
Legacies from three former manufactured-gas plants: impacts on groundwater quality

Robert H. Abrams · Keith Loague

Abstract Groundwater contamination due to accidental releases of mono- and polycyclic aromatic compounds (MAHs and PAHs) from decommissioned manufactured-gas plants is an ongoing and litigious problem. The MAHs and PAHs are derived from coal tar, which was a by-product of the gas-manufacturing process. While originally designed to contain coal tar, the manufactured-gas plant structures that remain today have often degraded over time and are not completely leak-proof. Over a period of many years, subsurface water has seeped into and out of the structures, resulting in groundwater contamination. This was particularly true once the tops of the structures were removed. In this study, process-based simulations were conducted to estimate the groundwater-quality impacts of accidental releases of dissolved naphthalene ($C_{10}H_8$) from the sites of three former manufactured-gas plants. The results from one-dimensional, transient, unsaturated, near-surface fluid-flow and solute-transport simulations served as input to three-dimensional saturated subsurface fluid-flow and solute-transport simulations. The simulation results and sensitivity analysis reported here indicate that accidental releases of naphthalene had significant, negative impacts on groundwater quality at each of the three sites.

Résumé La contamination d'une nappe par relargage accidentel de composés aromatiques mono- et polycycliques (HAM et HAP) à partir d'usines à gaz abandonnées est un problème persistant et litigieux. Les HAM et les HAP proviennent du goudron de charbon qui était un sous-produit du procédé de fabrication du gaz. Alors qu'elles étaient prévues pour contenir du

goudron, les structures des usines à gaz qui restent actuellement se sont souvent dégradées avec le temps et ne sont plus étanches. En plusieurs années, les eaux de surface se sont infiltrées dans ces structures et en sont ressorties, en provoquant une contamination des eaux souterraines. Ceci s'est produit en particulier lorsque les toits des bâtiments ont été enlevés. Dans cette étude, des simulations basées sur les processus ont été réalisées pour évaluer les impacts de relargages accidentels de naphthalène ($C_{10}H_8$) sur la qualité de l'eau souterraine à partir de sites de trois anciennes usines à gaz. Les résultats de simulations d'écoulement de fluide et de transport de soluté près de la surface, en une dimension, en régime transitoire et en milieu non saturé ont été utilisés comme entrées de simulations d'écoulement de fluide et de transport de soluté d'eau souterraine à trois dimensions et en milieu saturé. Les résultats des simulations et l'analyse de sensibilité fournis ici montrent que les relargages accidentels de naphthalène ont des impacts négatifs significatifs sur la qualité de l'eau en chacun des trois sites.

Resumen La contaminación de las aguas subterráneas debido a vertidos accidentales de compuestos aromáticos mono- y policíclicos (MAHs y PAHs) en plantas de producción de gas abandonadas es un problema continuo y actual. Los MAHs y PAHs se derivan del alquitrán de hulla, que a su vez es un subproducto del proceso de manufactura del gas. Aunque las plantas de gas fueron diseñadas para contener alquitrán, las estructuras existentes hoy día se han ido degradando con el tiempo y no son estancas. Durante un período de muchos años, las aguas subsuperficiales han ido percolando a través de las estructuras, provocando la contaminación de las aguas subterráneas. Esto se comprobó al retirar las cubiertas de las estructuras. En este estudio, se han hecho simulaciones basadas en los procesos químicos para estimar la afección causada a la calidad de las aguas subterráneas por los vertidos accidentales de naftaleno disuelto ($C_{10}H_8$) en tres plantas de gas antiguas. Los resultados de simulaciones unidimensionales, en transitorio, para el flujo no saturado cercano a la superficie y el transporte de solutos, han sido utilizados para alimentar un modelo tridimensional de flujo y transporte en medio saturado. Los resultados y el análisis de sensibilidad mos-

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trados aquí indican que los vertidos accidentales de naftaleno tuvieron un impacto negativo considerable en la calidad de las aguas subterráneas en los tres sitios.

Keywords numerical modeling · contamination · groundwater quality · solute transport · USA

Introduction

Background

From the early 1800s to about 1950, manufactured-gas plants were operated in the United States to produce gas from coal, coke, or oil (e.g., Edison Electric Institute 1984; Gas Research Institute 1987). Most manufactured-gas plants were located in the midwestern and northeastern regions of the country (Electric Power Research Institute 1992). By the time these manufactured-gas plants began to close down in the 1930s and 1940s, because of the construction of interstate natural-gas pipelines, about 2,000 plants had been constructed throughout the United States (Landemeyer et al. 1998).

The contamination legacy resulting from the production of manufactured gas poses a significant and ongoing problem to groundwater quality. Leaks and spills have contributed to the contamination of manufactured-gas plant sites. Much of the contamination appears to be the result of accidental releases of mono- and polycyclic aromatic hydrocarbons (MAHs and PAHs) that are present in the manufacturing by-products. Coal tar was perhaps the most abundant by-product and had significant economic value. Coal tar was sold for multiple uses, such as explosives, pesticides, pharmaceutical preparations, pipe coatings, plastics, road tar, roofing pitch, and wood preservatives (McNeil 1981). Because of its commercial value, coal tar was usually stored in underground holding tanks and tar wells until removal from the site occurred, usually by rail. The holding tanks and tar wells were designed and built to contain the coal tar, using the technology of the day.

After a manufactured-gas plant was decommissioned, some amount of the coal tar was often left in the underground structures. When removed from service, the typical site of a manufactured-gas plant was dismantled, converted to a utility maintenance area and/or substation, or sold to a third party (Electric Power Research Institute 1996). Fifty years later, many holding tanks, tar wells, and other structures that were left behind when the plants were closed remain as sources of contamination that often need to be remediated.

Today, as utility companies proceed with the remediation of sites of former manufactured-gas plants, the issue of financial responsibility is raised. The cost of investigating and remediating a typical site has been estimated to range from \$1,000,000–9,000,000 (Gas

Research Institute 1990). As a result, many utility companies are pursuing reimbursement (through litigation) from insurance companies with which liability policies were held (Fels et al. 1996). These liability policies were typically written to cover exposure to conditions that resulted in property damage that was neither expected nor intended (Fels et al. 1996). Two central issues in the litigation are (1) determining whether the release of contaminants (and the timing thereof) was unexpected and unintended, and (2) ascertaining whether property damage occurred.

The purpose of the study reported here was to address the two issues listed above in a “what if” mode for three sites of former manufactured-gas plants. To accomplish this, physically based numerical models of unsaturated and saturated fluid flow and solute transport were applied to the three sites. The relevant boundary-value problems were constructed such that the sources of contamination could only be from structures that were intended to contain and store coal tar (e.g., holding tanks and tar wells). Using the best available data, the question was asked, “Could contamination emanating from the designated sources cause undesirable impacts to groundwater quality?” If the answer is no, then it follows, in a hypothesis-testing mode, that a liability policy should not be activated. If the answer is yes, then it should not be possible to reject the hypothesis that the resulting groundwater contamination was accidental (unexpected and unintended), and therefore a liability policy would be activated.

Objectives

Driven by a recent civil action, the objective of the effort reported here was to consider whether there have been off-site impacts to groundwater quality at three sites of former manufactured-gas plants during a 20-year period of insurance coverage (1949–1969). The impact of accidental releases of dissolved naphthalene ($C_{10}H_8$) on groundwater quality was estimated in this study by simulating fluid flow and solute transport through the unsaturated near-surface and the saturated subsurface.

Methods

The analyses presented here are founded on process-based simulations. In this study, three different models were used to simulate subsurface fluid flow and solute transport. All of the simulations reported here were conducted in an uncalibrated mode based upon the best available data. Only subsurface contamination sources for the three sites (e.g., holding tanks and tar wells) were considered in this study.

Source Composition and Concentration

Naphthalene is among the most common compounds in coal tars to dissolve into groundwater at many former manufactured-gas plant sites (Murarka et al. 1992; Durant et al. 1995). For example, Lee et al. (1992) determined that various naphthalenes were the dominant components in the eight coal tars that they studied. Because naphthalene is among the most soluble of the coal-tar constituents (32,000 µg/L), it is often considered to provide a worst-case indicator of groundwater contamination (Luthy et al. 1994).

The basic premise of the unsaturated near-surface naphthalene transport simulations undertaken in this study is the assumption of the presence of coal tar in structures such as storage tanks and tar wells. Dissolution, which is a function of aqueous solubility, is the primary release mode of coal tar constituents to the environment (Lee et al. 1992; Murarka et al. 1992). Since the structures were typically constructed from bricks and mortar and may have degraded due to age or outside stimuli, they are not completely leak-proof. Meteoric water percolating through the unsaturated near-surface and flowing groundwater could enter a structure and come into contact with the coal tar inside. The assumption was made for this study that the naphthalene component of the coal tar would become dissolved in water that entered a structure. Once the water was contaminated, it leaked out of the structure and produced a plume of naphthalene-contaminated groundwater. For example, dissolution from a single, buried, coal-tar source has been reported to generate a naphthalene plume with concentrations of >4,500 µg/L, at a site in the northeastern United States (Murarka et al. 1992).

The aqueous solubility of naphthalene was used as a basis for estimating the source concentrations for the simulations in this study. However, the aqueous solubility of a pure compound is not a valid way to estimate the aqueous concentrations that result from dissolution of a complex mixture, such as coal tar (Lee et al. 1992). Based upon the Raoult's law and its assumption of ideality, the dissolved concentrations of the various compounds are usually treated as being some fraction of the individual compound's aqueous solubility, where the fraction is based upon the fraction of that compound in the coal tar (e.g., Landmeyer

et al. 1998; Lane and Loehr 1992; Lee et al. 1992; Luthy et al. 1994).

The composition and quantity of coal tar that was produced as a by-product was a function of the feed-stock and the manufacturing process; coal tars from manufactured-gas plants vary from one site to another (Lee et al. 1992). Also, how and where coal tars were stored has an impact on their current state in terms of the availability of the constituents of interest (Murarka et al. 1992). For these reasons, it is not reasonable to assume that samples of coal tar currently in the structures are representative of all the tars that were ever present. In addition, some of the sources have been removed and no coal tar sample is available. In light of the above complications, the naphthalene source concentration used in this study was a conservative 10% of the aqueous solubility (3,200 µg/L).

Models

The approach used in this study to simulate the subsurface transport of dissolved naphthalene is summarized in Table 1. The model used for the unsaturated near-surface simulations in this study was LEACHM (Hutson and Wagenet 1992). The models used for the saturated subsurface fluid-flow and solute-transport simulations are, respectively, MODFLOW (McDonald and Harbaugh 1988) and MT3D (Zheng 1992).

Unsaturated near-surface

The program LEACHM was used in this study to simulate unsaturated near-surface fluid flow and solute transport. The one-dimensional Richards' equation of transient, vertical soil-water movement that was used in this study is given by:

$$\frac{\partial}{\partial z} \left[K(\theta) \frac{\partial h}{\partial z} \right] = \frac{\partial \psi}{\partial t} C(\theta) \quad (1)$$

$$C(\theta) = \frac{\partial \theta}{\partial \psi} \quad (2)$$

where $C(\theta)$ is the differential water capacity; h is the hydraulic head, the pressure head plus the elevation

Table 1 Steps used to simulate fluid flow and transport of dissolved naphthalene through the unsaturated near-surface and saturated subsurface at three sites of former manufactured-gas plants

1. Approximate the climatic history (plant inception to 2000) using precipitation data for study areas.
2. Approximate the soil properties for each site based upon soil texture and measured values (see Table 2).
3. Approximate the operational history of each manufactured-gas plant based upon anecdotal evidence.
4. Simulate (with LEACHM) transient, vertical unsaturated fluid flow and transport of dissolved naphthalene for subsurface contamination sources (plant inception to 2000; see Fig. 3).
5. Obtain dissolved naphthalene concentrations at the water table (to be used in step 8) for each source (plant inception to 2000), based upon simulated last-day-of-the-year concentration profiles in step 4.
6. Approximate the geology and saturated hydraulic conductivity of each site, based upon well logs (see Fig. 2 and Table 3).
7. Simulate (with MODFLOW) three-dimensional, steady-state groundwater flow for each site (see Fig. 2).
8. Simulate (with MT3D) three-dimensional, transient, saturated transport of dissolved naphthalene for each site (plant inception to 2000; see Fig. 4).

head (L); ψ is the pressure head (L); t is time (T); and z is the elevation (L). The soil-water-retention relationship (Campbell 1974), for $\theta < \theta_c$, is given by:

$$\psi(\theta) = a \left(\frac{\theta}{\theta_s} \right)^{-b} \quad (3)$$

where θ is the volume fractional water content (L^3/L^3); θ_s is the volumetric water content at saturation (L^3/L^3); and a and b are constants, although a is sometimes regarded as the air-entry value, $\psi_a(L)$. When $\theta \geq \theta_c$ the pressure head is estimated as:

$$\psi(\theta) = a \left(\frac{\left(1 - \frac{\theta}{\theta_s}\right)^{\frac{1}{2}} \left(\frac{\theta_c}{\theta_s}\right)^{-b}}{\left(1 - \frac{\theta_c}{\theta_s}\right)^{\frac{1}{2}}} \right) \quad (4)$$

where

$$\theta_c = \frac{2b\theta_s}{1+2b} \quad (5)$$

The hydraulic-conductivity relationship (Campbell 1974) is given by:

$$K(\theta) = K_s \left(\frac{\theta}{\theta_s} \right)^{2b+3} \quad (6)$$

where K_s is the saturated hydraulic conductivity (L/T).

The one-dimensional advection-dispersion equation for the vertical, transient transport of a decaying solute that was used in this study is given by:

$$\frac{\partial}{\partial z} \left[\theta D(\theta, q) \frac{\partial c}{\partial z} - qc \right] - \theta k_{ru} c = \frac{\partial \theta c}{\partial t} \quad (7)$$

where c is the aqueous-phase concentration in the unsaturated subsurface (M/L^3); q is the macroscopic (Darcy) water flux (L/T); $D(\theta, q)$ is a lumped parameter that includes the effects of molecular diffusion and mechanical dispersion (L^2/T); and k_{ru} is the rate constant of the first-order reactions in the unsaturated subsurface (1/T). LEACHM contains a correction for numerical dispersion that forces the minimum value of the dispersivity to be $0.16 \Delta z/\theta$. In this study, hydrodynamic dispersion in the unsaturated near-surface was taken to be represented by numerical dispersion.

For this study, simulated profiles of dissolved naphthalene concentration, $c(z, t)$, were used to estimate chemical loading to the water table (x, y, z, t) on an annual basis. Each source was represented as a group of contiguous finite-difference cells in the x, y direction that could be represented by a single, one-dimensional vertical soil column, and hence a single LEACHM simulation. The aggregate of the dissolved naphthalene concentrations loaded to the water table for each grid element (each year), $c(x, y, z, t)$, make up the annual loading files for the three-dimensional transient, saturated, subsurface-transport simulations.

Saturated subsurface

The program MODFLOW was used in this study to simulate saturated, subsurface-fluid flow. The three-dimensional, steady-state, groundwater-flow equation that was used in this study is given by:

$$\frac{\partial}{\partial x_i} \left(K_{ii} \frac{\partial h}{\partial x_i} \right) + q_w = 0 \quad (8)$$

where K_{ii} is a principal component of the saturated hydraulic conductivity tensor along the x_1 , x_2 , and x_3 axes (L/T); h is the hydraulic head (L); and q_w is the volumetric flux per unit volume of the saturated porous media representing the sources and/or sinks of water (1/T).

The program MT3D was used in this study to simulate solute transport in the saturated subsurface. The three-dimensional, transient advection-dispersion equation for solute transport in a saturated groundwater flow system with a decaying solute that was used in this study is given by:

$$\frac{\partial}{\partial x_i} \left(\mathbf{D}_{ij} \frac{\partial C_w}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (\mathbf{v}_i C_w) + \frac{q_w}{n_e} C_p - k_{rs} C_w = \frac{\partial C_w}{\partial t} \quad (9)$$

where x_i is the distance along the respective Cartesian coordinate axis (L); \mathbf{D}_{ij} is the tensor of hydrodynamic dispersion coefficients (L^2/T); C_w is the concentration of the dissolved solute in the saturated subsurface (M/L^3); \mathbf{v}_i is the average linear pore-water velocity vector (L/T); n_e is the effective porosity of the porous medium (dimensionless); C_p is the concentration of the solute dissolved in sources and/or sinks (M/L^3), $C_p = c$ for sources [see equation (7)]; k_{rs} is the rate constant of the first-order reactions in the saturated subsurface (1/T); and t is time (T). Equations (8) and (9) are linked through the average linear pore-water velocity term, which is given by:

$$\mathbf{v}_i = - \frac{K_{ii} \partial h}{n_e \partial x_i} \quad (10)$$

where the principal components of the velocity vector, along the x_1 , x_2 , and x_3 axes, are v_{x_1} , v_{x_2} , and v_{x_3} .

Simulation Assumptions

For the "what if" unsaturated near-surface and saturated-subsurface simulations undertaken in this study, it was assumed that (1) the decay rates for naphthalene were first-order with constant rate coefficients, and (2) sorption was not significant. Retardation was not included in the simulations reported here due to the lack of data on soil organic carbon for the three sites.

Case Studies

The three former manufactured-gas plant sites included in this study are referred to herein as site A, site B, and site C. The subsurface structures at each of the three sites were assumed to extend from the ground surface to approximately 4 m in depth (Dale Helmers, Northern Indiana Public Service Co., personal communication 1996). At sites A and B, field investigations indicated that the bottoms of some structures were below the water table (Dale Helmers, Northern Indiana Public Service Co., personal communication 1996 and 1998). For the site A structures, the depth of the leaks in the unsaturated near-surface was simulated to be 1.5 m, which is approximately half the distance between the surface and the water table (see Table 2). For the site B structures, the depth of the leaks in the unsaturated near-surface was simulated to be 2.4 m, because there was evidence that a significant leak had occurred at 2.4 m (8 ft) depth (Dale Helmers, Northern Indiana Public Service Co., personal communication 1996). For the site C structures, the depth of the leaks in the unsaturated near-surface was simulated to be 4.0 m, because the water table is below the bottoms of all the subsurface structures.

As discussed above, the unsaturated near-surface simulations were conducted with source concentrations of 10% of the aqueous solubility for naphthalene. For the saturated zone, the simulations were conducted with and without dispersion. The sources at each site were activated at different times during the course of each structure's history, due to operational needs at each plant and new construction. The sources were "turned on" in the simulations reported here based upon anecdotal evidence and Sanborn Fire Insurance maps (Dale Helmers, Northern Indiana Public Service Co., personal communication 1998). The sources were only "turned off" in the simulations reported here if a source were physically removed from a site.

Input Data

The monthly precipitation records used in this study to drive the unsaturated near-surface simulations for each of the three sites were obtained from the National Climatic Data Center (Table 2). These precipitation records provided monthly totals for the station of interest, but gave no information regarding precipitation intensity, duration, or the days that individual events actually occurred. For this study, the data were disaggregated to daily values by assuming that precipitation occurred every day at a uniform rate from midnight to 1 a.m. For the months and years in which precipitation data were not available, the average value from all available data for that particular month was used.

Table 2 summarizes the base-case input parameters for the transient LEACHM simulations in this study. For the unsaturated near-surface, estimates of the soil hydraulic properties were based upon soil texture (b , ψ_a , K_s) and measured values (K_s) at each site. The naphthalene half-life was taken from Howard et al. (1991). The upper boundary condition was designated as a flux-controlled surface boundary (i.e., non-ponded infiltration). The lower boundary condition was simulated as being the water table (i.e., $\psi=0$). The initial condition for the soil profile was uniform and relatively dry (i.e., $\psi=-150$ m). Each simulation was conducted from the inception year of a particular site through the year 2000.

Table 3 summarizes the input parameters for the steady-state MODFLOW and transient MT3D simulations. Figures 1 and 2 show the saturated, subsurface fluid-flow and solute-transport boundary-value problems used in this study for the three sites. Figure 1 shows the lateral boundary conditions for each site, and the locations and designations of each source. The lower, horizontal boundary was designated as a no-flow boundary in all simulations. The lower boundary was located at a distance far enough from the sources so as to not have a significant effect on the migration of the solute plumes. The upper boundary was the water table. For sites A and C (Fig. 1a, c), the average

Table 2 Input data for base-case unsaturated-zone simulations with LEACHM. b is a constant in Campbell's (1974) soil-water retention equation, ψ_a is the air-entry value, and K_s is the saturated hydraulic conductivity

Parameter	Site A	Site B	Site C	
Precipitation data ^a (station number)	124837	123037	124837	
Average depth to water table (m)	3.0	4.4	6.0	
Soil horizon	1	1	1	2
Depth of soil horizon ^b (m)	0.0–3.0	0.0–4.4	0.0–3.6	3.6–6.0
Space increment, Δz (m)	0.02	0.02	0.02	0.02
Half-life ^c (d)	48	48	48	48
b^d (–)	4.1	7.12	4.6	4.1
ψ_a^d (m)	0.121	0.299	0.154	0.121
K_s (m/d)	1 ^b	3×10^{-2b}	1 ^e	5 ^e
Silt ^b (%)	10	22	10	0
Clay ^b (%)	10	22	10	0

^a<http://www.ncdc.noaa.gov/pub/data/coop-precip/indiana.txt>

^bDale Helmers (Northern Indiana Public Service Co., personal communication 1996 and 1998)

^cHoward et al. (1991)

^dClapp and Hornberger (1978)

Table 3 Input data for saturated-zone simulations with MODFLOW and MT3D

Parameter	Site A			Site B			Site C
Δx (m)	5.3			4.7			6.0
Δy (m)	4.5			6.7			6.6
Δz (m)	1.0			1.0			2.0
Half-life (d) ^a	258			258			258
n_e^b (%)	Fill	Sand	Clay	Fill	Alluvium	Till	Alluvium
K_s^b (m/d)	20	25	10	15	20	10	20
	1	10	9×10^{-5}	3×10^{-2}	4×10^{-1}	3×10^{-2}	2

^aHoward et al. (1991)

estimated recharge (from LEACHM) for the entire simulation period was applied as a steady flux across the water table. For site B (Fig. 1b), recharge was not applied; a steady-state distribution of hydraulic head was estimated from field measurements and the recharge flux was assumed to be included implicitly in the head distribution. Figure 2 shows two views of the three-dimensional spatial distributions of saturated hydraulic conductivity estimated for each site. For the saturated-subsurface transport simulations in which dispersion was considered, the horizontal and transverse dispersivities were each set to 1.0 m. Solutes were allowed to flow out of the simulation domain only at constant-head boundaries.

Site Descriptions

Site A

The hydrostratigraphic units for site A are illustrated in Fig. 2a. The bedrock in the area of site A is composed primarily of Devonian and Mississippian shale that occurs at 45–90 m below the ground surface. The overlying sediments consist of Pleistocene glacial outwash deposits of sand and gravel that contain interbedded layers of silt and clay. Four distinct soil layers exist at site A. The uppermost layer is fill that is mostly 2 m thick but increases to 5 m near the river. The fill is composed of loose, black and brown, medium sand and gravel with some silt and red brick fragments. Beneath the fill is a layer of outwash sand and gravel with interbedded gravel and silt that is 2–5 m deep. A 25-m-thick clay layer separates the upper two layers from 40–45 m of sand and gravel outwash. There were three sources for the site A simulations (Fig. 1a). Source 1 was active from 1871–2000, source 2 was active from 1890–2000, and source 3 was active from 1907–2000 (Dale Helmers, Northern Indiana Public Service Co., personal communication 1998).

Site B

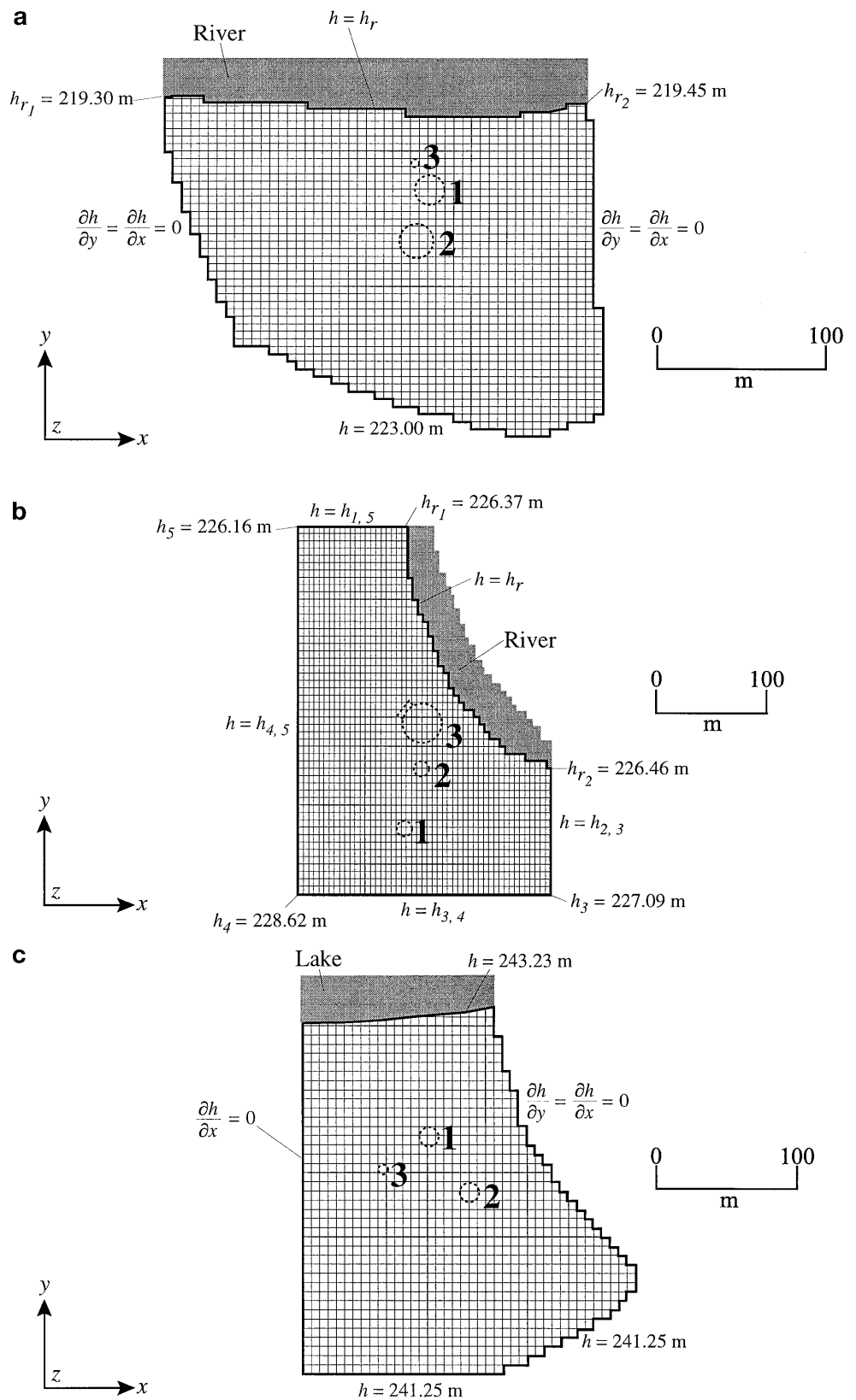
The hydrostratigraphic units for site B are illustrated in Fig. 2b. The bedrock in the area of site B is mostly composed of Devonian shale and limestone and older sedimentary rocks (Fleming 1994). The overlying sediments consist of Pleistocene glacial deposits. Three

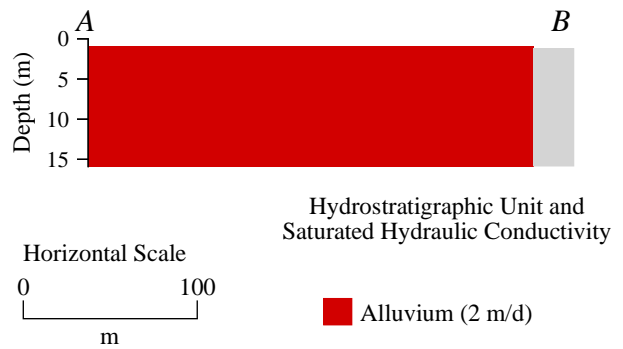
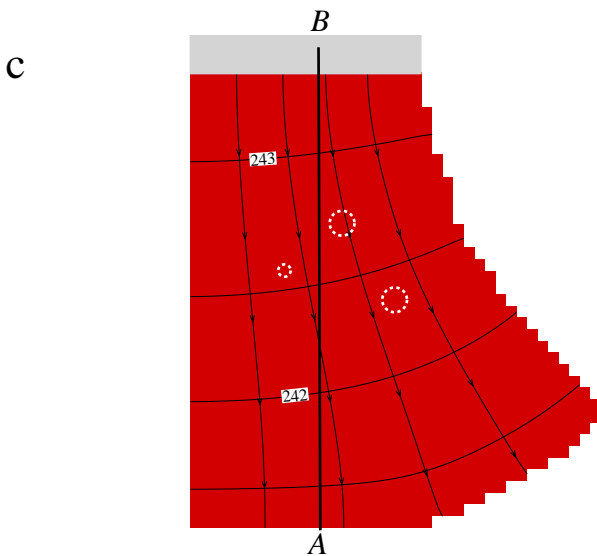
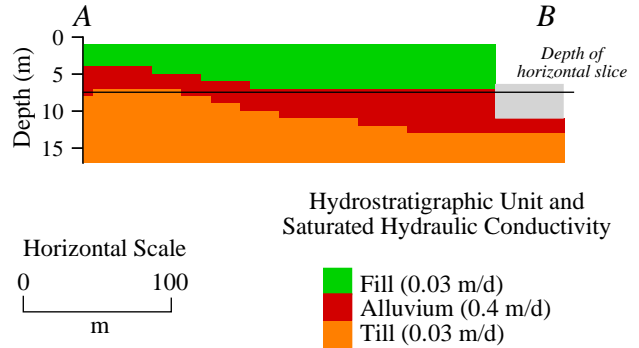
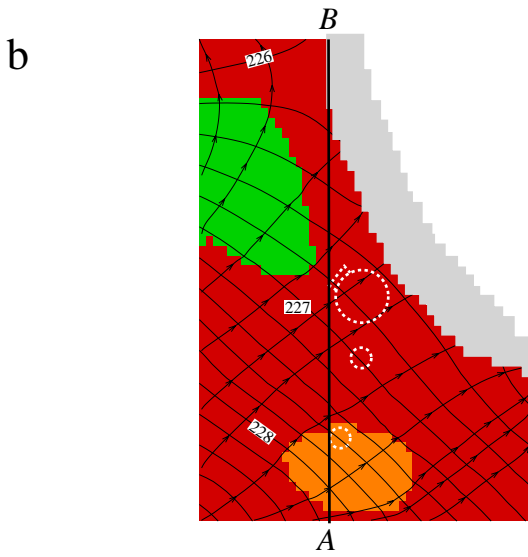
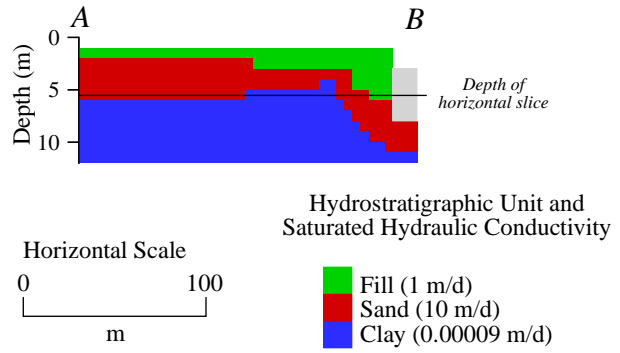
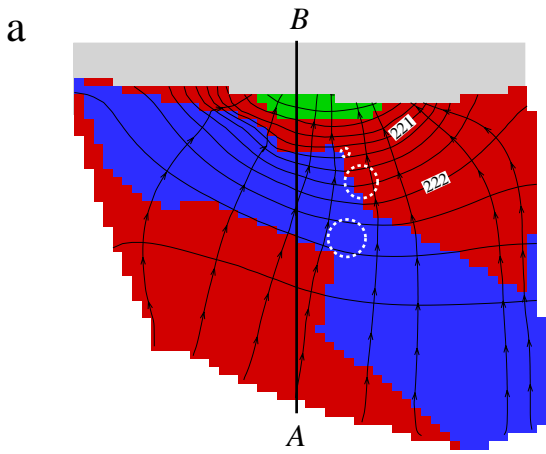
distinct soil layers exist at site B. The uppermost layer is fill that is 2–6 m thick, with an average thickness of 4 m. The fill consists of sand with silt, clay, glass, cinders, coal, wood, and brick fragments. Beneath the fill is a layer of alluvium that ranges in thickness from 2–6 m, with an average thickness of 4 m. The alluvium is primarily sand, with silt and gravel present. Beneath the alluvium is a gray, basal till that is at least 12 m thick. The till is composed of silt with clay, fine sand, and gravel. There were three sources for the site B simulations (Fig. 1b). Source 1 was active from 1853–1994, source 2 was active from 1896–2000, and source 3 was active from 1910–1996 (Dale Helmers, Northern Indiana Public Service Co., personal communication 1998). Source 3 is actually two separate structures (see Fig. 1b); the large circular structure was a holder and the smaller, rectangular structure immediately adjacent to it was a tar separator. Sources 1 and 3 were removed in 1994 and 1996, respectively (Dale Helmers, Northern Indiana Public Service Co., personal communication 1996).

Site C

The hydrostratigraphic units for site C are illustrated in Fig. 2c. The bedrock in the area of site C is primarily Devonian and Mississippian shale and is overlain by Pleistocene glacial sediments. Two aquifers exist at site C. The deep aquifer is composed of sand and gravel and is partially confined. The shallow aquifer is unconfined. The deep aquifer is overlain by 5–15 m of clay ablation till. In general, locations exist where the two aquifers are hydraulically connected, but at the site location the aquifers are completely separate. The upper 12–15 m of strata are interbedded fine sands with varying amounts of silt and gravel and 2–3 m of fill. Below 15 m is a thick layer of fine sand. A deep, basal till layer, composed of dense dark gray clay, occurs at approximately 60 m depth. There were three sources for the site C simulations (Fig. 1c). Source 1 was active from 1855–1996, source 2 was active from 1855–2000, and source 3 was active from 1912–2000 (Dale Helmers, Northern Indiana Public Service Co., personal communication, 1998). Source 1 was removed in 1996 (Dale Helmers, Northern Indiana Public Service Co., personal communication 1996).

Fig. 1 Site maps showing finite-difference grids and boundary-value problems for **a** site A, **b** site B, and **c** site C. Specified head boundaries along which hydraulic head is not spatially constant were calculated as linear interpolations between values shown at the two ends. *Subscript r* refers to the hydraulic head adjacent to a river. Contamination sources are shown as *dashed circles* labeled with a **bold numeral**. Numbers correspond to source numbers in Fig. 3





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Fig. 2 Site maps and vertical sections showing spatial distribution of hydrostratigraphic units and saturated hydraulic conductivities for **a** site A, **b** site B, and **c** site C. Map views show results of saturated-zone fluid-flow simulations performed with MODFLOW, using boundary-value problems shown in Fig. 1. Steady-state hydraulic heads (m) and some flow lines are shown for the layer indicated on vertical sections. Since there is only one hydrostratigraphic unit for site C, the groundwater flow solution can be considered to be representative of all layers of the boundary-value problem. Contamination sources are shown as *white dashed circles* (see Fig. 1)

Results

The results presented here are for sites A, B, and C, in which the depth of the leak from the source structures in the unsaturated near-surface at each site was 1.5, 2.4, and 4.0 m, respectively. For sites A and B, these are not the worst-case scenarios, because the bottoms of some structures are actually below the water table. For site C, the results shown do represent the worst-case scenario (leaking from or near the bottoms of the structures).

Unsaturated Near-Surface

Simulated concentration histories (with LEACHM) of dissolved naphthalene loaded to the water table for each of the three sites for each of the three sources are presented in Fig. 3. The range and variability of the simulated loading concentrations are shown in Fig. 3. For example, the loading concentrations at site A span three orders of magnitude, whereas at site B the range is two orders of magnitude. The variability with time is caused by the variable precipitation rates and amounts. The portions of the plots where the loading concentration is constant with time represent time periods when precipitation data were not available and the average values were used. Even though the distance to the water table is approximately the same for site B and site C, the maximum loading concentration differs by a factor of approximately seven. The different loading concentrations for sites B and C are related to the soil properties at the two sites (e.g., K_s is greater for site C; see Table 2), which in turn leads to different residence times for naphthalene in the unsaturated near-surface and thus different amounts of decay. The timing of when the different sources were turned on and off is also shown in Fig. 3.

Saturated Subsurface

The results from the steady-state groundwater flow simulations (with MODFLOW) are presented in Fig. 2 as contour lines of hydraulic head and flow lines for each of the three sites. The effect of the geology (K_s) on flow direction is shown in Fig. 2a, b; i.e., flow lines refract in several locations where contrasts in K_s

occur. The groundwater velocities at each of the three sites (estimated with MODFLOW) and the water-table loading concentrations of dissolved naphthalene (Fig. 3) for the three sources at each of the three sites (estimated with LEACHM) serve as input to the transient solute-transport simulations (with MT3D). The results from the three-dimensional, transient solute-transport simulations are shown as two-dimensional snapshots for the year 1959 in Fig. 4. The snapshots in Fig. 4 show the maximum simulated concentration of dissolved naphthalene in any given vertical column of finite-difference cells. In this manner, the three-dimensional solution to the solute-transport equation can be displayed as a two-dimensional plot without losing any of the essential concentration information. The left-hand side of Fig. 4 shows results for simulations in which advective transport was the sole cause of solute flux. The right-hand side of Fig. 4 shows results for simulations in which advective transport and dispersion were the joint cause of solute flux. The snapshots in Fig. 4 each show that dissolved naphthalene is simulated to migrate to the edge of the boundary-value problem (i.e., beyond the site boundary).

Only snapshots for 1959 are shown in Fig. 4. Other snapshots during the 20-year insurance-coverage period (i.e., 1949–1969) show both larger and smaller dissolved naphthalene plumes, as the plumes expand and contract due to the amount of precipitation. The simulation results shown in Fig. 4 indicate an impact on groundwater quality. Figure 4 also illustrates the large difference in the predicted behavior of the dissolved naphthalene plumes in groundwater at the three different sites, both in terms of distance migrated and in the extent of relatively high concentrations.

The impact that dispersion has on the simulation results for the three sites is illustrated in Fig. 4; the solute plumes that were subject to dispersion cover a larger area with peak concentrations that are somewhat lower. The snapshots for site A (Fig. 4a) illustrate the effects of dispersion quite well. The groundwater flow pattern near the sources (see Fig. 3a) focuses flow directly toward the river, so that the results without dispersion show almost “plug” flow from the sources to the river. In contrast, the simulation with dispersion includes a flux that acts against the advective-focusing of flow lines, generating a more spread-out concentration distribution. In both cases, dissolved naphthalene concentrations of tens of micrograms per liter are estimated to flow directly into the river.

Figure 4b shows results for site B. The dissolved naphthalene plume migrated a shorter distance away from the sources and at lower concentrations. Figure 4c shows simulation results for site C. As with site A (Fig. 4a), the effects of dispersion are pronounced. The right-hand side of Fig. 4c shows a solute plume in which the regions of high concentrations are considerably smaller than on the left-hand side of Fig. 4c.

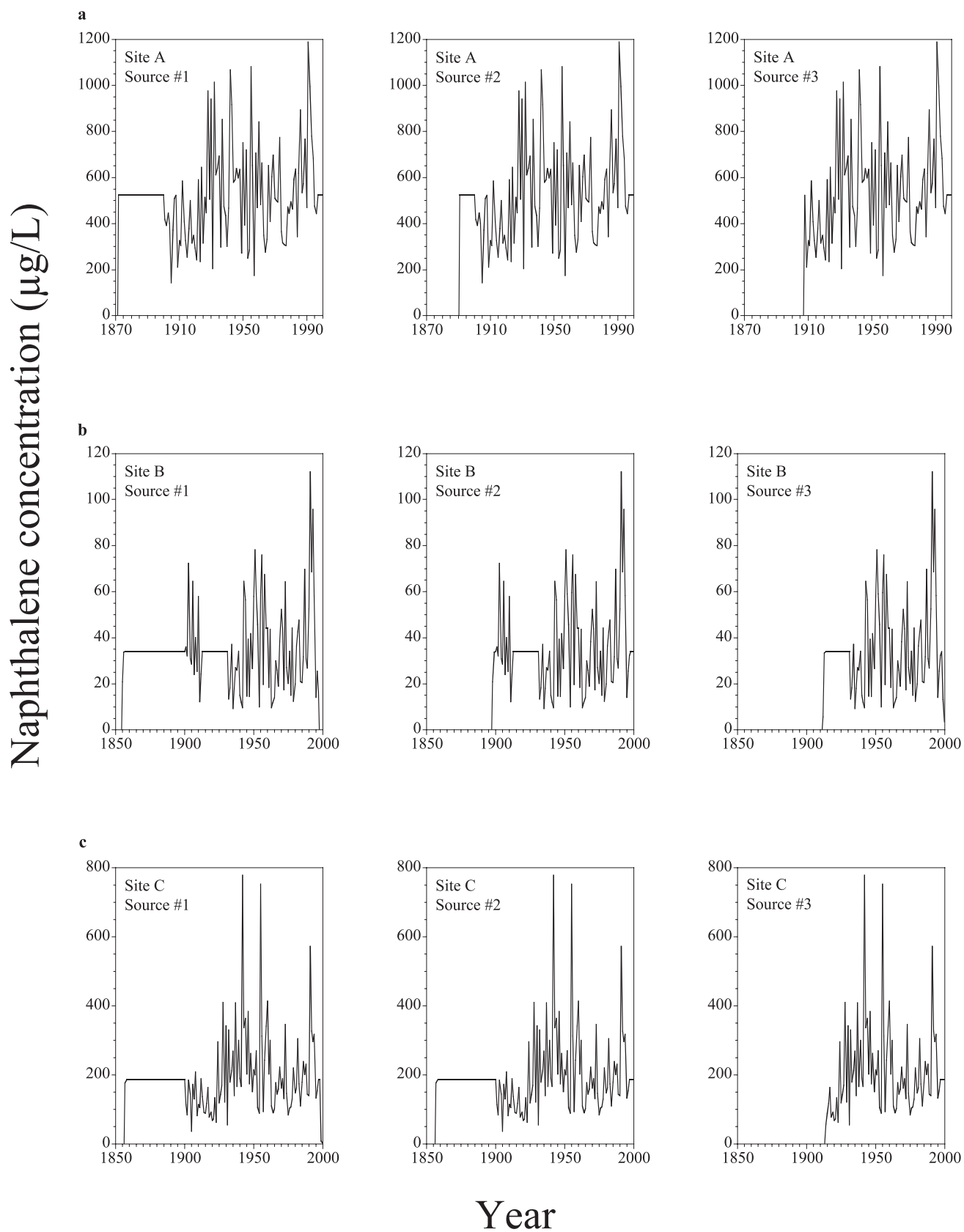


Fig. 3 Results from nine unsaturated-zone fluid-flow and solute-transport simulations performed with LEACHM showing dissolved concentration of naphthalene loaded to the water table for **a** site A, **b** site B, and **c** site C. Concentration histories for the three sources for each of the three sites are shown. *Source numbers* refer to maps shown in Fig. 1

There is a subtle difference in the results for dispersion for site B and site C (Fig. 4b, c, respectively). In Fig. 4b, the results with dispersion show that the leading edge of the solute plume has moved farther away from the sources than without dispersion. In contrast, Fig. 4c shows that the solute plume with dispersion did not move as far as the plume without dispersion.

Discussion

The simulation results presented in Figs. 3 and 4 illustrate the non-intuitive interplay between the effects of dissolved naphthalene movement through the unsaturated near-surface (e.g., soil hydraulic properties, precipitation rate), chemical properties (half-life), consideration of the depth of leak, and the effect of geology on the resulting dissolved naphthalene plumes in the saturated subsurface. An important implication of this interplay is that “back-of-the-envelope” calculations of the fate of dissolved MAHs and PAHs in the subsurface would not be capable of providing a reasonable assessment of impacts on groundwater quality.

Impact of Geology/Dispersion

The site stratigraphy plays an important role in how contaminants move in the subsurface. For example, at sites A and B, layers of lower conductivity material are immediately below the relatively thin, primary water-transmitting layers (Fig. 2). At site C, a single, thick, high-conductivity layer exists (Fig. 2). At site B, in the presence of dispersion, the low-conductivity layers below the main flow horizon force the simulated leading edge of the naphthalene plume to move out ahead of the advective front (see Fig. 4). Because no such layers exist at site C, dispersion smears out the leading edge by allowing increased spreading in the vertical direction, causing the advective front to move out ahead of the leading edge that was simulated with advection and dispersion.

Sensitivity Analysis

The simulated water-table loading concentrations of dissolved naphthalene in this study are conditional on the values of several parameters, some of which are more uncertain than others. To address the uncertainty, a sensitivity analysis was performed (using LEACHM), for each of the three sites, in which the values of b , ψ_a , K_s , $t_{1/2}$, and the depth to the water

table were varied. The results from the ten cases that make up the sensitivity analysis are compared with the base-case results in Fig. 5.

For cases 1–4, the values of b and ψ_a were adjusted up and/or down one soil textural class from the base-case texture in accordance with values reported by Clapp and Hornberger (1978). If the soil texture was at one of the delimiters, then that particular case was not necessary. For cases 5 and 6, respectively, the value of K_s was increased and decreased by 50% of the base-case value. For cases 7 and 8, respectively, the depth to the water table was increased and decreased by 50% from the base case value. For both cases 9 and 10, the value of $t_{1/2}$ was decreased. For each of the ten permutations of the base-case simulations, only one parameter was modified at a time from the base-case value. For example, in case 5 for site A, the value of K_s was increased to 2.0 m/d (from 1.0 m/d), while the values of b and ψ_a , the depth to the water table, and $t_{1/2}$ were kept at 4.1, 0.121 m, 3.0 m, and 48 d, respectively.

Figure 5 illustrates that the simulated loading to the water table is most sensitive to the depth to the water table and the half-life. For all three sites, decreasing the depth to the water table resulted in the leak occurring below the water table; hence the water-table loading concentration was the same as the source concentration (i.e., 3,200 $\mu\text{g/L}$). Increasing the depth to the water table resulted in significant water-table loading concentrations in all but one case (case 7, site B; Fig. 5b). Decreasing the half-life reduced the concentration of dissolved naphthalene that was loaded to the water table, as expected. The water-table loading concentrations are relatively insensitive to all the other adjustable parameters. In all cases except two (cases 7 and 9 for site B; Fig. 5b), significant concentrations of dissolved naphthalene still reach the water table.

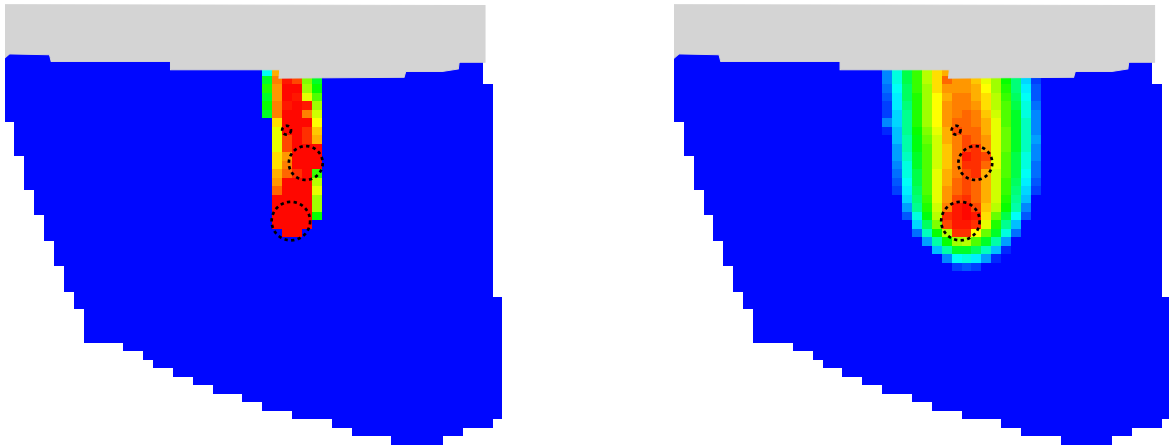
The results in Fig. 5 suggest that the estimation of soil properties would have to contain significant errors before the predicted water-table loading concentration would be greatly in error. Errors related to the chemical half-life are more difficult to quantify. For example, Durant et al. (1995) report that the half-life of naphthalene ranged from 11–169 d under aerobic conditions and from 84–144 d under anaerobic (nitrate and sulfate present) conditions in experiments that they performed. In most cases, errors in the measured

Fig. 4 Results from six saturated-zone solute-transport simulations performed with MT3D showing dissolved naphthalene concentrations at the end of 1959 for **a** site A, **b** site B, and **c** site C. Concentration shown at each horizontal location is the maximum concentration for the vertical column of finite-difference cells at that location. *Left* Results with advection only; *right* results with advection and dispersion. Naphthalene leaching results, shown in Fig. 3, were input to MT3D simulation results shown here

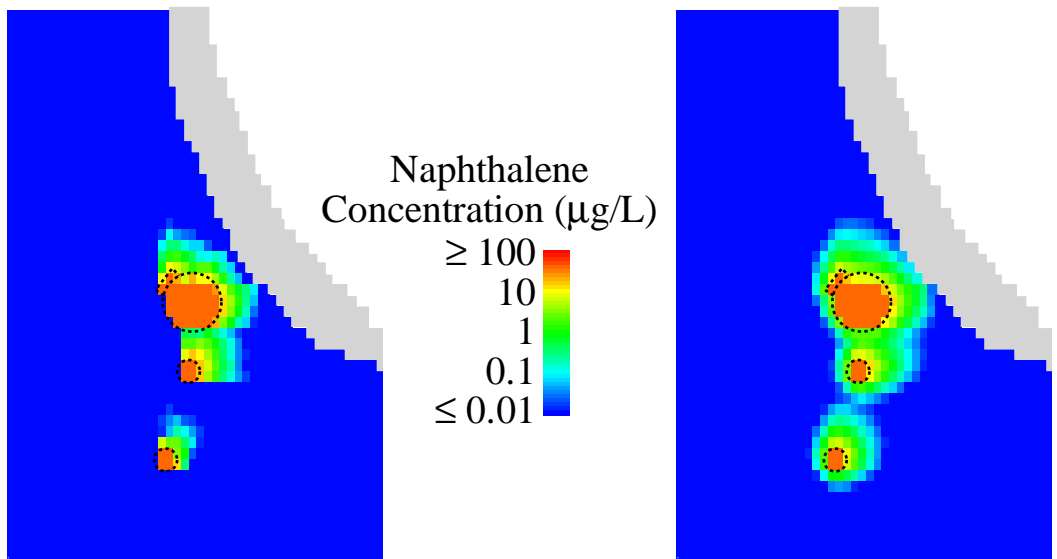
Advection

Advection and Dispersion

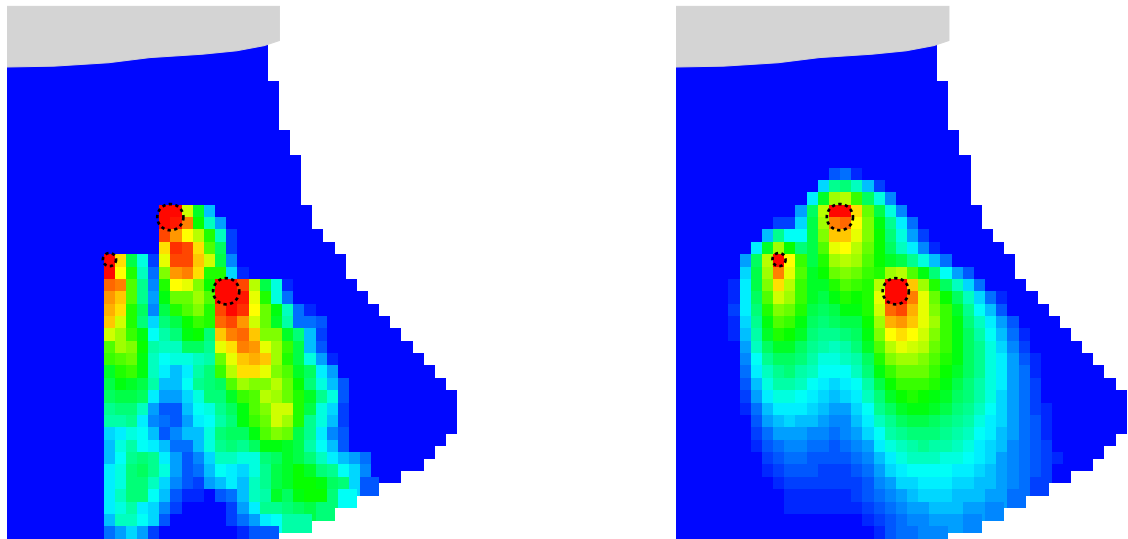
a



b



c



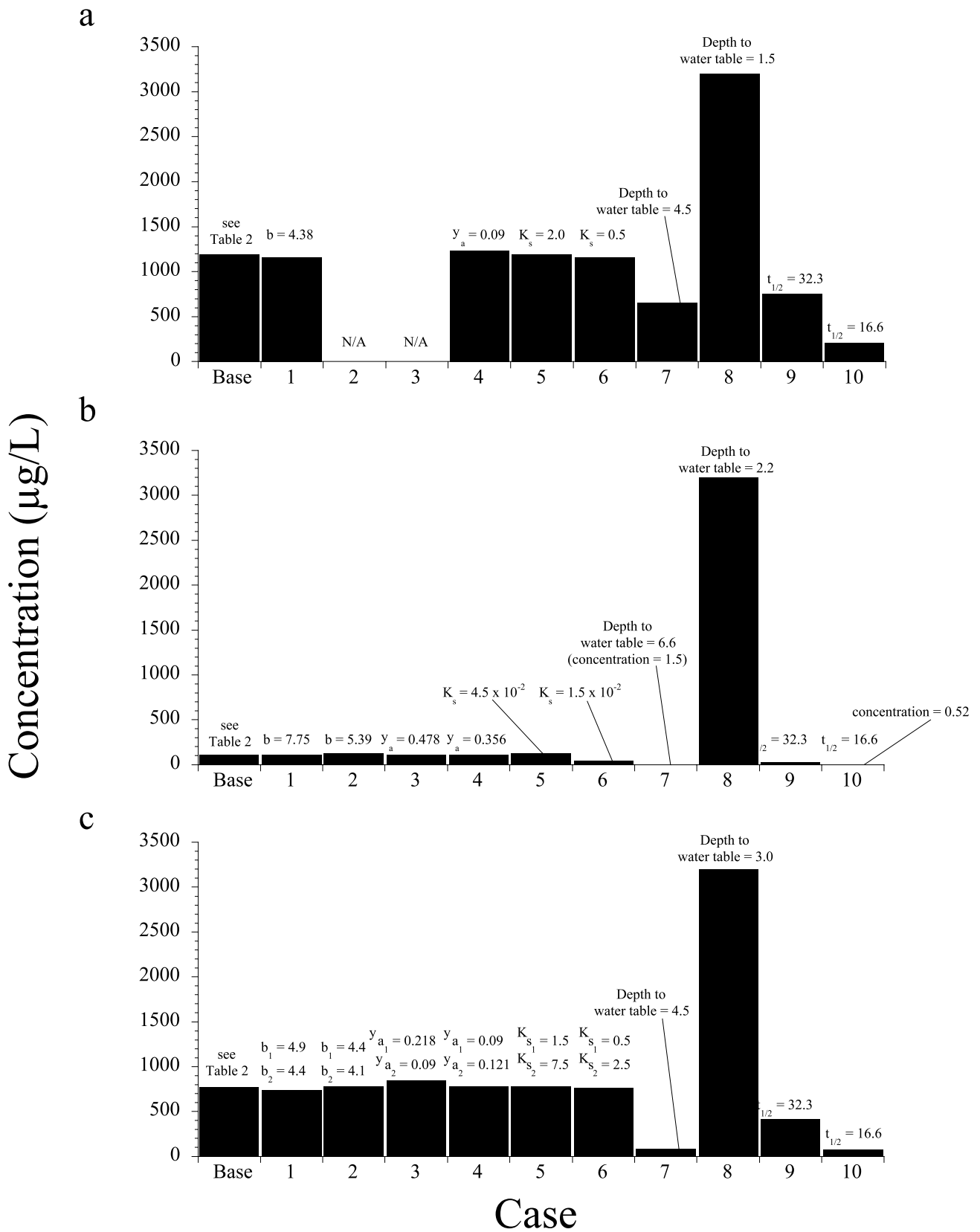


Fig. 5 Results of sensitivity analyses performed with LEACHM showing dissolved concentrations of naphthalene loaded to the water table for **a** site A, **b** site B, and **c** site C. Parameters $b(-)$, ψ_a (m), K_s (m/d), depth to water table (m), and $t_{1/2}$ (d) were varied individually for the different cases, while other parameters were kept at their base-case values

depth to the water table would not be a major concern. It is unlikely for the depth to the water table to be consistently incorrect by $\pm 50\%$ in most field studies.

The two variables that are not included in the sensitivity analysis reported here are the naphthalene source concentration and the precipitation history. The naphthalene source concentration used in this study (i.e., 10% of the aqueous solubility, or 3,200 $\mu\text{g/L}$) was conservative. Increasing the value of the source concentration would only reinforce the conclusions that have already been made. The impact of changes in the precipitation rate, duration, and/or timing are, at a basic level, captured by changing the chemical half-life. For example, increasing the precipitation rate would increase the leaching rate and subsequently decrease the amount of decay

Conclusions

Decommissioned manufactured-gas plants have led to a legacy of groundwater contamination due to accidental releases of MAHs and PAHs from subsurface structures. In the study reported here, process-based numerical simulations were conducted to estimate the impacts on groundwater quality resulting from three former manufactured-gas plants. The simulation results reported here, for the unsaturated near-surface and the saturated subsurface, indicate that accidental releases of naphthalene have most likely resulted in significant, negative offsite impacts on groundwater quality at each of the three sites considered in this study.

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