Risk-based monitored natural attenuation — a case study

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Abstract

The term "monitored natural attenuation" (MNA) refers to a reliance on natural attenuation (NA) processes for remediation through the careful monitoring of the behavior of a contaminant source in time and space domains. In recent years, policymakers are shifting to a risk-based approach where site characteristics are measured against the potential risk to human health and the environment, and site management strategies are prioritized to be commensurate with that risk. Risk-based corrective action (RBCA), a concept developed by the American Society for Testing Materials (ASTM), was the first indication of how this approach could be used in the development of remediation strategies.

This paper, which links ASTM's RBCA approach with MNA, develops a systematic working methodology for a risk-based site evaluation and remediation through NA. The methodology is comprised of seven steps, with the first five steps intended to evaluate site characteristics and the feasibility of NA. If NA is effective, then the last two steps will guide the development of a long-term monitoring plan and approval for a site closure. This methodology is used to evaluate a site contaminated with oil from a pipeline spill. The case study concluded that the site has the requisite characteristics for NA, but it would take more than 80 years for attenuation of xylene and ethylbenzene, as these chemicals appear in the pure phase. If fast remediation is sought, then efforts should be made to remove the contaminant from the soil. Initially, the site posed a serious risk to both on-site and off-site receptors, but it becomes acceptable after 20 years, as the plume is diluted and drifts from its source of origin. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Monitored natural attenuation; RBCA; Natural attenuation; MNA; Site remediation; Pollution control

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1. Introduction

It is estimated that in the next three decades between 373 billion and 1.694 trillion dollars will be required to remediate hazardous waste sites in the USA [1]. The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and the Resource Conservation Act (RCRA) will mandate the bulk of this expenditure. According to estimates made by the US EPA, around 330,000 sites in the USA are contaminated. Out of these, more than 2000 are on the CERCLA national priority list and between 1500 and 3000 are RCRA sites, while 295,000 sites are categorized as leaking underground fuel tank sites [2,3]. The hundreds of billions of dollars slated for the cleanup of these sites will not benefit health care, education, social security, or infrastructure renewal. It might be defensible if the money provided an equivalent benefit to human health or the environment [3]. In 1994, the National Research Council's (NRC) review of technologies concluded that, "conventional technologies has restored contaminated groundwater to regulatory standards at 8 of 77 sites evaluated in the previous studies" [4]. In the most recent comprehensive review NRC stated that, "Although considerable efforts have been invested in groundwater and soil cleanup, the technologies available for these cleanups are relatively rudimentary" [5,6].

Soil and groundwater contamination and remediation problems are worldwide. An estimate of the number of such contaminated sites is alarming: 50,000 sites in Germany, 110,000 sites in the Netherlands, and 10,000 sites in Denmark require remediation. Similarly, there are more than 200,000 ha of contaminated land within the United Kingdom [7], where the cost of remediation of the soil and the associated groundwater could easily exceed 10,000 million pounds [8].

The risks associated with soil and groundwater contamination are significant, but conventional cleanup may be more costly in terms of litigation, financing, remediation, public relations, land transfer and associated development. Increasing public awareness and the introduction of environmental legislation have created a state of exaggerated risk perception associated with contaminated soils. The remedial goals for contaminated sites are often unnecessarily stringent, giving rise to vastly inflated costs for soil and groundwater cleanup. As a result, many old contaminated sites lie undeveloped because the estimated remedial costs are much higher than the land value [6]. Quantifying real risk rather than allowing perceived risk to dominate decision-making processes would enable a more cost-effective and targeted response to contaminated site problems [9].

In recent years, many countries have rewritten rules and passed legislation to facilitate the judicious allocation of remediation resources to expedite remediation and project closures [3,10,34]. To accomplish these goals, policymakers are shifting to a risk-based approach where site characteristics are measured against the potential risk to human health and the environment. Subsequently, site management strategies are prioritized to be commensurate with that risk. Risk-based corrective action (RBCA), a concept developed by the American Society for Testing Materials (ASTM), was the first formalization of the use of this approach in the development of remediation strategies. By focusing on actual and potential risks, the goal of protecting human health and the environment is expeditiously achieved.

The concept reported in this paper links ASTM's RBCA approach with natural attenuation (NA), and develops a systematic working methodology for risk-based site evaluation and

remediation through NA. Subsequent sections give a brief description of the methodology, followed by an application.

2. Risk-based corrective action (RBCA)

Before examining the RBCA process, it is important to define risk and the risk assessment process. In the present context, risk is related to the toxicity of a chemical(s) as well as exposure to that chemical(s). Risk assessment is a calculation of the total risk to human health and the environment [9] and involves: (i) data collection and evaluation; (ii) toxicity assessment; (iii) exposure assessment; and (iv) risk characterization. Toxicity assessment analyzes a contaminant on the basis of its carcinogenic and non-carcinogenic characteristics; exposure assessment considers current and possible future contaminant exposure; and risk characterization seeks to predict the net effect of toxicity and exposure.

The ultimate objective of environmental cleanup is the minimization of health risk in a cost-efficient and timely fashion. Cleanup decisions and site characterization should reflect the interplay between cost and health risk reduction [11–13]. Cleanup targets must be part of this balancing act because both cost and risk reduction depend directly on the definition of "clean" for a particular site. Attempts have been made to define protocols for the cleanup decision-making process; the most notable of these is the RBCA approach. Recognizing that all sites are different, the RBCA approach relies on a tiered approach or gradual response to site characterization and remediation efforts in soil and groundwater contamination. The initial site screening places individual sites in specific tiers, depending on the potential risk and specific site characteristics. Remediation efforts concentrate on those sites which pose the greatest health risk. Site characterization efforts are specifically directed to collecting the necessary information for risk-based decision-making. The RBCA approach calibrates cleanup efforts to reflect the risk to human health and the environment. The urgency for cleanup is proportional to the health threat and focuses on adjusting the cleanup to the potential future use of the site. This is a better approach than assuming that all aquifers will be used for drinking water.

The RBCA approach [14] involves three tiers: Tier 1 involves a traditional initial site assessment based on source characterization, the potential for exposure, the extent of contaminant migration, and a summary of the site characterization results. Contaminant concentrations are compared with risk-based screening levels (RBSLs) derived from conservative default fate-and-transport and risk assessment parameters. If the results of a Tier 1 assessment, which is based on conservative default parameters, are unacceptable due to cost or feasibility considerations, additional site information can be collected for reassessment according to Tier 2 criteria. In general, a Tier 1 evaluation identifies sites which require no further action. For sites which exceed the Tier 1 limit, Tier 2 analysis provides a more cost-efficient basis for an evaluation of remedial measures.

Tier 2 involves the use of site-specific data (instead of Tier 1 default levels) to develop site-specific target levels (SSTLs), which are based on the site's relevant physical and chemical characteristics, augmented by analytical fate-and-transport and risk assessment modeling. This measures migration and attenuation of contaminants from the source area(s). As with Tier 1, site conditions in Tier 2 are analyzed to determine achievable, appropriate, and economical remedial action goals. Tier 1 RBSLs and Tier 2 SSTLs represent concentration

limits for constituents within the source zone. However, SSTLs differ from RBSLs in three significant ways [15,16]:

1. site-specific data is used to calculate risk-based cleanup goals;
2. human exposure to affected media may occur not only at the source zone, but at a separate point of exposure (POE); and
3. the effects of NA on constituent concentrations during lateral transport from the source to an off-site POE are considered in the SSTL calculation.

If Tier 2 remedial measures are unacceptable, additional site information can be collected for a reassessment according to Tier 3 criteria.

Tier 3 involves a further expanded site assessment with SSTLs based on more sophisticated statistical, fate-and-transport and risk assessment models. Tier 3 is rarely used because of the complexity of the models and the requirement for highly specific data, without a significant improvement in the predictions. A simplified architecture of RBCA is shown in Fig. 1 [9].
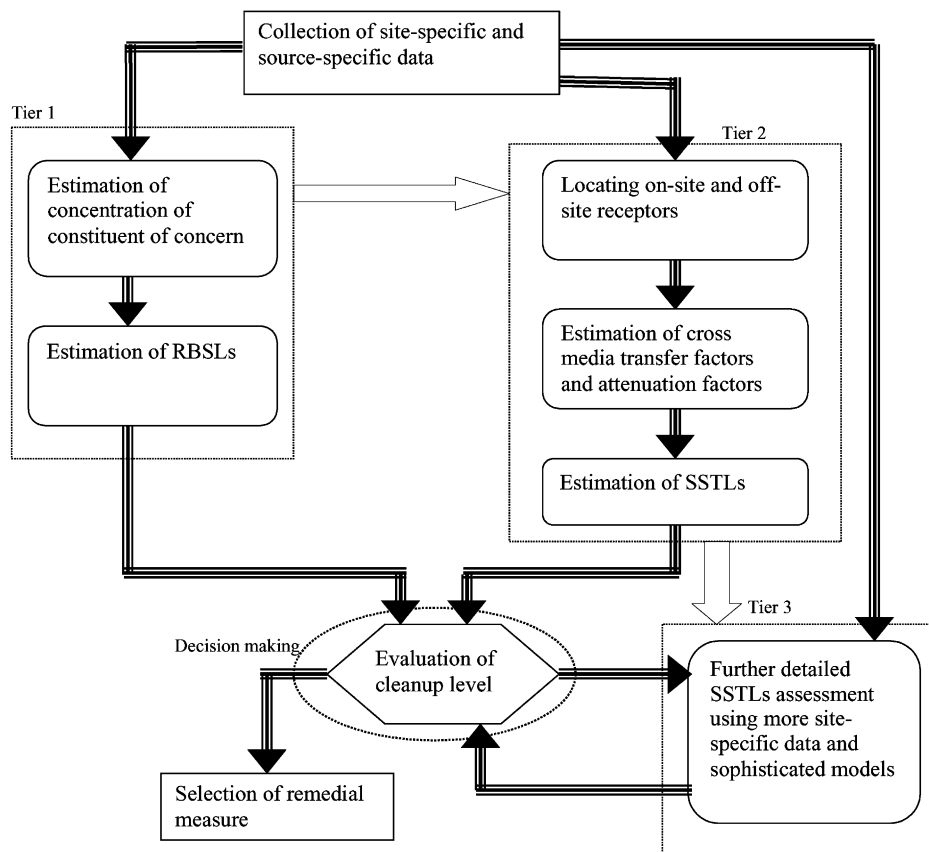

Fig. 1. Simplified architecture of RBCA system.

3. Monitored natural attenuation (MNA)

MNA refers to the observed reduction in contaminant concentrations as the contaminant migrates from the source to the environmental media and EPA [17] defines MNA as follows:

The term monitored natural attenuation, as used in this directive, refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored site cleanup approach) to achieve site-specific remedial objectives within a time frame that is reasonable compared to that offered by other more active methods.

The naturally attenuating processes at work in such a remediation approach include a variety of in situ physical, chemical, or biological processes, which under favorable conditions act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and groundwater [6,18,34]. These in situ processes include biodegradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization of contaminants. A particular NA site may include any or all of these processes. Naturally attenuating contaminant plumes can expand, remain stable, or shrink, depending on trends in the spatial variation of contaminant concentrations over time. A common feature of all attenuating plumes is a decline in the contaminant concentration with time and down-gradient from the source.

Generally, the nature of the groundwater system and the behavior of the contaminants complicate the study of the MNA process. Contaminants in the subsurface distribute themselves among various media (soil, water, and soil vapor) and can exist in different phases (aqueous, non-aqueous, and vapor). Additionally, processes such as dissolution, sorption, and biodegradation control their fate and transport. Many of these processes are still poorly understood. Nonetheless, significant progress has been made in the last decade in quantifying NA of contaminants in groundwater systems [10,34]. Field protocols, analytical and numerical models, and numerous databases have emerged from field characterization studies [15,19,20].

4. Methodology for risk-based monitored natural attenuation (RBMNA) evaluation

The most comprehensive cleanup protocol that includes a consideration of NA has been proposed by AFCEE [21] and Wiedemeier et al. [22,23]. In this paper, we have developed a more efficient and compact methodology by combining the RBCA approach with the MNA evaluation system earlier proposed by Wiedemeier et al. [23]. This new methodology is named RBMNA and is described below (Fig. 2).

4.1. Step 1: review of available data and risk characterization

This step involves Tiers 1 and 2 of RBCA. In this step, the available site data is used to compute the risk to on-site receptors as in Tier 1 of RBCA. If the computed risk is higher than the threshold, either engineering remediation or further analysis using Tier 2 of RBCA
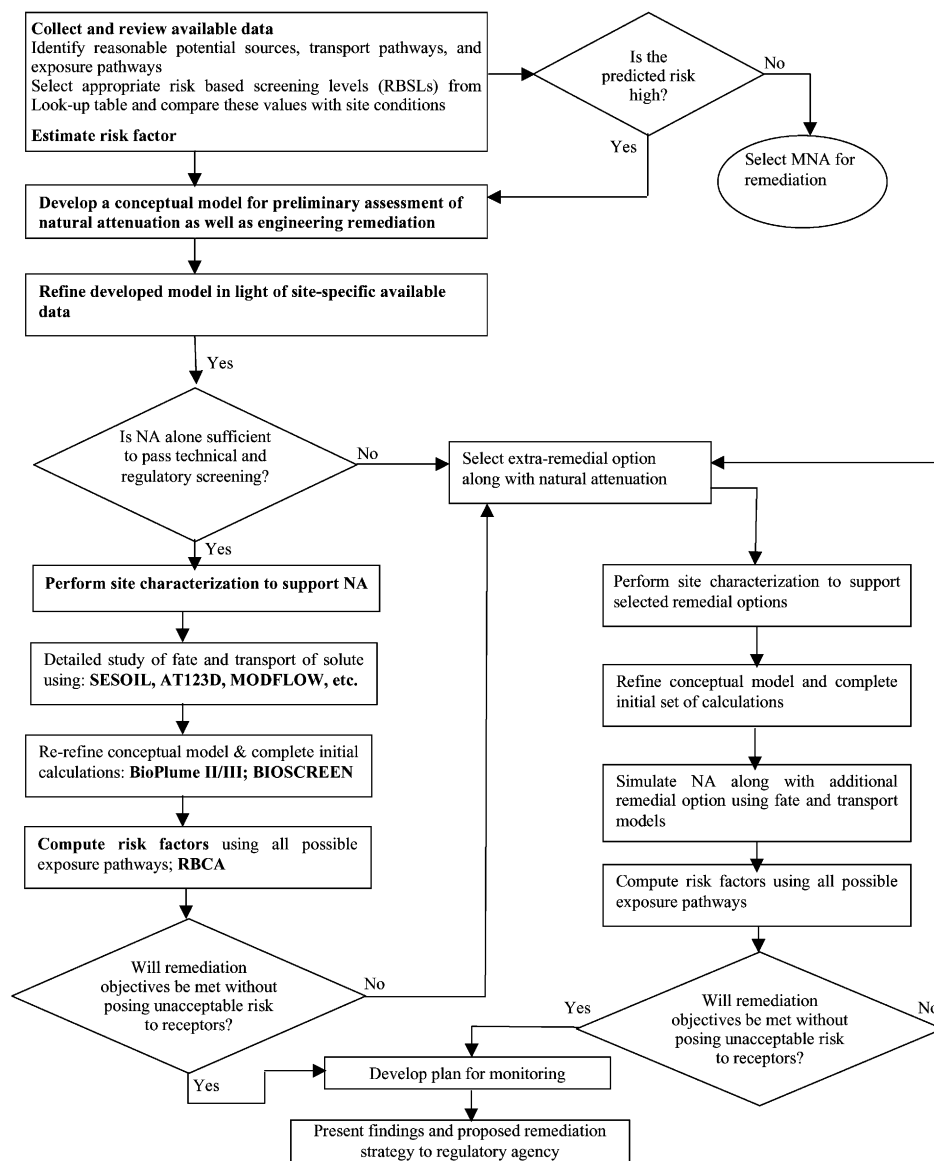
Fig. 2. Methodology for risk-based monitored natural attenuation remediation process.

is required. Based on the risk potential estimated earlier (through Tiers 1 and 2 of RBCA) and available site data, the site is evaluated for NA as the remedial option. If the site has the potential for NA, a detailed evaluation study is conducted using steps 2 to 5 (discussed below). The data collected in this step include the nature and extent of the contamination and the duration of release. The nature of the contaminant is particular important.

4.2. Step 2: developing a conceptual model

This step focuses on the development of the conceptual model required for the integration of contaminant history, and the assessment of biogeochemical attenuation, site hydrology data, and exposure duration and pathways.

4.3. Step 3: refining the conceptual model

This step involves filling in the gaps identified in the previous steps and the collection of data, particularly those which track NA in the subsurface and are important for risk computation, such as electron acceptor levels (e.g. O_2, NO_3^-, Fe^{3+}) which point to oxidation of the hydrocarbons. The conceptual model developed in step 2 is modified using recently available data. Wiedemeier et al. [19,23] highlight the use of contaminant contour maps, as well as electron acceptor, metabolic by-product, and alkalinity maps for such purposes. Sorption, biodegradation and other processes also need to be assessed. A detailed discussion of this step and the required data has been presented by Brady et al. [3].

4.4. Step 4: modeling of NA using analytical and/or numerical fate-and-transport models

This step, the most important of the RBMNA methodology, models transport of contaminant in soil and groundwater and attenuation due to dilution, transformation, degradation, and adsorption, etc.

The modeling of NA simulates solute transport affected by advection, dispersion, sorption, and biodegradation as well as groundwater flow fields in which contaminants are transported. Models which simulate groundwater flow and solute transport are classified according to the mathematical technique used to solve the governing mathematical expressions. Analytical models provide an exact solution to the flow and transport governing equations and associated initial boundary conditions. Numerical models, on the other hand, give an approximate solution to the problem [19,20].

NA models predict migration and degradation of dissolved contaminant plumes. These models also predict contaminant concentrations in a receptor well, and estimate the time required for contaminants to reach a potential receptor. The modeling of NA involves: (i) a conceptual model as an idealized representation of the natural system; (ii) a mathematical model representing controlling mechanisms in mathematical terms; (iii) solution of the mathematical model; (iv) calibration of the solution by adjusting the computed response with the natural system; (v) validation of the accuracy of the model's prediction; and (vi) simulation based on the calibrated solution of the conceptual model.

Analytical models are useful in defining the magnitude of a contaminant problem. If limited data is available or hydrological conditions are simple, an analytical model simulates contaminant fate and transport. Numerical models are less burdened by simplified assumptions and are capable of addressing more complicated problems. If the required data is available, numerical models can handle surface heterogeneity and varying aquifer parameters. The resolution of numerical model results depends upon the degree of discretization of the site and associated parameters. Numerical models require an understanding of the dimensional distribution of both aquifer hydraulic properties and contaminants. The

implementation of numerical models is relatively more complex than analytical models. The final decision whether to use an analytical or a numerical model is based on the complexity of the problem, data availability, and the importance of the results generated by the models. A list of available analytical and numerical models for NA modeling is presented in Table 1.

The ultimate objective of NA modeling is to effectively reproduce the chemical and physical behavior of a site from a fundamental understanding of the processes, so that the long-term behavior of a plume can be confidently predicted. For details of fate-and-transport modeling of contaminants see Hossein and Rose [24], Oelkers et al. [25], McDonald and Gelston [26], Hetrick and Scott [27], Clark and Richardson [35] and Wiedemeier et al. [19]. A variety of codes developed to perform these calculations include BIOPLUME II and III [20,28] which have been used to argue successfully for the NA option for fuel hydrocarbons. In all likelihood, the latest version of BIOSCREEN [29], will be used with increasing frequency to support remediation of organic contaminants by NA.

4.5. Step 5: exposure pathway analysis

This step analyzes the most likely pathways for contaminant exposure and computes the associated risk for current and reasonable future scenarios. Unlike step 1, which is used as a screening tool, this step uses the results of a detailed fate-and-transport model in computing contaminant concentration and risk estimation as with Tier 3 of RBCA. Engineering remediation options are selected according to the severity of the risk; if the risk posed is not severe, the feasibility of MNA as a remediation option is explored. If NA is demonstrably effective, a long-term monitoring plan is developed.

4.6. Step 6: preparation of long term monitoring (LTM) plan

A long-term monitoring (LTM) plan includes the site, the number of monitoring wells, the frequency of monitoring, and analysis. Two type of monitoring wells are advisable: LTM wells to determine if plume behavior changes, and point of compliance (POC) wells to detect contaminant movement outside the negotiated perimeter of a contaminant. LTM wells should be uniformly distributed throughout the contaminant area, while POC wells are placed at both hypothetical and existing receptor positions. The distribution of LTM wells is dependent upon the size and type of the contaminant site, and should be sufficient in number to represent the plume behaviors. By their function, LTM wells should include analyses for contaminant levels, and if the contaminants are organic, these wells should include electron acceptor analysis. In the same situation, POC wells should sample for contaminant levels as well as for dissolved oxygen [19,22]. The sampling frequency should depend upon the trend observed in previous samples.

4.7. Step 7: obtaining approval for MNA

Negotiations with regulators are critically important. For fuel hydrocarbons, the argument for MNA relies primarily on three observations:

- *Trend of contaminant disappearance*. The best supporting evidence for NA is a demonstration of a rapid decrease in contaminant concentration with time.

Table 1
Important analytical and numerical models for transport modeling [19]

Model	Capabilities
Analytical models	
AGU-10	Analytical flow, advective solute transport, advective–depressive transport with decay and without decay
AT123D	Based on analytical solution for transient one-, two- and/or three-dimensional transport in a homogenous isotropic aquifer with uniform regional flow. Allows for retardation, dispersion, and first-order decay, with differing source configuration and boundary conditions
1-D	Package of five analytical solutions of one-dimensional advective–depressive transport equation with adsorption, dispersion, and first-order decay options
PLUME, PLUME2D	Analytical models for calculating point concentrations of solutes. Includes advection, dispersion, retardation, and first-order decay. Source terms can be varied over time
PRINCE	Proprietary package of 10 analytical solute transport and flow models, widely referred to as the Princeton Analytical Models. Advection, dispersion, retardation and first-order decay can be simulated, along with a wide range of source terms
SOLUTE	Menu-driven set of five different programs provide the user with nine different types of analytical solute transport models
USGS-SOL	Analytical solutions describing advective–depressive transport, as well as first-order decay and retardation. Includes one-, two-, and three-dimensional models
WALTON35	Set of 35 analytical and numerical models for a variety of groundwater flow and solute transport problems
BIOSCREEN	Natural attenuation decision support system for simulating the nature of dissolved hydrocarbons. Based on Domenico analytical solute transport model that simulates groundwater flow, linear isotherm sorption, three-dimensional dispersion, first-order and instantaneous decay used as a screening tool to determine whether attenuation is feasible at a particular site
Numerical models	
AQUA	Two-dimensional, transient groundwater flow and transport. Aquifer may be heterogeneous and anisotropic. Can simulate advection, dispersion, linear sorption and decay
ASM	Aquifer simulation model for two-dimensional modeling of groundwater flow and solute transport. Uses random-walk method for solute transport, and can simulate advection, dispersion, linear sorption, and decay. Aquifer can be heterogeneous and anisotropic
BIO1D	One-dimensional model for simulation of biodegradation and sorption of hydrocarbons. Transport of substrates and electron acceptors is considered, assuming a uniform flow field. Several biodegradation models are available
BIOPLUME II	Two-dimensional model for simulating transport of single dissolved hydrocarbon species under the influence of oxygen-limited biodegradation, first-order decay, linear sorption, advection, and dispersion. Aquifer may be heterogeneous and anisotropic. It is a public domain code
BIOPLUME III	Successor to BIOPLUME II. Two-dimensional model for reactive transport of multiple hydrocarbons under the influence of advection, dispersion, sorption, first-order decay, and reactant-limited biodegradation

Table 1 (*Continued*)

Model	Capabilities
BioTrans	Proprietary two-dimensional finite-element transport code requiring flow velocity data from another code. Models transport of multiple species under the influence of advection, dispersion, sorption, first-order decay, and oxygen-limited biodegradation. Allows internal computation of source terms due to dissolution of NAPL
FEMSEEP	Simple programs for solving steady-state groundwater flow and solute transport problems in simplified two- and three-dimensional systems. Transport under the influence of advection, dispersion, linear sorption, and first-order decay may be simulated using finite elements methods
FEMWATER and FEMWASTE	Finite-element flow (FEMWATER) and transport (FEMWASTE) models. FEMWATER can simulate variably saturated conditions in two- and three-dimensions. FEMWASTE can simulate transport in one-, two-, and three-dimensions. The system may be heterogeneous and anisotropic and the code can account for advection, dispersion, first-order decay, and three types of sorption. It is a public domain code
FLONET, FLOWTRANS	Two-dimensional steady-state groundwater flow (FLONET) and transient solute transport (FLOTRANS) models for cross-sectional problems. FLOTRANS is an extension of FLOWNET that can simulate transport under the influence of advection, dispersion, linear sorption, and first-order decay
FTWORK	Block-centered finite-difference model for one-, two-, and three-dimensional flow and transport. The transport includes advection, dispersion, and first-order decay and two types of sorption (linear and non-linear)
MODFLOW	Block-centered finite-difference code for steady-state and transient simulation of groundwater flow in two- and three-dimensions. Can be used to generate flow fields that may be coupled with a wide variety of transport models, e.g. MT3D, BioTrans, and RAND3D
MODFLOP	Extension of MODFLOW, includes a package that uses non-linear regression techniques to estimate model parameters under constraints given by modeler. Model input includes statistics for analyzing parameter estimates and the model to quantify the reliability of the resulting model
MT3D	Three-dimensional transport model for simulation of advection, dispersion, linear or non-linear sorption, and first-order decay of single species. Uses the modular structure similar to MODFLOW
RAND3D	Three-dimensional version of random walked algorithm. Designed to be coupled with MODFLOW input files for calculations of velocity vector files used to run the code. Used for transient simulation of advection, dispersion, linear sorption, and zero order, first-order, or variable order decay
RT3D	Modification of MT3D. RT3D (reactive transport in three-dimensions) is designed to describe multi-species transport and reactions, including attenuation of chlorinated compounds and their daughter products. Also included are modules for aerobic, instantaneous BTEX reactions and multiple-electron-acceptor kinetically limited BTEX reactions
SWICHA	Three-dimensional element code for simulating steady-state and transient flow and transport in confined aquifer
TRAGET	Code for simulating two- and three-dimensional flow and transport under a wide variety of conditions. Can simulate advection, dispersion, diffusion, sorption, and first-order decay

- *Loss of electron donors*. Depressed electron donor (e.g. O_2, NO_3^-, SO_4^{2-}, etc.) levels, relative to a measured background, provide evidence for the degradation of organic matter and the effectiveness of NA.
- *Degradation products*. Fe^{2+}, H_2S, CO_2, and CH_4 are produced during the degradation of fuel hydrocarbons. Elevated levels relative to the background also suggest degradation of the contaminant and the effectiveness of NA.

5. Application of RBMNA to evaluate NA on a hydrocarbon spill site

5.1. Problem statement and site characteristics

On 11 October, 1996, a 48 in. pipeline which connected a refinery to a transportation terminal, ruptured, releasing a significant volume of crude oil. Fig. 3 depicts the site layout, the location of the monitoring well, and the contaminated area. To maintain confidentiality, site details, including the name, are omitted. A preliminary investigation provided the following information:
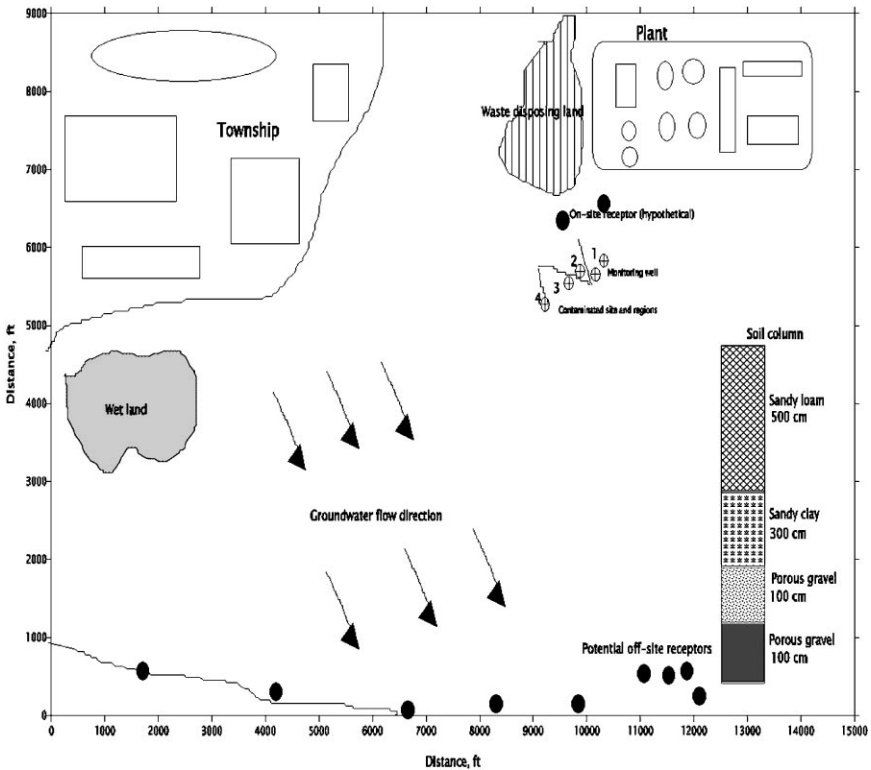

Fig. 3. Site layout and location of spill.

- The shallow groundwater was approximately 10–15 m below the ground surface.
- The groundwater was of good quality and needed to be protected.
- The rupture caused the release of about 150,000 barrels of oil on the ground surface.
- An area of about $81,000 \, \text{m}^2$ was contaminated due to the spillage.
- Out of five wells drilled for a preliminary investigation, two wells had a thick accumulation of oil, while the remaining three wells did not have any oil content.
- The contaminant plume was expected to move down the water table gradient towards the southeast, and away from the community. There was no potential receptor within 1.5 km downstream from the site.
- The soil strata were comprised of fractures, solution cavities, and a relatively impermeable layer just over the aquifer. The general soil profile of the area is depicted in Fig. 3.

In the present study, this site is evaluated for NA using RBMNA. To account for the heterogeneity of the area, the total contaminated zone is divided into four regions. Regions 3 and 4 have fracture flow, and are modeled using high permeability soil (sand), whereas regions 1 and 2 are modeled using the original soil strata (sand, clay, and gravel). Additionally, a geological study reveals that region 1 contains an impermeable layer of clay in the third layer of soil (300 cm thick). The results of this study are summarized according to RBMNA.

6. Results and discussions

Step 1. As the oil spill is not old, there is little data available about the fate and transport of the contaminant. However, a preliminary study collected important details about the site and the contaminant. These details were subsequently used to estimate the risk potential to on-site and off-site receptors (Tiers 1 and 2 of RBCA). A residential on-site receptor was considered in the analysis. According to RBCA's Tier 1 study, the concentration of benzene at the on-site receptor was predicted to be more than 10 times higher than the risk-based screening level (RBSL) of benzene. The analysis predicts a concentration 100% higher than the SSTLs for the off-site receptor (according to RBCA's Tier 2). This necessitated the detailed investigation discussed in the following steps.

Steps 2 *and* 3. A conceptual model of the site and the attenuation process was developed. As stated earlier, the site is comprised of four regions to account for the heterogeneity of the area. Subsequent data related to hydrology and electron receptors observed at the site is compiled in Table 2. It is clear from the tabulated data that the site has good potential for NA, as the concentration of electron acceptors in the background is high, and hydrological conditions favor NA. In Table 2, the size of the aquifer is considered infinite because of the large size of the aquifer ($\sim$100 km^2). There is little data available about contaminant migration, plume geometry, and attenuation characteristics; however, this information would be generated by fate-and-transport modeling of the contaminants.

Step 4. In this step, three computer-aided tools were used to study the transportation and transformation of the contaminant in different zones: SESOIL [27,30,31] for contaminant modeling in an unsaturated zone; AT123D for fate and migration of contaminants in a saturated zone [27,30,31]; and BIOSCREEN for NA [29]. The results are summarized below.

Table 2
Initial set of conditions used in the present study

Parameters	Region 1	Region 2	Region 3	Region 4
Average ambient temperature ($^\circ$C)	35	35	35	35
Average ambient pressure (kPa)	101.35	101.35	101.35	101.35
Number of soil layers	4	4	4	3
Number of sub-layers	2	2	2	2
Thickness of soil layer (cm)	500, 300, 100, 100	600, 200, 100, 100	600, 200, 150, 50	600, 300, 100
Soil type	Sandy clay with porous gravel and clay loam	Sandy clay loam with porous gravel	Loamy sand with porous gravel	Loamy sand with porous gravel
Application area (cm^2)	1.63E+08	1.63E+08	1.63E+08	1.63E+08
Site latitude ($^\circ$)	21.56	20.40	15.56	18.45
Loading rate of benzene (μg/cm^2)	2.5E+06	2.5E+06	2.5E+06	2.5E+06
Loading rate of toluene (μg/cm^2)	5.0E+06	5.0E+06	5.0E+06	5.0E+06
Loading rate of ethylbenzene (μg/cm^2)	7.5E+06	7.5E+06	7.5E+06	7.5E+06
Loading rate xylene (μg/cm^2)	1.0E+07	1.0E+07	1.0E+07	1.0E+07
Background concentration of O_2 (mg/l)	1.65	1.95	1.90	2.0
Background concentration of NO_3^- (mg/l)	0.7	1.5	0.98	1.15
Background concentration of SO_4^{2-} (mg/l)	22.2	23.2	23.7	24.5
Background concentration of Fe^{3+} (mg/l)	16.6	17.4	18.8	15.4
Background concentration of CH_4 (mg/l)	1.5	3.5	4.5	3.5
Size of aquifer (cm^2)	Infinite	Infinite	Infinite	Infinite
Depth of aquifer (cm)	2000	2000	2000	2000

6.1. Modeling of vadose zone

The soil column was modeled for four layers (Fig. 3, Table 2) with the contaminant loaded on the uppermost layer. The thickness and characteristics of the soil column layers vary with the region. Transportation and transformation of the main components of the crude oil (benzene, toluene, ethylbenzene, and xylene in the soil column) were simulated for a period of 80 years using SESOIL. The simulated results for benzene in region 1 predict that most of the benzene would be either volatilized (∼76%) or biodegraded (∼24%, Table 3). Therefore, in the soil in region 1, the benzene leachate concentration is negligible. This is similar to toluene. Ethylbenzene and xylene, however, mainly stay in the pure phase in the soil column and a substantial fraction is biologically degraded (∼10%). The pure phase of ethylbenzene and xylene acts as a non-aqueous phase liquid (NAPL), which is a continuous source of contaminant to the groundwater.

In region 2, the contaminants show rapid transportation (Table 3). As with region 1, a major portion of the benzene is volatilized; however, a substantial amount is transported with moisture to the groundwater (∼1%), causing a moderately high leachate concentration. Toluene shows a comparatively slower movement: toluene is either volatilized or degraded (41 and 58%, respectively), and only a small amount reaches the groundwater (Table 3). Xylene shows a comparatively fast movement; however, a large portion remains in the pure phase in the soil (∼88%), and a small fraction (<4%) is degraded. A similar trend is observed for ethylbenzene (Table 3).

Region 3, which is modeled as a fracture flow, shows an exceptionally high rate of contaminant transportation (Table 4). Benzene moves fastest and about 6% reaches the groundwater, causing a high leachate concentration in the groundwater. However, a major portion of benzene (about 87%) is volatilized. Toluene also moves quite fast: about 57% is volatilized, 42% is biologically degraded, and only a small amount (<1%) reaches the groundwater (Table 4). Xylene moves faster than ethylbenzene, with about 90% remaining in the pure phase in the soil/groundwater, and acts as continuous source for the groundwater contamination plume. Similar to xylene, a major portion of ethylbenzene (66%) remains in the pure phase, but a considerable portion is either biologically degraded or volatilized (27%).

The results of region 4 follow the trend for region 3. The values of various parameters in this region are lower than those observed for region 3 (Table 4).

6.2. Modeling of saturated zone

The saturated zone is located about 10 m below the ground surface. This aquifer is about 20 m thick. Transportation and transformation of chemicals in the aquifer were modeled using AT123D [27,31,32]. As with the unsaturated zone modeling, the same four zones were also studied for four different constituents. A continuous source was considered for ethylbenzene and xylene present in the pure phase; for benzene and toluene, an instantaneous source was assumed.

As stated earlier, the movement of contaminant in region 1 is slow. The concentration of benzene and toluene in the aquifer is negligible (Fig. 4) because of the lengthy duration of these constituents in the soil, where they are either biologically degraded or volatilized.
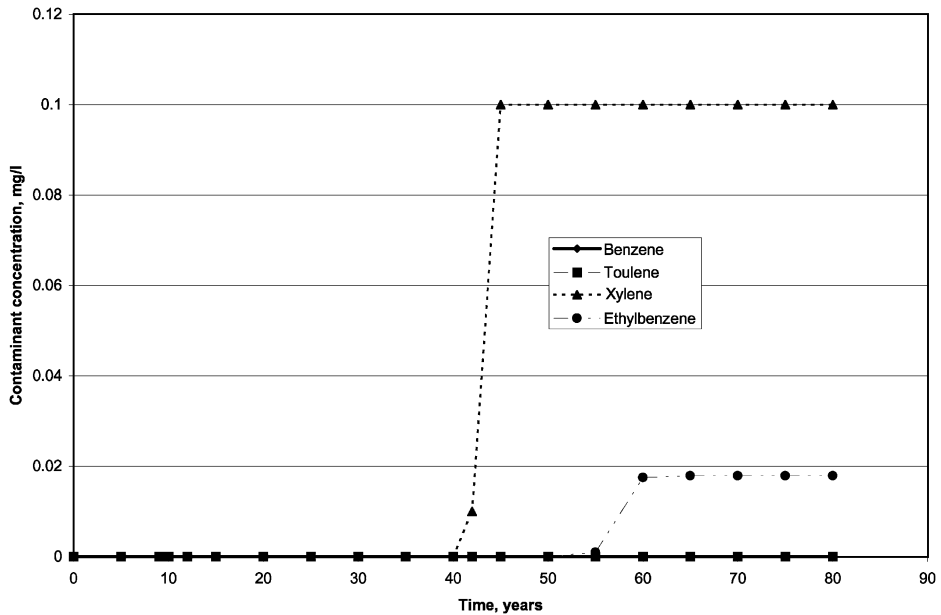
Table 3
Summary of modeling results for contamination distribution in the soil for regions 1 and 2

Process of contaminant distribution	Region 1				Region 2			
	Benzene	Toluene	Ethyl benzene	Xylene	Benzene	Toluene	Ethyl benzene	Xylene
Volatilized (kg)	3.10E+5	2.05E+5	1.18E+5	7.96E+4	3.52E+5	3.36E+5	2.23E+5	1.22E+5
Soil air (kg)	3.65E−7	2.88E−8	8.48E+2	5.74E+2	1.76E−8	8.74E−8	1.44E+3	8.95E+2
Surface run-off (kg)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
In wash load (kg)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Adsorbed in soil (kg)	4.62E−8	9.87E−9	5.07E+2	4.27E+2	3.80E−9	1.60E−8	1.32E+3	1.13E+3
Pure phase (kg)	0.0	0.0	9.60E+5	1.46E+6	0.0	0.0	9.05E+5	1.42E+6
Metal complexed (kg)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Immobile CEC (kg)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
In soil moisture (kg)	6.55E−7	4.53E−8	1.17E+3	1.37E+3	1.53E−8	2.08E−8	8.64E+2	1.03E+3
Biodegradation (kg)	9.72E+4	6.09E+5	1.15E+5	8.44E+4	5.33E+4	4.78E+5	8.90E+4	6.68E+4
Groundwater run-off (kg)	1.92E−4	2.27E−8	1.42E+0	8.03E+0	1.75E+3	8.86E+1	9.80E+2	2.41E+3
Total contaminant input (kg)	4.07E+5	8.15E+5	1.22E+6	1.63E+6	4.07E+5	8.15E+5	1.22E+6	1.63E+6
Maximum leachate concentration (mg/l)	1.8.0E−3	3.92E−08	1.04E+0	3.98E+0	1.33E+3	5.12E+0	2.98E+1	7.02E+1
Year to reach maximum groundwater concentration (year)	42.67	48.58	57.58	45.58	13.92	18.00	23.83	16.83
Length of simulation (year)	80	80	80	80	80	80	80	80

Table 4
Summary of modeling results for contamination distribution in the soil for regions 3 and 4

Process of contaminant distribution	Region 3				Region 4			
	Benzene	Toluene	Ethyl benzene	Xylene	Benzene	Toluene	Ethyl benzene	Xylene
Volatilized (kg)	3.54E+5	4.62E+5	2.16E+5	1.18E+5	3.67E+5	6.43E+5	2.74E+5	1.50E+5
Soil air (kg)	3.34E−8	3.92E−8	1.38E+3	8.48E+2	2.01E−8	8.23E−8	1.61E+3	1.01E+3
Surface run-off (kg)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
In wash load (kg)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Adsorbed in soil (kg)	4.49E−9	1.38E−9	7.73E+2	6.51E+2	1.95E−9	2.16E−8	6.69E+2	5.73E+2
Pure phase (kg)	0.0	0.0	5.38E+5	1.46E+6	0.0	0.0	4.63E+5	1.42E+6
Metal complexed (kg)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Immobile CEC (kg)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
In soil moisture (kg)	1.74E−8	1.74E−8	4.88E+2	5.74E+2	1.27E−8	4.56E−8	7.06E+2	8.45E+2
Biodegradation (kg)	3.03E+4	3.47E+5	4.82E+4	3.58E+4	3.52E+4	5.78E+5	7.12E+4	5.35E+4
Groundwater run-off (kg)	2.26E+4	4.39E+3	8.74E+3	1.35E+4	5.19E+3	9.56E+2	3.34E+3	6.45E+3
Total contaminant input (kg)	4.07E+5	8.15E+5	8.15E+5	1.63E+6	4.07E+5	1.22E+5	8.15E+5	1.63E+6
Maximum leachate concentration (mg/l)	1.68E+3	8.02E+1	9.81E+1	1.39E+2	1.52E+3	2.05E+1	6.26E+1	1.02E+2
Year to reach maximum groundwater concentration (year)	6.87	7.75	10.83	7.00	9.92	11.75	15.0	10.83
Length of simulation (year)	80	80	80	80	80	80	80	80

Fig. 4. Trend for contaminant concentration (centerline of plume) in aquifer for region 1.

After 40 years, a maximum xylene concentration of about 0.1 mg/l occurs in the aquifer and persists at least for the next 40 years. In the case of ethylbenzene, a concentration of about 0.018 mg/l occurs in the aquifer after 55 years of release and is maintained at this level. The slow movement of contaminant in region 1 results from the presence of an impermeable soil layer, a low hydraulic gradient, and the conductivity of the aquifer.

In region 2, a high concentration of benzene ($\sim$180 mg/l) is observed after 10 years of release; this concentration reduces to 8 mg/l within 10 years, and is negligible in the next 15 years (Fig. 5). A similar trend is observed for toluene, but its maximum concentration is quite low ($\sim$1 mg/l) and occurs after 18 years of release (Fig. 5), and becomes negligible after 45 years of release. In the case of xylene, maximum concentration (20 mg/l) is observed after 20 years of release, reduced to 18 mg/l in the next five years, and maintained at this level for the next 40 years (Fig. 5). For ethylbenzene, a concentration of approximately 4 mg/l is observed after 20 years of release and remains at this level for another 60 years. These results (after 10 years of release) are compared with the observed values of individual benzene, toluene, ethylbenzene, and xylene (BTEX) constituent concentrations in the monitoring well of region 2. The values predicted by the model strongly agree with the observed values.

The result of fate-and-transport modeling in the saturated zone of region 3 is presented in Fig. 6. This region was modeled for fracture flow. As evident from Fig. 6, the benzene concentration in the aquifer appears after just 1 year of release. After 18 years it reaches its maximum concentration level of 1450 mg/l, and thereafter decreases sharply. After 25 years of release, the concentration of benzene in the aquifer is negligible. The excessively high concentrations of benzene in the aquifer after 10 years of release, as predicted by the model,
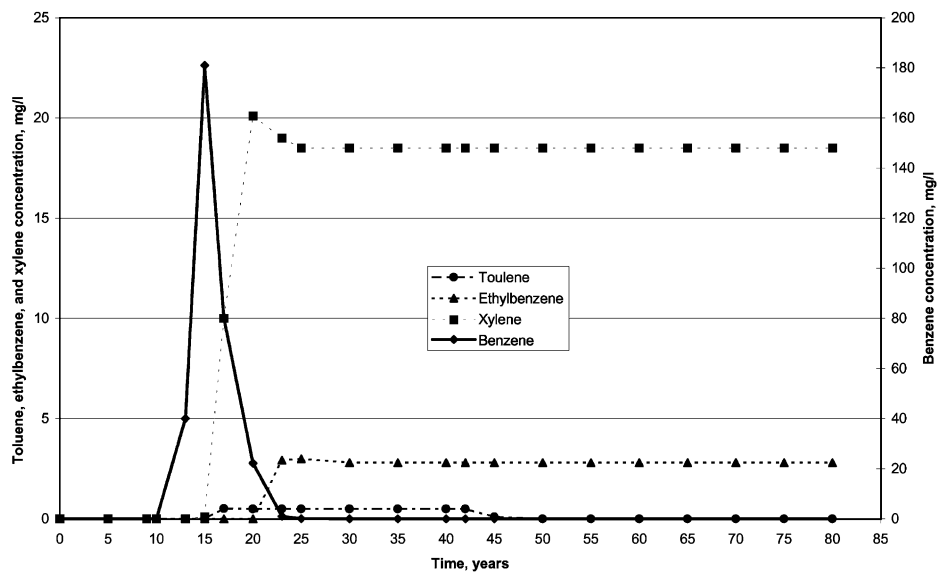
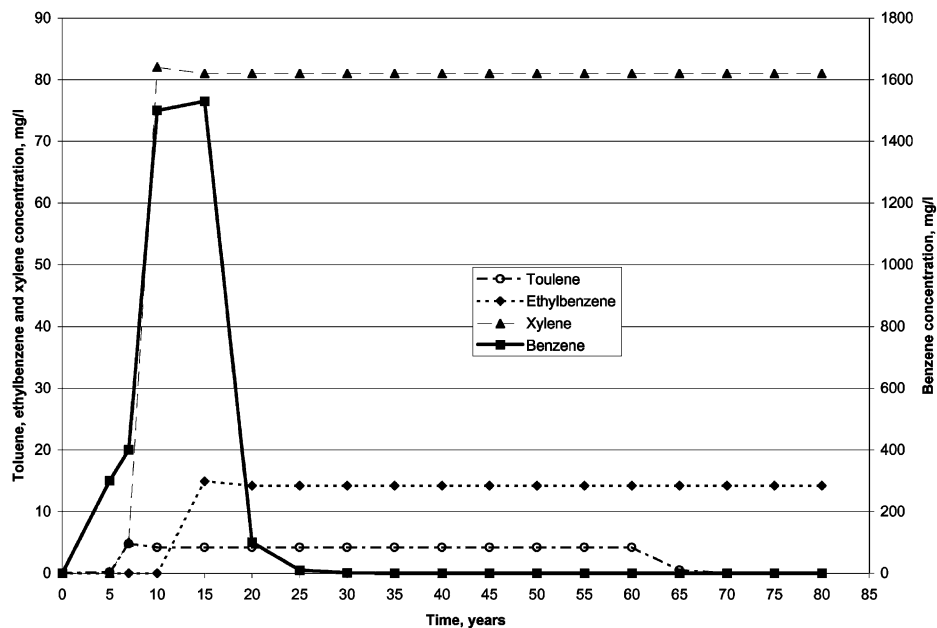Fig. 5. Trend of contaminant concentration (centerline of plume) in aquifer for region 2.

Fig. 6. Trend of contaminant concentration (centerline of plume) in aquifer for region 3.

are compared with the observed values in the monitoring well, and indicates that these values are well matched. As shown in Fig. 6, the increasing trend for toluene starts after the fifth year of release and reaches its maximum (∼5 mg/l) in the next few years. Thereafter, it maintains this level for another 50 years, and becomes negligible after 65 years of release. The trend for xylene is similar to that for benzene except that the maximum concentration (82 mg/l), observed on the 10th year of release, is maintained for the next 70 years (Fig. 6). The maximum concentration of ethylbenzene is observed after 15 years of release and is maintained for the next 70 years (Fig. 6). The model's prediction for ethylbenzene and xylene also agrees with the observed values.

The trend of contaminant concentration in the aquifer of region 4 is presented in Fig. 7. It is evident from this figure that a maximum concentration of benzene (∼375 mg/l) will be observed in the 12th year of release. Subsequently, this concentration will reduce to a negligible level after 30 years of release. A similar trend is observed for xylene, but there is no depleting trend, and the maximum concentration is maintained for a longer duration (more than 80 years, Fig. 7). For toluene, the maximum concentration (2.0 mg/l) is observed after the 12th year of release, and will be maintained for the next 50 years (Fig. 7). The trend for ethylbenzene concentration is similar to xylene; however, the maximum concentration will be relatively lower (Fig. 7).

Analysis of these results (for of four regions) reveals that in most regions the concentration of benzene and toluene initially show an increasing trend, followed by a depleting trend. With time, fresh leachate from the soil comes in contact with the aquifer. Although there is a depletion of contaminant due to processes occurring in the aquifer (biodegradation, dilution, dispersion, etc.), the rate of fresh leachate addition to the aquifer is higher than
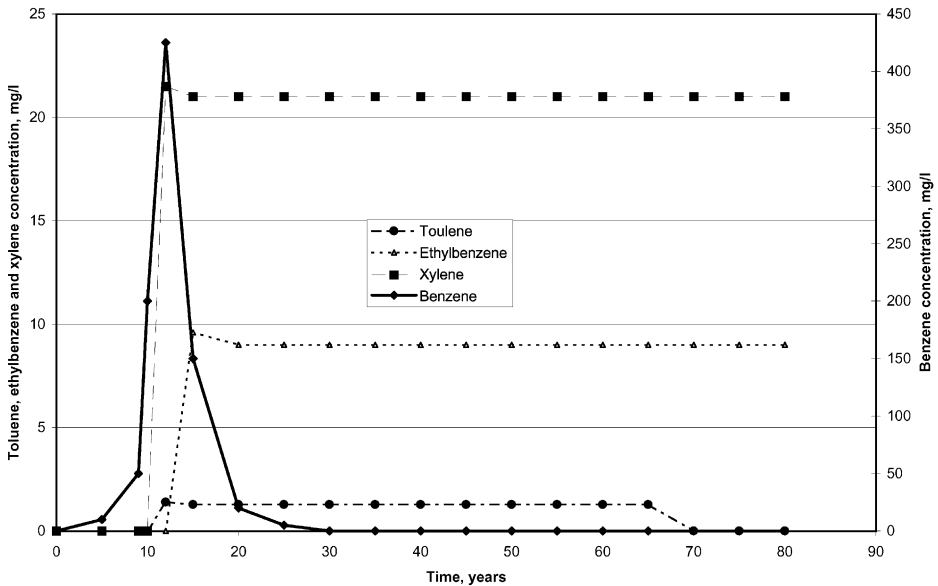

Fig. 7. Trend of contaminant concentration (centerline of plume) in aquifer for region 4.

the rate of depletion, resulting in an increasing trend. This is verified by the fact that the maximum concentration of contaminant in the aquifer will always be less than the maximum leachate concentration. As the rate of fresh leachate addition to the aquifer ceases, the trend changes (a depleting trend begins). The main processes modeled in the present study are dilution, dispersion, and biodegradation. No substantial depleting trend is observed with ethylbenzene and xylene because these constituents are largely stored in the pure phase (as NAPL), which acts as a slow but continuous source of contaminant. A decrease in the concentration is observed only when the pure phase is exhausted or removed externally.

6.3. Natural attenuation modeling

The remediation of aquifer contamination was modeled using the NA processes of biodegradation, absorption, dilution, and dispersion (with biodegradation the dominant
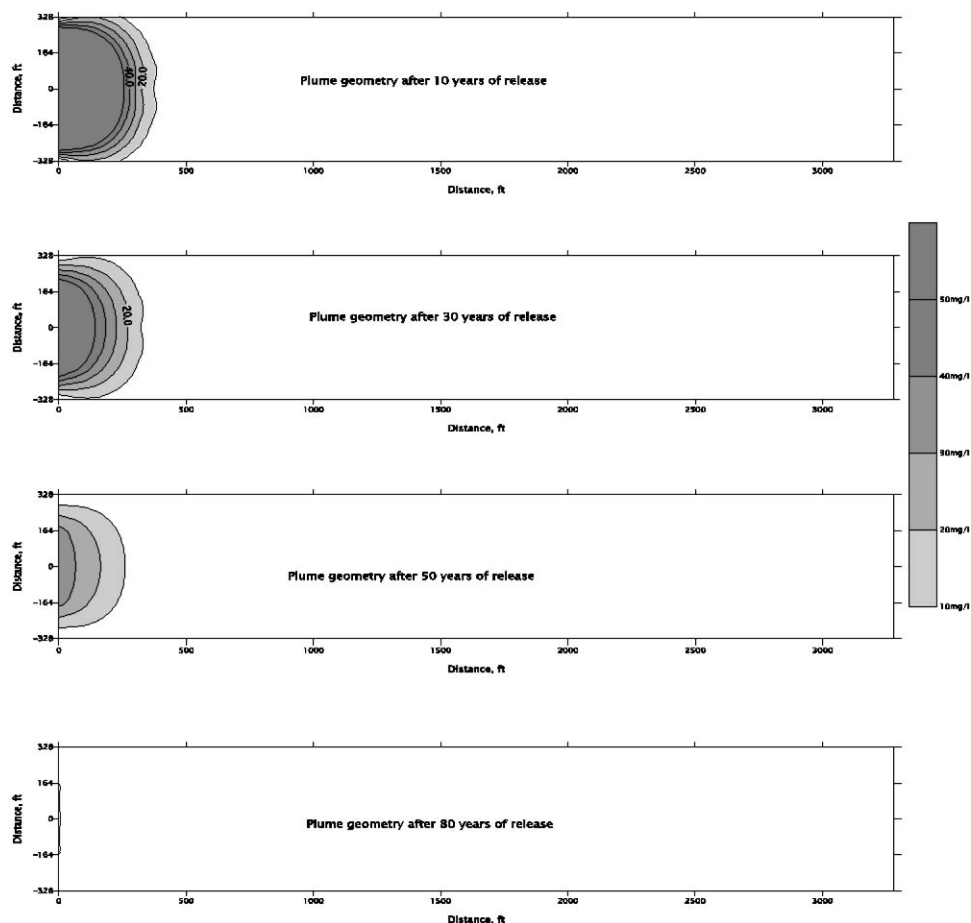
Fig. 8. Benzene plume geometry at different durations for region 3, based on first-order decay model.

process). As seen in Table 2, a high background concentration of electron acceptors favors biodegradation. There are two approaches in modeling the biodegradation of organic contaminants: first-order decay and instantaneous reaction. The first approach is independent of the concentration of electron acceptors and depends only on the concentration of the organic pollutant. In recent years, it has been observed that the limited availability of electron acceptors (O_2 with aerobic reactions and NO_3^-, SO_4^{2-}, Fe^{3+} ions with anaerobic reactions) controls the reaction rate rather than the contaminant concentration. Therefore, a first-order decay model overestimates biodegradation. This has been verified by many field studies; see particularly Rifai et al. [20].

In the present analysis, the performance of both models (first-order and instantaneous reaction models) was evaluated for benzene in region 3 (Figs. 8 and 9). A close evaluation of
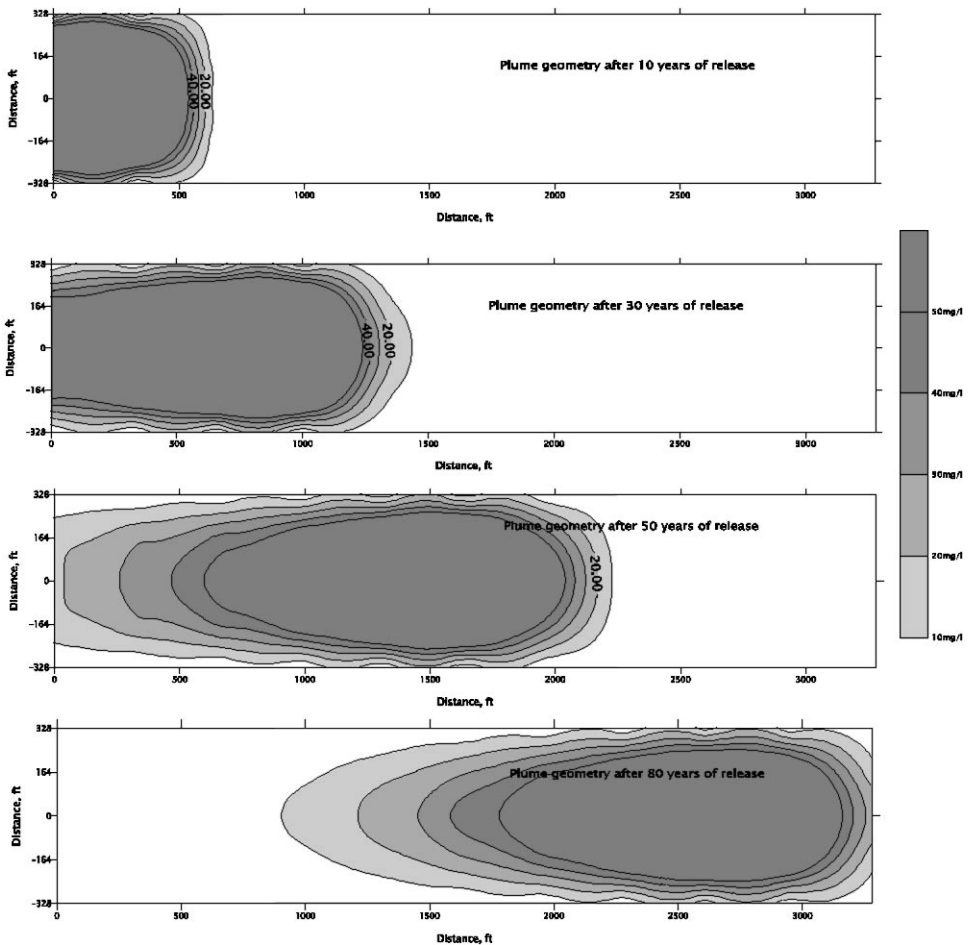
Fig. 9. Benzene plume geometry at different durations for region 3, based on instantaneous reaction model.

these figures reveals that after 10 years of release, contaminant plumes in the first-order decay model are confined to 500 ft longitudinally and about 280 ft laterally. On the other hand, the instantaneous reaction approach (electron acceptor concentration as limiting concentration) models the plume dimension as 650 ft by 320 ft. After 50 years of release, the first-order decay model predicts an almost exhausted plume, whereas the instantaneous approach predicts a plume of 1200 ft long and 200 ft wide with the center relocated about 1300 ft from the point of release. Although there is insufficient data to validate which model is best suited for this case study, as a precaution, the instantaneous model was used for subsequent analysis.

The plumes of BTEX for region 3 are presented in Figs. 9–12. It is evident from Fig. 9 that the benzene plume for the first 30 years of release shows an expanding trend, extending to more than 1300 ft longitudinally and about 300 ft laterally. Subsequently, these plumes start
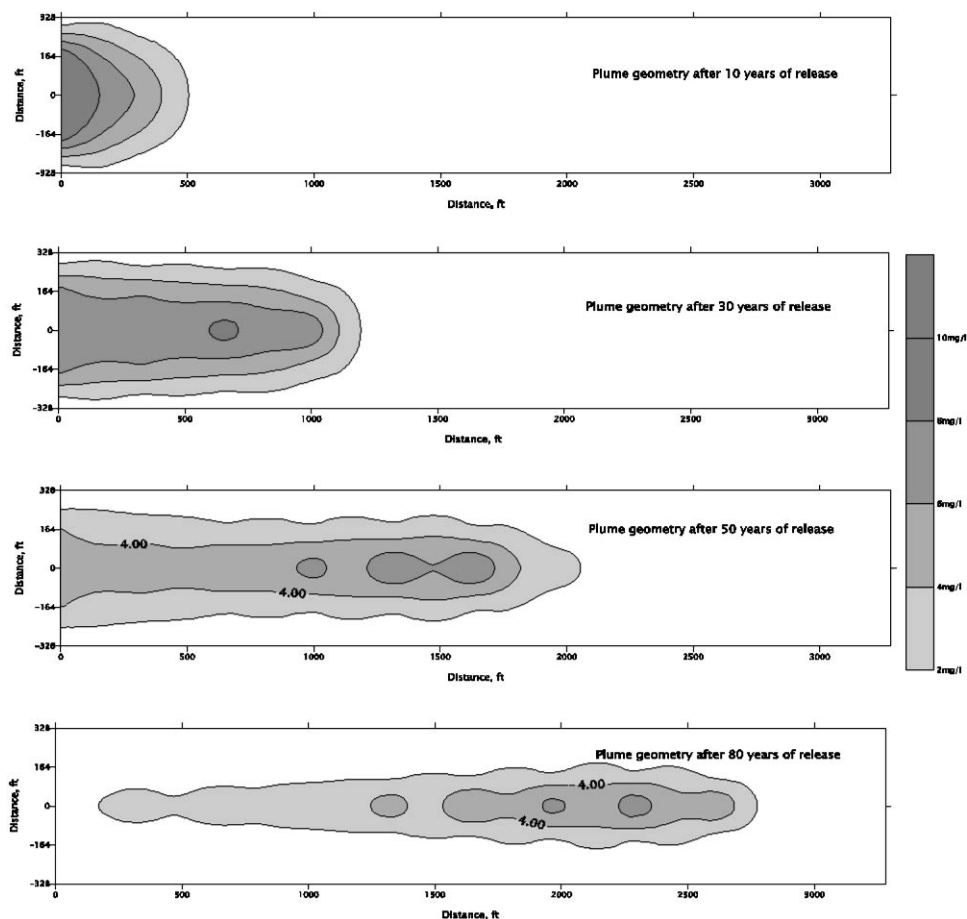
Fig. 10. Toulene plume geometry at different durations for region 3, based on instantaneous decay model.
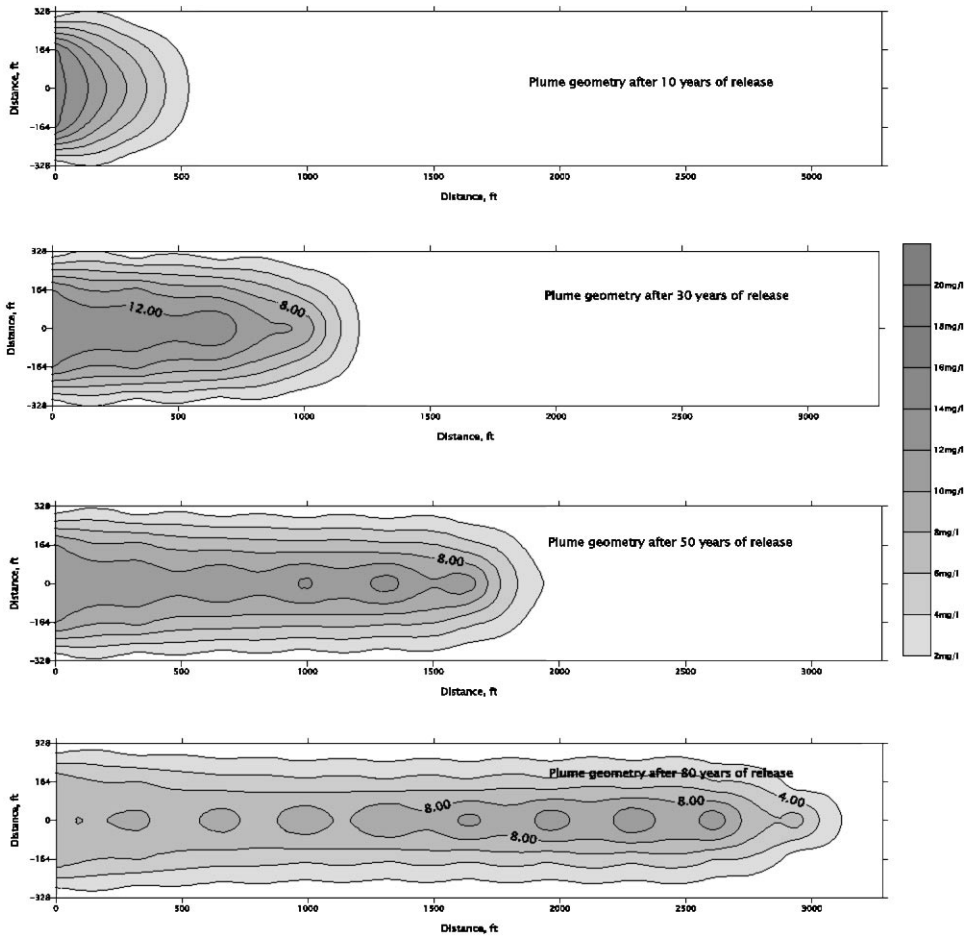
Fig. 11. Ethylbenzene plume geometry at different durations for region 3, based on instantaneous decay model.

shrinking (Fig. 9). After 50 years of release, the plume shrinks to 1200 ft, and in the next 30 years it further shrinks to 1000 ft longitudinally and 200 ft laterally. The large dimensions of the benzene plume (10 mg/l) after 30 and 50 years are a matter of concern. The plume (Fig. 9) also moves as a slug and shows less dilution on the downstream side, whereas the long tail is on the upstream side. This occurs because the excessively high concentration of dissolved benzene in the aquifer acts as a source and moves as a slug. Due to a low hydraulic gradient and conductivity, the downstream dilution is comparatively lower than the upstream concentration. Plumes of toluene at different times are shown in Fig. 10. A toluene plume of 2 mg/l moves in a downstream direction but is simultaneously exhausted. After 50 years of release, the plume extends up to 2000 ft from the release point, but shrinks to about 40% in the lateral direction. After 80 years of release, the plume resembles a long tail with negligible thickness.
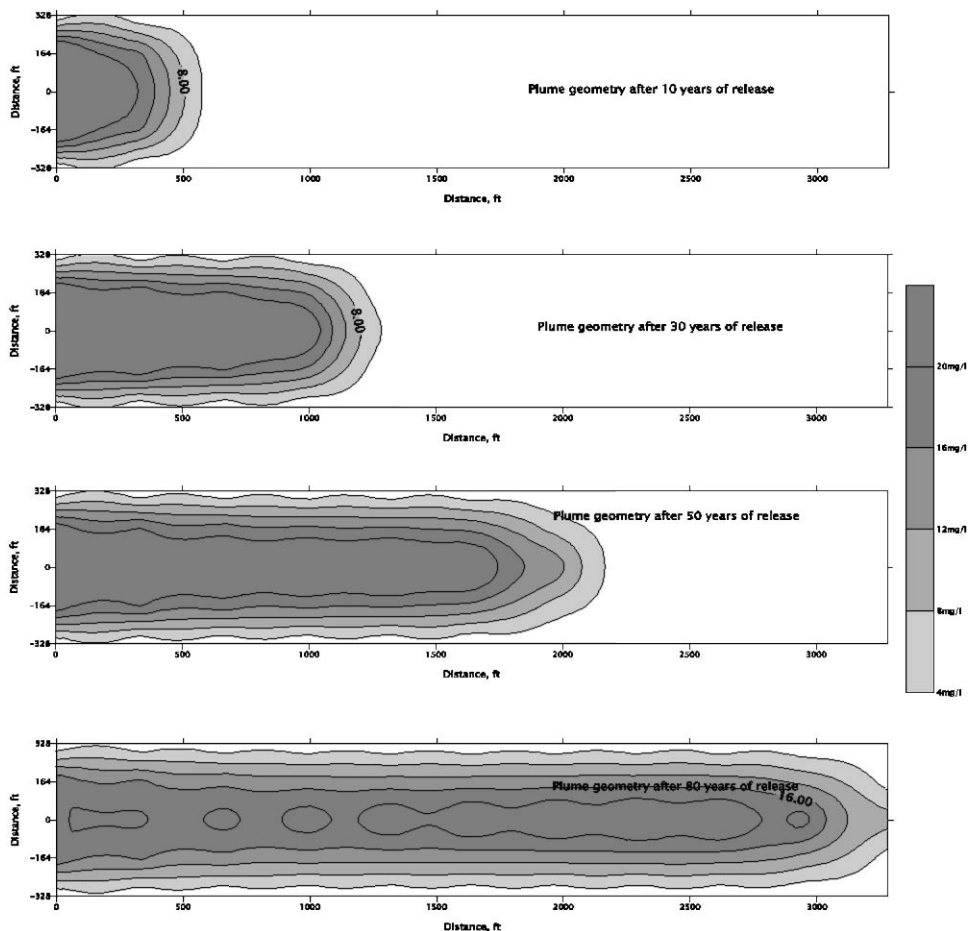
Fig. 12. Xylene plume geometry at different durations for region 3, based on instantaneous reaction model.

Fig. 11 depicts the plume of ethylbenzene at different durations. Initially, a plume of 2 mg/l concentration (outermost in Fig. 11) extends only up to 500 ft longitudinally. In the next 40 years, it extends to about 1900 ft longitudinally with little lateral shrinking (Fig. 11). It is alarming to note that after 80 years of release, the plume expands to more than 3000 ft. A similar trend is observed for xylene (Fig. 12). The plume that was initially limited to 600 ft expands to a distance of more than 3000 ft downstream after 80 years of release. In summary, plumes of benzene, ethylbenzene, and xylene are of concern; Figs. 10–12 demonstrate that these plumes extend to larger distances compared to regions 1, 2 and 4. Although the core of each plume is being depleted and shrinks in a lateral direction, its expansion in the direction of flow is alarming.

The benzene plume over time in region 4 is presented in Fig. 13. It is clear from the figure that it takes about 30 years for the plume to obtain a stable shape of 500 ft by 300 ft; this plume
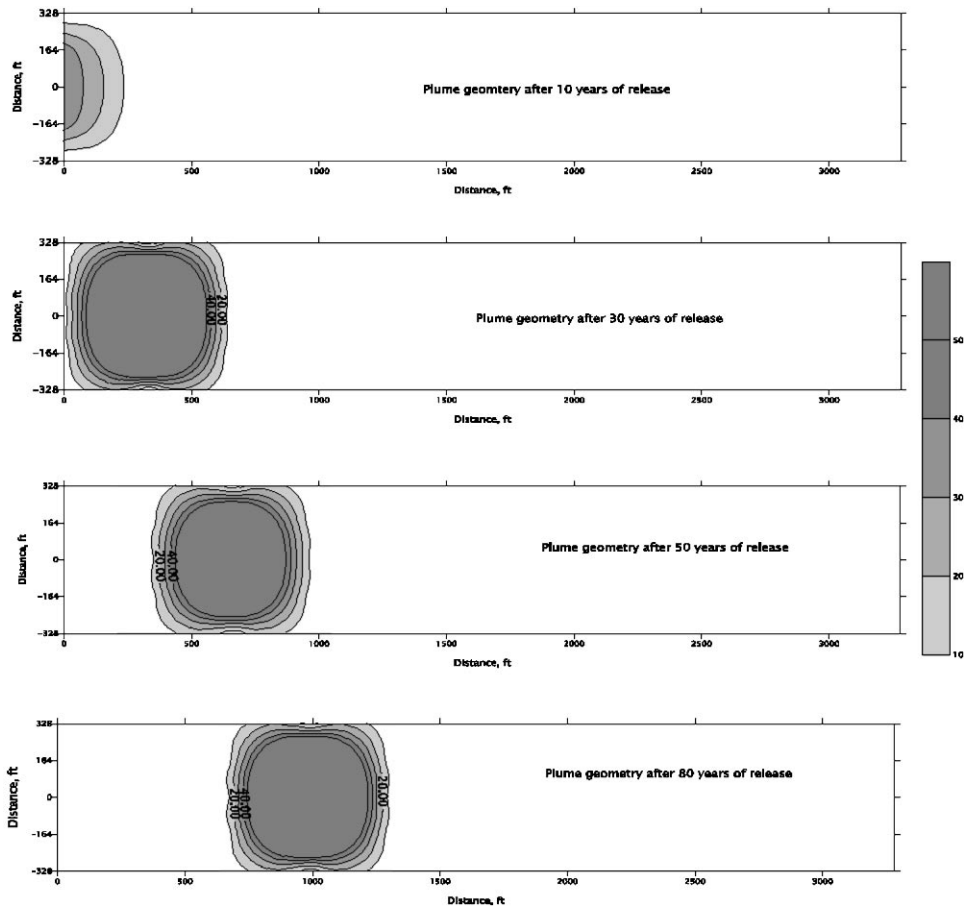
Fig. 13. Plume geometry at different durations for region 4, based on instantaneous reaction model.

is considerably smaller than the one observed in region 3. In subsequent years, the plume size remains almost constant (Fig. 13). A similar trend is observed for toluene; however, the size of its plume is comparatively smaller, and after 30 years of release it is 350 ft by 150 ft. The plume geometry for ethylbenzene and xylene is similar. After 30 years of release, plumes of xylene and ethylbenzene have spread to 800 ft downstream and 260 ft laterally. Like the benzene plume, these plumes have stabilized and no further expansion is observed. Unlike region 3, this region does not show much depletion as it was modeled considering a continuous source.

The plume geometry for benzene and other constituents in region 2 differ little from region 4. This region was modeled considering a continuous source due to the presence of the contaminant in the pure phase. In the case of benzene, almost the same plume geometry was observed, but this time the plume moved downstream less than region 4.

The plumes for toluene and other chemicals are almost the same as those observed in region 4.

Region 1 shows interesting results. For benzene and toluene, for the initial periods of 45 years from the date of release, the plumes are limited to only 200 ft, and in the next 10 years are exhausted completely. The plume for ethylbenzene shows a similar trend and expands only to 150 ft downstream; however, this plume remains for more than 80 years.

The above study concludes that NA is effective in all regions, but region 3 is of particular concern: although the plumes are shrinking, they are large. The suitability of NA in this region depends upon the risk posed by these plumes to the potential receptors.

Step 5. Once the contaminant concentrations at different locations with time are known, the risk to potential on-site and/or off-site receptors can be estimated. In the present study, a residential location 400 ft from the release source was considered an on-site receptor. Potential off-site receptors were located about 5000 ft from the point of release in a downstream direction. The complete exposure flow chart used in the risk computation is shown in Fig. 14. The RBCA Chemical Release version 1.2 [11–13,33] was used for base risk computations. The results of this step are presented in Table 5 clarifies that region 1 does not pose any risk at any time. Regions 2 to 4 pose immediate on-site risks, but at no time is there a threat to the off-site receptors. The risk becomes acceptable after 20 years of release. By taking appropriate precautionary measures, the present risk can be minimized and the site maintained for MNA.

Steps 6 *and* 7. It is evident from the above study that MNA can be used as an effective remediation alternative for the case presented in this paper. However, extensive monitoring is required to ensure that the constituents behave as predicted and no further complexities occur. For this purpose, an extensive monitoring plan should be developed. The complete results from steps 1 to 6 need to be documented in a well-defined manner and submitted to a regulatory agency for evaluation and approval.
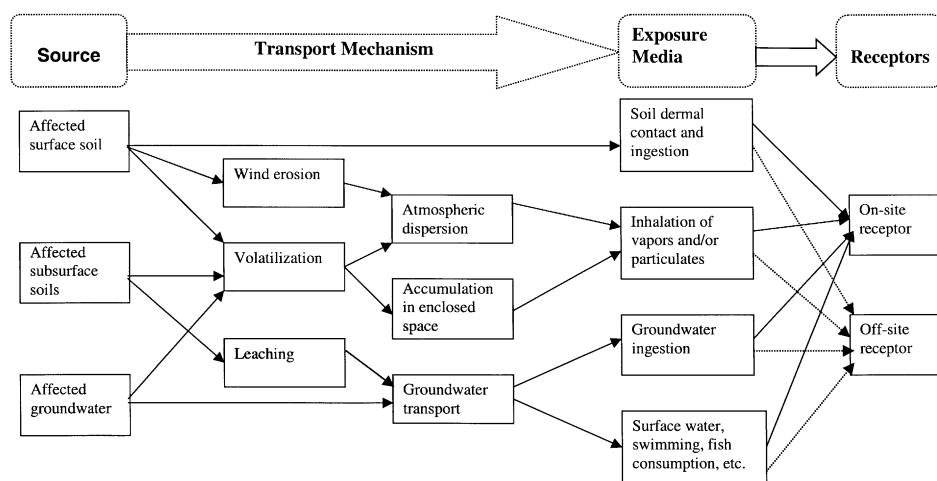

Fig. 14. Simplified flowchart of exposure pathways.

Table 5
Summary of risk factors and hazard quotient at different durations in different regions

Region	After 10 years				After 30 years				After 50 years			
	On-site[a]		Off-site[b]		On-site[a]		Off-site[b]		On-site[a]		Off-site[b]	
	CRF[c]	HQ[d]	CRF[c]	HQ[d]	CRF[c]	HQ[d]	CRF[c]	HQ[d]	CRF[c]	HQ[d]	CRF[c]	HQ[d]
Region 1	2.1E−07	1.5E−03	4.4E−12	1.0E−05	2.1E−07	1.5E−03	4.4E−12	1.0E−05	2.1E−07	1.5E−03	4.4E−12	1.0E−05
Region 2	2.5E−06	1.1E+0	5.9E−12	2.7E−06	5.4E−08	1.1E−1	2.1E−13	5.0E−07	5.4E−08	1.1E−1	2.1E−13	5.0E−07
Region 3	4.6E−04	2.2E+1	2.5E−09	1.7E−06	1.0E−07	4.0E−1	1.5E−11	3.2E−09	5.4E−12	1.0E−05	4.5E−14	3.0E−09
Region 4	4.3E−04	2.1E+1	1.6E−09	1.5E−06	5.0E−08	2.0E−1	1.0E−11	2.5E−09	1.0E−12	6.0E−06	1.8E−14	1.0E−09

[a] The estimation of cumulative risk factor (CRF) and hazard quotient (HQ) has been done considering as on-site residential area (which in reality it is not). This is done as a precaution. In the estimation of CRF and HQ on-site, all possible exposure pathways have been considered.

[b] The off-site calculation considered a distance of 1500 m from the source of release. Off-site was located downstream from the groundwater flow, and a residential area.

[c] CRF is estimated for carcinogens constituents.

[d] HQ estimated for non-carcinogen constituents.

7. Summary and conclusion

Hydrocarbon spills, which cause contamination of the soil and groundwater, are a worldwide problem. The cleanup of these contaminated sites using a conventional remediation process is cost-prohibitive and does not ensure complete recovery of the site. NA is a remediation approach where natural physical, chemical, and/or biological processes under favorable conditions act without human intervention to reduce the mass, toxicity, mobility, volume or concentration of contaminants in soil and groundwater. These in situ processes include biodegradation, dispersion, dilution, sorption, volatilization, chemical or biological stabilization, and transformation or destruction of contaminants. A particular NA site may include any or all of these.

This paper links ASTM's RBCA approach with NA. A systematic working methodology was presented for risk-based site evaluation and remediation through NA. Application of this methodology used a real life case study: the first step predicted a high risk on-site and a moderate risk off-site; subsequent steps predicted that at the initial stage a high concentration of benzene was a major concern in most of the regions. In region 3, highly concentrated plumes of contaminants (benzene, ethylbenzene, and xylene) were observed for longer durations at greater distances. However, due to the remote location of the site, it did not pose much threat to off-site receptors. Although the site posed a substantial on-site risk in the initial period (10 years) of release, it became acceptable as the plume was diluted and drifted from the point of release. Plumes of xylene and ethylbenzene persisted for longer durations, as a major portion of these constituents were present in the pure phase in the soil column. This pure phase acted as a continuous source of contaminant to the saturated zone. If fast remediation is sought, then efforts should be made to remove the contaminant from the soil. Since benzene and toluene do not occur in the pure phase, the chronic effects of these constituents are of little concern.

In brief, this study concludes that NA can be used as an effective measure for remediation of the present site, but efforts are needed to develop an extensive monitoring program to control the present on-site risk. If early remediation is sought, efforts are required to clean up the pure phase. In our opinion, depending on the duration of remediation and the risk involved, a combination of engineering remediation and NA would be an optimal approach.

References

[1] M. Russell, E.W. Colgalazier, M.R. English, Hazardous Waste Remediation: The Task Ahead, Waste Management Research and Education Institute, University of Tennessee, USA, 1991.
[2] EPA, Cleaning up the Nation's Waste Sites: Markets and Technology Trends, USEPA, Office of Solid Waste and Emergency Response, Washington, DC, 1993.
[3] P.V. Brady, M.V. Brady, D.J. Borns, Natural Attenuation: CERCLA, RBCA's and the Future of Environmental Remediation, Lewis Publishers, New York, 1999.
[4] National Research Council (NRC-1994), Alternatives for Groundwater Cleanup, National Academy Press, Washington, DC.
[5] National Research Council (NRC-1997), Innovations in Ground Water and Soil Cleanup: From Concept to Commercialization, National Academy Press, Washington, DC.
[6] J.A. MacDonald, Natural Attenuation for Groundwater Cleanup, Environmental Science and Technology, 2000, pp. 346A–353A.

[7] T. Cairney, Contaminated Land, Blockier, London, 1993, 4 pp.

[8] B. Ellis, K. Gorder, Intrinsic bioremediation: an economic option for cleaning up contaminated land, Chem. Ind. 9 (1999) 1–6.

[9] F.I. Khan, T. Husain, Risk based corrective action's volatilization factors — modifications and improvement, J. Soil Contam. 2000 (submitted after revision).

[10] E. Nyer, P. Mayfield, J. Hughes, Beyond the AFCEE Protocol for Natural Attenuation, GWMR, summer issue, 1998, pp. 70–76.

[11] J.A. Connor, J. Charles, J. Newell, P. Nevein, H.S. Rifai, Guidelines for use of groundwater spreadsheet models in risk-based corrective actions design, in: Proceedings of the NGWA Petroleum Hydrocarbons Conference, Houston, TX, November 1994.

[12] J.A. Connor, C.J. Newell, M.W. Malander, Parameter estimation guidelines for risk-based corrective action modeling, in: Proceedings of the NGWA Petroleum Hydrocarbon Conference, Houston, TX, November 1996.

[13] J.A. Connor, L.B. Richard, J.P. Nevein, R.T. Fisher, RBCA Tool Kit for Chemical Releases, Ground Water Services, Inc., 2211 Norfolk, Houston, TX, 1998.

[14] ASTM, Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites, E1739-95, 100 Bar Harbor, West Conshohocken, PA, 1995.

[15] T. Husain, R. Hejazi, F.I. Khan, Remediation of Petroleum Contaminated Sites Using Monitored Natural Attenuation Approach, Presented in Chemistry and Industry, Bahrain, 30 October–1 November 2000.

[16] RAAG, Evaluation of Risk Based Corrective Action Model, Remediation Alternative Assessment Group, Memorial University of Newfoundland, St John's, NF, Canada, 2000.

[17] EPA, Draft Interim Final OSWER on Monitored Natural Attenuation Policy, Directive 9200.4-17, US EPA, Office of Solid Waste and Emergency Response, Washington, DC, 1997.

[18] J.S. Heath, Introduction: guidance on natural attenuation in soils and groundwater, J. Soil Contam. 8 (1) (1999) 3–7.

[19] T.H. Wiedemeier, C.J. Newell, H.S. Rifai, J.T. Wilson, Natural Attenuation of Fuels and Chlorinated Solvents in the Subsurface, Wiley, New York, 1999, pp. 1–26.

[20] S.H. Rifai, C.J. Newell, J.R. Gonzales, J.T. Wilson, Modeling natural attenuation of fuels with BIOPLUME III, J. Environ. Eng. 126 (5) (2000) 428–438.

[21] AFCEE, Review of State Regulations Regarding Natural Attenuation as a Remedial Option, Technical Brief, US Air Force Center for Environmental Excellence, San Antonio, TX, 1994, 7 pp.

[22] T.H. Wiedemeier, J.T. Wilson, D.H. Kampbell, R.N. Miller, J.E. Hansen, Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater, US Air Force Center for Environmental Excellence, San Antonio, TX, 1995.

[23] T.H. Wiedemeier, M.A. Swanson, D.E. Moutoux, E.K. Gordon, J.T. Wilson, B.H. Wilson, D.H. Kampbell, J.E. Hansen, P. Haas, F.H. Cahpelle, Overview of the technical protocol for natural attenuation of chlorinated aliphatic hydrocarbons in groundwater under development for the US Air Force for Environmental Excellence, in: Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Groundwater, Dallas, TX, 11–13 September 1996, EPA/540/r-96.

[24] G. Hossein, C.W. Rose, Modeling Chemical Transport in Soils: Natural and Applied Contaminants, Lewis Publishers, Boca Raton, FL, 1992.

[25] E. Oelkers, C.I. Steefel, P. Lichtner, Reactive Transport in Porous Media, Mineralogical Society of America, Washington, DC, 1996.

[26] J.P. McDonald, G.M. Gelston, Commentary on fate and exposure models: description of the multimedia environmental pollution assessment system version 3.2 with application to hypothetical soil contamination scenarios, J. Soil Contam. 7 (3) (1998) 283–300.

[27] D.M. Hetrick, S.J. Scott, Fate and exposure models: selecting the appropriate model for a specific application SESOIL and AT123D models, J. Soil Contam. 7 (3) (1998) 301–309.

[28] H.S. Rifai, C.J. Newell, J.R. Gonzales, S. Dendrou, L. Kennedy, J. Wilson, BioPlume III Natural Attenuation Decision Support System Version 1.0 User's Manual, US Air Force Center for Environmental Excellence, Brooks Air Force Base, San Antonio, TX, 1997.

[29] C.J. Newell, R.K. McLeod, J.R. Gonzales, J.T. Wilson, BIOSCREEN Natural Attenuation Decision Support System Version 1.3, EPA/600/R-96/087, US EPA, Washington, DC, 1996.

[30] M. Bonazountas, D.H. Hetrick, P.T. Kostecki, E.J. Calabrese, SESOIL in Environmental Fate and Risk Modeling, Amherst Scientific Publishers, Amherst, 1997, 661 pp.

[31] ESC SESOIL and AT123D, Integrated Contaminant Transport and Fate Modeling Users Guide, Environmental Software Consultants, Inc., Madison, WI, 2000.

[32] G.T. Yeh, H. Trussel, J. Hoopes, AT123D: Analytical Transient One, Two and Three Dimension Simulation of Waste Transport in the Aquifer System, Wisconsin Department of Natural Resources, WI, 1987.

[33] GSI, RBCA Toolkit for Atlantic RBCA and RBCA Toolkit for Chemical Release, Ground Water Services, Inc., 2211 Norfolk, Houston, TX, 1998.

[34] J.A. MacDonald, M.C. Kavanaugh, Restoring contaminated groundwater: an achievable goal? Environ. Sci. Tech. 23 (1994) 362–368.

[35] K.E. Clark, M.G. Richardson, Fate and transport models: selecting the appropriate model for specific application, J. Soil Contam. 7 (3) (1998) 267–274.