'BackGroundColor',[0.8 0.8 0.8],...
    'string',sprintf('Max quantity :  %d  l',max_qty),'FontSize',12,'HorizontalAlignment','left');

uicontrol('style','text','pos',[620 410 200 25], 'BackGroundColor',[0.8 0.8 0.8],...
    'string','XY scale:','FontSize',12,'HorizontalAlignment','left');
sf_field=uicontrol('Style','edit','Position',[720 415 70 25],'FontSize',12,...
    'Callback','chem_spills("modify_sf")','String',sf);
uicontrol('style','text','pos',[800 410 100 25], 'BackGroundColor',[0.8 0.8 0.8],...
    'string','m','FontSize',12,'HorizontalAlignment','left');


uicontrol('style','text','pos',[620 370 200 25], 'BackGroundColor',[0.8 0.8 0.8],...
    'string','Z scale:','FontSize',12,'HorizontalAlignment','left');
zsf_field=uicontrol('Style','edit','Position',[720 375 70 25],'FontSize',12,...
    'Callback','chem_spills("modify_zsf")','String',zsf);
uicontrol('style','text','pos',[800 370 100 25], 'BackGroundColor',[0.8 0.8 0.8],...
    'string','m','FontSize',12,'HorizontalAlignment','left');

uicontrol('style','text','pos',[620 330 200 25], 'BackGroundColor',[0.8 0.8 0.8],...
    'string','Time:','FontSize',12,'HorizontalAlignment','left');
st_field=uicontrol('Style','edit','Position',[720 335 70 25],'FontSize',12,...
    'Callback','chem_spills("modify_st")','String',st);
uicontrol('style','text','pos',[800 330 100 25], 'BackGroundColor',[0.8 0.8 0.8],...
    'string','days','FontSize',12,'HorizontalAlignment','left');

uicontrol('style','text','pos',[550 190 350 25], 'BackGroundColor',[0.8 0.8 0.8],...
    'string',sprintf('Maximum depth:  %3.2f m',zmax),'FontSize',12,'HorizontalAlignment','left');

raza_max=max(r_max)*sf/(2*Ts);
uicontrol('style','text','pos',[550 150 350 25], 'BackGroundColor',[0.8 0.8 0.8],...
    'string',sprintf('Maximum impact radius: %3.2f m',raza_max),'FontSize',12,'HorizontalAlignment','left');

buton5=uicontrol('Style','Pushbutton','Position',[650 50 200 30],...
    'Callback','chem_spills("4D_analysis")','String','Spatial-temporal analysis',...
    'ToolTipString','Go to Spatial-temporal analysis');

lat_start_m=lat_start-km2deg(raza_max/1000);
lat_stop_m=lat_stop+km2deg(raza_max/1000);
long_start_m=long_start-km2deg(raza_max/1000)/distance(lat_start,0,lat_start,1);
long_stop_m=long_stop+km2deg(raza_max/1000)/distance(lat_start,0,lat_start,1);
t_start_m=datestr(datenum(t_start)-st,23);

if (datenum(t_end)-datenum(t_start))>90

    t_end=datestr(datenum(t_start)+90,23);
    set(t_end_field,'string',t_end);

end


timeoutA=logintimeout(5);
connA=database('Spills','','');
ping(connA);
SQLT=sprintf('SELECT ALL
ID,LATITUDE,LONGITUDE,DATE,CHEMICAL,Quantity_in_Liters,Percent_concentration,REGION FROM
CHEMICAL_SPILLS WHERE CHEMICAL = "%s" AND REGION = "%s" AND DATE BETWEEN #%s# AND
#%s# AND LATITUDE BETWEEN %3.6d AND %3.6d AND LONGITUDE BETWEEN %3.6d AND
%3.6d',chem,reg,t_start_m,t_end,lat_start_m,lat_stop_m,long_start_m,long_stop_m);
```

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```matlab
cursorA=exec(connA,SQLT);
cursorA=fetch(cursorA,100);
Spills_data_m=cursorA.Data;
close(cursorA);
close(connA);

nr_conc=size(Spills_data,1);
nr_conc_m=size(Spills_data_m,1);

if nr_conc==nr_conc_m
    uicontrol('style','text','pos',[100 100 750 50], 'BackGroundColor',[0.7 0.7 0.7],...
        'string',[{sprintf('%d chemical spill(s) found in the selected area',nr_conc)};{'No chemical spills adjacent to the
selected area & time were included'}],'FontSize',12); %,'HorizontalAlignment','left');

elseif nr_conc_m-nr_conc==1
    uicontrol('style','text','pos',[100 100 750 50], 'BackGroundColor',[0.7 0.7 0.7],...
        'string',[{sprintf('%d chemical spill(s) found in the selected area',nr_conc)};{sprintf('%d chemical spill adjacent
to the selected area & time has been included',nr_conc_m-nr_conc)}],'FontSize',12); %,'HorizontalAlignment','left');

else
    uicontrol('style','text','pos',[100 100 750 50], 'BackGroundColor',[0.7 0.7 0.7],...
        'string',[{sprintf('%d chemical spill(s) found in the selected area',nr_conc)};{sprintf('%d chemical spills adjacent
to the selected area & time have been included',nr_conc_m-nr_conc)}],'FontSize',12); %,'HorizontalAlignment','left');

end

elseif strcmp(action,'modify_sf');

    sf=str2num(get(sf_field,'string'));
    chem_spills('analysis');

elseif strcmp(action,'modify_zsf');

    zsf=str2num(get(zsf_field,'string'));
    chem_spills('analysis');


elseif strcmp(action,'modify_st');

    st=str2num(get(st_field,'string'));
    chem_spills('analysis');

elseif strcmp(action,'4D_analysis');


    xmax=round(deg2km(distance(lat_start,long_start,lat_start,long_stop))*1000);
    ymax=round(deg2km(distance(lat_start,long_start,lat_stop,long_start))*1000);
    tmax=datenum(t_end)-datenum(t_start);

    cc=zeros(100,100,Ts,tmax);
    xcc=linspace(0,xmax,100);
    ycc=linspace(0,ymax,100);
    zcc=linspace(0,zsf,Ts);
    tcc=10^-20:1:tmax-1;

    xcube = 0:xmax:min(sf*100,xmax*100)-1;
    ycube = 0:ymax:min(sf*100,ymax*100)-1;
    %zcube = 0:100:(zmax-1)*100;
    zcube = linspace(0,zsf*100,Ts);
    tcube = 10^-20:1:st-1;
    [Ycube,Xcube,Zcube,Tcube] = ndgrid(ycube,xcube,zcube,tcube);
    X0=sf*100/2;
    Y0=sf*100/2;
    Z0=0;
    T0=0;
```

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```
    for i=1:size(Spills_data_m,1)
ci=conc4D(Spills_data_m{i,6},WFV,DC,SBD,WPV*100,LD*100,FODRW,FODRS,Xcube,X0,Ycube,Y0,Zcube,Z0,Tc
ube,T0);
        xi=round(deg2km(distance(lat_start,long_start,lat_start,Spills_data_m{i,3}))*1000*100/xmax);
        if Spills_data_m{i,3}<long_start
            xi=-xi;

        end

        yi=round(deg2km(distance(lat_start,long_start,Spills_data_m{i,2},long_start))*1000*100/ymax);
        if Spills_data_m{i,2}<lat_start
            yi=-yi;

        end


        xx=Spills_data_m{i,4};
        ti=datenum(sprintf('%s/%s/%s',xx(6:7),xx(9:10),xx(1:4)))-datenum(t_start);


        xs_cc=max(xi-fix(size(xcube,2)/2),1);
        xe_cc=max(min(xi+round(size(xcube,2)/2-1),100),1);
        ys_cc=max(yi-fix(size(ycube,2)/2),1);
        ye_cc=max(min(yi+round(size(ycube,2)/2-1),100),1);
        ts_cc=max(ti,1);
        te_cc=min(ti+st-1,tmax);

        if (xi-fix(size(xcube,2)/2))>0
            xs_ci=1;
        else
            xs_ci=modul(xi-fix(size(xcube,2)/2))+2;
        end

        xe_ci=size(xcube,2)-(max(xi+round(size(xcube,2)/2-1),100)-100);


        if (yi-fix(size(ycube,2)/2))>0
            ys_ci=1;
        else
            ys_ci=modul(yi-fix(size(ycube,2)/2))+2;
        end

        ye_ci=size(ycube,2)-(max(yi+round(size(ycube,2)/2-1),100)-100);

        if ti>0
            ts_ci=1;
        else
            ts_ci=modul(ti)+2;
        end

        if (ti+st-1)<tmax
            te_ci=st;
        else
            te_ci=tmax-ti+1;
        end

cc(ys_cc:ye_cc,xs_cc:xe_cc,:,ts_cc:te_cc)=cc(ys_cc:ye_cc,xs_cc:xe_cc,:,ts_cc:te_cc)+ci(ys_ci:ye_ci,xs_ci:xe_ci,:,ts_ci:t
e_ci);
        clear ci xi yi ti xs_cc xe_cc ys_cc ye_cc ts_cc te_cc xs_ci xe_ci ys_ci ye_ci ts_ci te_ci
    end

    t_current=round(tmax/2);
    x_current=round(25*xmax/100);
    y_current=round(50*ymax/100);
    z_current=1;
    c_lim=1;
    scalare_cc=max(max(max(max(cc))))*10^-4;

    NF=figure(4);
```

```
set(NF,'backingstore','off','NumberTitle','off',...
    'Resize','off','Position',[2 2 1398 1018],'color', [0.8 0.8 0.8],...
    'Name','Spatial-temporal spills analysis','Menubar','none','Pointer','crosshair');
tip_text1=uicontrol('Style','text','Position',[1080 10 300 30],...
    'BackgroundColor',[0.8 0.8 0.8],...
    'ForegroundColor','blue','String','Spatial-temporal spills analysis V1.1 @ 2003-2004 ');
pause(0.0001);

uicontrol('style','text','FontSize',12,'pos',[15 870 100 40],'BackGroundColor',[0.8 0.8 0.8], ...
    'string','Position:');

uicontrol('style','text','FontSize',12,'pos',[20 820 60 40],'BackGroundColor',[0.8 0.8 0.8], ...
    'string','Time:');
t_field=uicontrol('Style','edit','Position',[80 830 50 35],'FontSize',10,...
    'Callback','chem_spills("set_t")','String',num2str(t_current));
uicontrol('style','text','FontSize',12,'pos',[130 820 60 40],'BackGroundColor',[0.8 0.8 0.8], ...
    'string','days');

uicontrol('style','text','FontSize',12,'pos',[20 770 60 40],'BackGroundColor',[0.8 0.8 0.8], ...
    'string','X:');
x_field=uicontrol('Style','edit','Position',[80 780 50 35],'FontSize',10,...
    'Callback','chem_spills("set_x")','String',num2str(x_current));
uicontrol('style','text','FontSize',12,'pos',[130 770 60 40],'BackGroundColor',[0.8 0.8 0.8], ...
    'string','m');

uicontrol('style','text','FontSize',12,'pos',[20 720 60 40],'BackGroundColor',[0.8 0.8 0.8], ...
    'string','Y:');
y_field=uicontrol('Style','edit','Position',[80 730 50 35],'FontSize',10,...
    'Callback','chem_spills("set_y")','String',num2str(y_current));
uicontrol('style','text','FontSize',12,'pos',[130 720 60 40],'BackGroundColor',[0.8 0.8 0.8], ...
    'string','m');

uicontrol('style','text','FontSize',12,'pos',[20 670 60 40],'BackGroundColor',[0.8 0.8 0.8], ...
    'string','Z:');
z_field=uicontrol('Style','edit','Position',[80 680 50 35],'FontSize',10,...
    'Callback','chem_spills("set_z")','String',num2str(z_current));
uicontrol('style','text','FontSize',12,'pos',[130 670 60 40],'BackGroundColor',[0.8 0.8 0.8], ...
    'string','m');

buton1=uicontrol('Style','Pushbutton','Position',[40 570 140 30],...
    'Callback','chem_spills("create_movie")','String','Dynamics',...
    'ToolTipString','Create time-spatial evoution');

buton2=uicontrol('Style','Pushbutton','Position',[40 620 140 30],...
    'Callback','chem_spills("select_xy")','String','Set position',...
    'ToolTipString','Select the point for analysis');

uicontrol('style','text','pos',[600 560 100 40], 'BackGroundColor',[0.8 0.8 0.8],...
    'string','Colormap:','FontSize',12);
culoare=uicontrol('style','popup',...
    'string','jet|hsv|pink|cool|bone|hot',...
    'Position',[700 570 80 30],...
    'callback','chem_spills("selectie_culoare")','ToolTipString','Colormap selection');

uicontrol('style','text','FontSize',12,'pos',[10 500 100 40],'BackGroundColor',[0.8 0.8 0.8], ...
    'string','Climit:');
c_field=uicontrol('Style','edit','Position',[90 510 56 35],'FontSize',10,...
    'Callback','chem_spills("conc")','String',num2str(c_lim));
uicontrol('style','text','FontSize',12,'pos',[150 500 100 40],'BackGroundColor',[0.8 0.8 0.8], ...
    'string','[Kg/m^3]');

t_slide = uicontrol('style','slider','units','pixels','Position',[160 65 500 16],...
    'min',1,'max',tmax,'Sliderstep',[1 1/(Ts+20)],'val',t_current, ...
    'callback','chem_spills("set_t1")','string',num2str(t_current));

uicontrol('style','text','FontSize',12,'pos',[330 20 160 40],'BackGroundColor',[0.8 0.8 0.8], ...
    'string','Time [days]');
pause(0.000001);

chem_spills('distrib');
```

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```
chem_spills('conc');
% Calculate conc max
[ccmax,t_ccmax]=max(max(max(max(cc))));

% Calculate the max depth
izccmax=size(cc,3);
for i=1:size(cc,3)
    if isempty(find(cc(:,:,i,:)>scalare_cc))
        izccmax=i;
        %tz_ccmax=
        break
    end
end
z_ccmax=(izccmax-1)*zsf/Ts;

tz_ccmax=size(cc,4);
for i=1:size(cc,4)
    if ~isempty(find(cc(:,:,izccmax-1,i)>scalare_cc))
        tz_ccmax=i;
        %tz_ccmax=
        break
    end
end

%Calculate area max
for i=1:size(cc,4)
    Ai(i)=size(find(cc(:,:,1,i)>scalare_cc),1);
end
[A_ccmax tA_ccmax]=max(Ai);
A_ccmax=A_ccmax*xmax*ymax/10000;

uicontrol('style','text','FontSize',12,'pos',[800 400 600 100],'BackGroundColor',[0.8 0.8
0.8],'HorizontalAlignment','left', ...
    'string',[{'Maximal values:                    Time'};{sprintf('    Max impact area:       %5.2f m^2
%3d days',A_ccmax,tA_ccmax)};{sprintf('    Max concentration:    %5.2f Kg/m^3       %3d
days',ccmax,t_ccmax)};{sprintf('    Max depth:                %3.2f m              %3d days',z_ccmax,tz_ccmax)}]);

%chem_spills('calc');

elseif strcmp(action,'distrib');
    figure(NF);
    H_subplot=subplot(2,2,1);
    chem_spills('selectie_culoare');
    H_image=imagesc(xcc,ycc,cc(:,:,z_current,t_current),[0, 10*scalare_cc]);

    %colormap(map_g);
    axis square;
    set(gca,'Ydir','normal','XDir','reverse');
    %set(gca,'Ydir','normal');
    set(gca,'NextPlot','add');
    plot(x_current,y_current,'ro');
    plot(x_current,y_current,'r.');
    set(gca,'NextPlot','replace');

    H_title=title('Spatial distribution of concentration','FontSize',14,'FontWeight','bold');
    xlabel('x','FontSize',12,'FontWeight','bold');
    ylabel('y','FontSize',12,'FontWeight','bold','Rotation',0);

    % Calculate conc max
    [ccmax_current,zccmax_current]=max(max(max(cc(:,:,:,t_current))));

    % Calculate the max depth
    izccmax=size(cc,3);
    for i=1:size(cc,3)
        if isempty(find(cc(:,:,i,t_current)>scalare_cc))
            izccmax=i;

            break
        end
    end
```

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```
        zccmax_current=(izccmax-1)*zsf/Ts;
        A_current=size(find(cc(:,:,1,t_current)>scalare_cc),1)*xmax*ymax/10000;

    uicontrol('style','text','FontSize',12,'pos',[800 250 600 100],'BackGroundColor',[0.8 0.8
0.8],'HorizontalAlignment','left', ...
        'string',[{sprintf('Current values at t=%d days:',t_current)};{sprintf('    Impact area:          %5.2f
m^2',A_current)};{sprintf('    Max concentration: %5.3f Kg/m^3',ccmax_current)};{sprintf('    Depth:
%3.2f m',zccmax_current)}]);

    chem_spills('3D');


elseif strcmp(action,'3D');
    figure(NF);
    subplot(2,2,2);
    cla;
    set(gca,'DrawMode','fast');

    [yc,xc,zc,cs(:,:,:,t_current)]=subvolume(xcc,ycc,zcc,cc(:,:,:,t_current),[nan nan nan nan nan nan]);
    %zc=-zc;
    p = patch(isosurface(yc,xc,zc,cs(:,:,:,t_current),scalare_cc), 'FaceColor', 'blue', 'EdgeColor', 'none');
    p2 = patch(isocaps(yc,xc,zc,cs(:,:,:,t_current),scalare_cc), 'FaceColor', 'interp', 'EdgeColor', 'none');
    isonormals(yc,xc,zc,cs(:,:,:,t_current),p);
    axis ;
    %colormap(jet);
    axis([0 max(xcc) 0 max(ycc) 0 max(zcc)]);
    set(gca,'Ydir','normal','XDir','reverse','ZDir','reverse');
    %title(sprintf('Time: %s   Surface: %4.2f m^2',hour_convert(round(t(tc)*24*60),2),size(find(cc(:,:,1,tc)>1000),1)));
    %xlabel(sprintf('Depth: %4.2f m',size(find(cc(25,25,:,tc)>1000),2)/5*2));
    daspect([1 1 2]);
    grid on;
    xlabel('x','FontSize',12,'FontWeight','bold');
    ylabel('y','FontSize',12,'FontWeight','bold');
    zlabel('z','Rotation',0,'FontSize',12,'FontWeight','bold');
    colorbar
    camva(10);
    box on;
    camlight(40, 40);
    camlight(-20,-10);
    lighting gouraud;
    clear xc yc zc p p2 cs

    H_title=title('3D Spatial distribution of concentration');
    set(H_title,'FontSize',14,'FontWeight','bold');
    pause(0.00001)

elseif strcmp(action,'conc');

    c_lim=str2num(get(c_field,'string'));
    set(c_field,'string',num2str(c_lim));

    figure(NF);
    subplot(2,2,3);
    d=cc(round(100/ymax*y_current),round(100/xmax*x_current),z_current,:);
    %d=cc(round(100/ymax*y_current),round(100/xmax*x_current),z_current,:);
    conc(1:size(d,4))=d(1,1,1,1:size(d,4));
    plot(tcc,conc);
    title('Concentration at (X,Y,Z)','FontSize',14,'FontWeight','bold');
    %xlabel('Time [days]','FontSize',12,'FontWeight','bold');
    ylabel('Concentration [Kg/m^3]','FontSize',12,'FontWeight','bold');
    set(gca,'NextPlot','add','YLim',[0 max(max(conc),10^-10)]);
    plot(t_current-1,conc(t_current),'r.',t_current-1,conc(t_current),'ro');
    plot([0 max(tmax)],[c_lim c_lim],'r')
    set(gca,'NextPlot','replace');
    axis([0 max(tmax) 0 max(max(conc),10^-10)]);
    uicontrol('style','text','FontSize',12,'pos',[800 80 600 130],'BackGroundColor',[0.8 0.8
0.8],'HorizontalAlignment','left', ...
        'string',[{sprintf('Values at current position (x , y , z) = (%dm , %dm ,
%dm)',x_current,y_current,z_current)};{sprintf('    Conc max:          %5.3f Kg/m^3',max(conc))};{sprintf('    Conc:
```

```
%5.3f Kg/m^3',max(conc(t_current)))};{sprintf('    Conc/conc_limit:    %5.3f',max(conc(t_current))/c_lim)};{sprintf('
Time period where C > c_lim:    %d days',size(find(conc>=c_lim),2))}]);
    pause(0.01)

elseif strcmp(action,'select_xy');
    subplot(2,2,1);
    [x_current,y_current]=ginput(1);
    x_current=round(x_current);
    y_current=round(y_current);
    if x_current < 1,
        x_current=1;
    elseif x_current > max(xcc),
        x_current=max(xcc);
    end
    if y_current < 1,
        y_current=1;
    elseif y_current > max(ycc),
        y_current=max(ycc);
    end
    set(x_field,'string',num2str(x_current));
    set(y_field,'string',num2str(y_current));
    chem_spills('distrib');
    chem_spills('conc');

elseif strcmp(action,'calc');
    figure(NF);
    subplot(2,2,4);
    set(gca,'color',[ 0.7 0.7 0.7],'XTick',[],'YTick',[],'ZTick',[],'Box','on');
    title('Calculations','FontSize',14,'FontWeight','bold');

elseif strcmp(action,'set_t');
    t_current=str2num(get(t_field,'string'));
    set(t_field,'string',num2str(t_current));
    chem_spills('distrib');
    chem_spills('conc');

elseif strcmp(action,'set_t1');
    t_current=round(get(t_slide,'val'));
    set(t_field,'string',num2str(t_current));
    chem_spills('distrib');
    chem_spills('conc');


elseif strcmp(action,'set_x');
    x_current=str2num(get(x_field,'string'));

    if x_current < 1,
        x_current=1;
    elseif x_current > max(xcc),
        x_current=max(xcc);
    end
    set(x_field,'string',num2str(x_current));
    chem_spills('distrib');
    chem_spills('conc');

elseif strcmp(action,'set_y');
    y_current=str2num(get(y_field,'string'));
    if y_current < 1,
        y_current=1;
    elseif y_current > max(ycc),
        y_current=max(ycc);
    end

    set(y_field,'string',num2str(y_current));
    chem_spills('distrib');
    chem_spills('conc');


elseif strcmp(action,'set_z');
    z_current=str2num(get(z_field,'string'));
```

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```
        if z_current < 1, .
          z_current=1;
        elseif z_current > max(zcc),
          z_current=max(zcc);
        end

        set(z_field,'string',num2str(z_current));
        chem_spills('distrib');
        chem_spills('conc');

    elseif strcmp(action,'create_movie');
        % Time-spatial distribution movie
        t_current1=t_current;
        figure(NF);
        subplot(2,2,1);

        MOV=moviein(tmax);
        for i=1:tmax,
            subplot(2,2,1);
            imagesc(xcc,ycc,cc(:,:,1,i),[0, 10*scalare_cc]);
            set(gca,'Ydir','normal','XDir','reverse');
            %   set(gca,'Ydir','normal','XDir');
            axis square;
            %colormap(map_g);
            set(gca,'NextPlot','add');
            plot(x_current,y_current,'ro')
            plot(x_current,y_current,'r.')
            title('Spatial-temporal evolution at Z','FontSize',14,'FontWeight','bold');
            xlabel('x [m]','FontSize',14,'FontWeight','bold');
            ylabel('y [m]','FontSize',14,'FontWeight','bold');
            pause(0.00001)
            set(gca,'NextPlot','replace');

            MOV(:,i)=getframe;
            t_current=i;
            set(t_field,'string',num2str(t_current));
            set(t_slide,'val',t_current);

            [ccmax_current,zccmax_current]=max(max(max(cc(:,:,:,i))));
            izccmax=size(cc,3);
            for j=1:size(cc,3)
              if isempty(find(cc(:,:,j,i)>scalare_cc))
                izccmax=j;

                break
              end
            end
            zccmax_current=(izccmax-1)*zsf/Ts;


            A_current=size(find(cc(:,:,1,i)>scalare_cc),1)*xmax*ymax/10000;

            uicontrol('style','text','FontSize',12,'pos',[800 250 600 100],'BackGroundColor',[0.8 0.8
        0.8],'HorizontalAlignment','left', ...
                'string',[{sprintf('Current values at t=%d days:',t_current)};{sprintf('   Impact area:        %5.2f
        m^2',A_current)};{sprintf('   Max concentration: %5.2f Kg/m^3',ccmax_current)};{sprintf('   Depth:
        %3.2f m',zccmax_current)}]);

            chem_spills('3D');
            chem_spills('conc');
        end
    %   mpgwrite(MOV,colormap,'film.mpg');
    %   set(t_field,'string',num2str(t_current));
    %   chem_spills('set_t');

    elseif strcmp(action,'selectie_culoare'),
        valmap=get(culoare,'value');
        if valmap==1
            map_g=colormap(jet);
            map_g(1,:)=[0.9 0.9 0.9];
```

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```
      colormap(jet)
      colormap(H_subplot,map_g);
      maptype='jet';
   end
   if valmap==2
      map_g=colormap(hsv);
      map_g(1,:)=[0.9 .9 0.9];
      colormap(hsv);
      maptype='hsv';
   end
   if valmap==3
      map_g=colormap(pink);
      map_g(1,:)=[1 1 1];
      colormap(pink);
      maptype='pink';
   end
   if valmap==4
      map_g=colormap(cool);
      map_g(1,:)=[1 1 1];
      colormap(cool);
      maptype='cool';
   end
   if valmap==5
      map_g=colormap(bone);
      map_g(1,:)=[1 1 1];
      colormap(bone);
      maptype='bone';
   end
   if valmap==6
      map_g=colormap(hot);
      map_g(1,:)=[0.3 1 0.3];
      colormap(hot);
      maptype='hot';
   end
end
```