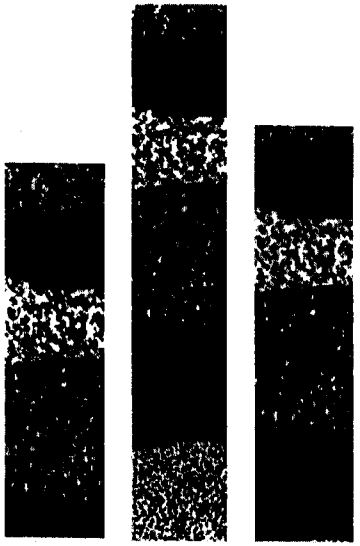
Natural Attenuation of Chlorinated Solvents, Petroleum Hydrocarbons, and Other Organic Compounds



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products in natural waters (Thurman et al., 1996). The lack of ESA formation suggests that ESA formation in nature primarily occurs in soils during runoff, whereas oxanillic acid formation predominantly occurs in the final receiving waters.

PRACTICAL CONCLUSIONS

Our studies have shown that environmentally relevant water conditions can be created in field microcosms to assess herbicide transformation phenomena in natural systems. Overall, herbicide decay rates were most rapid in warm nutrient-rich waters with the highest rates of decay being noted in methanogenic, anaerobic systems. These observations are significant because nutrient-rich water conditions often are present in areas where herbicide is the greatest. In principle, therefore, the highest rates of herbicide decay should also occur in waters most impacted by agricultural activity. On a policy level, our data suggest that waters that have not been historically exposed to previous agricultural or other human activity, or are innately low in nutrients, should be particularly protected from future herbicide exposure.

ACKNOWLEDGEMENTS

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EVALUATION OF A NOVEL NATURAL ATTENUATION SCENARIO

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ABSTRACT: Subsurface occurrences of DNAPL pools, residual in soil, and dissolved PAHs and BTEX in groundwater have been delineated at a former coal tar processing and coke production plant in New Jersey. A Brownfields remediation plan has been proposed for the site with the objective of stopping the discharge of DNAPL and impacted groundwater to an adjacent river, and limiting the potential for direct exposure to surface soil. As part of the remediation, over 4 million cubic yards of structural fill will be placed over the site, and containment walls will be installed along the river shoreline. The modeling analysis conducted to evaluate the plan had a unique aspect: it is expected that in the period immediately following fill placement and containment, most of the groundwater flowing off the site will originate from consolidation of the underlying compressible strata. Modeling results indicated that natural attenuation would achieve remedial objectives for the dissolved-phase plume.

INTRODUCTION

Brownfields programs are being advanced in many areas of the United States as a mechanism to encourage remediation and redevelopment of inactive industrial sites. Many inactive sites are contaminated with polycyclic aromatic hydrocarbons (PAHs), monoaromatic compounds (BTEX), and similar sparingly soluble, biodegradable organic compounds. The evaluation discussed herein examined the feasibility of implementing a Monitored Natural Attenuation (MNA) remedy for dissolved phase BTEX and PAHs at a Brownfield site, where the remedial and redevelopment strategies significantly change the hydrogeologic regime.

CONCEPTUAL MODEL DEVELOPMENT

Site Description

The study site encompassed 155 acres and operated as a coke production facility, coal tar processing facility, cyanide plant, and sulfuric acid production plant from 1917 until 1979 . The coal tar refinery (Figure 1) was the source of the greatest waste volumes and the most persistent organic compounds currently observed in site soil and groundwater. Elevated benzene concentrations have also been detected in shallow groundwater in the former coke plant area.

Site Hydrogeology

The most important hydrogeologic unit at the site, with regard to migration of constituents of interest (COIs), is an unconfined surficial fill. This unit is 6-20 ft (1.8-6.1 m) thick and composed primarily of coal, coke fines and sand. Below the

shallow fill lies a series of low-permeability units, including an organic silty peat (Meadow Mat), organic silty clay, silty varved clay, and glacial till (Figure 2). The Meadow Mat, organic silty clay, and varved clay are highly compressible and have only been subjected to minimal loading in their history, as most former plant structures were supported on pilings.

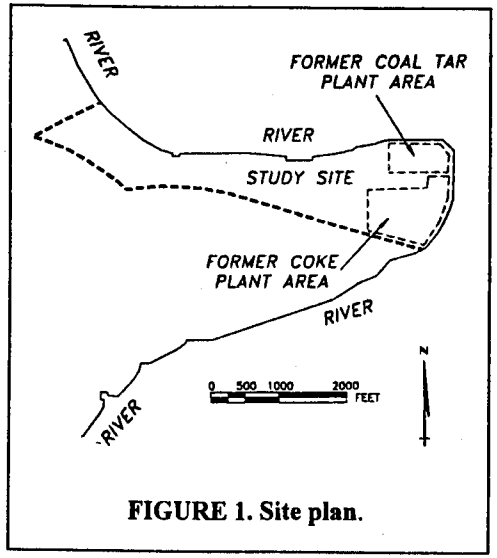

FIGURE 1. Site plan.

COI Distribution and Characterization

COIs are present at the site as both separate and dissolved phases. The separate phase liquid is coal tar that is slightly more dense than water, and therefore classified as a DNAPL. The DNAPL source area is the former coal tar processing facility, located in the northeast corner of the site, where DNAPL occurs as pools at the bottom of the fill unit, and as residual. The principal dissolved phase COIs (dpCOIs) derived from the coal tar are organic compounds: BTEX and PAHs. The dpCOIs occur over a somewhat larger area, but are confined to the site.

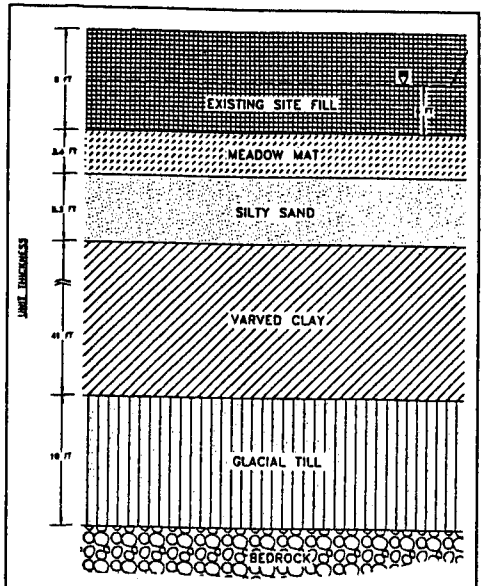

FIGURE 2. Site stratigraphy.

dpCOI Fate and Transport

The principal dpCOIs are sparingly soluble and variably biodegradable; the most mobile compounds also tend to be the most readily biodegradable. The mobility of the dpCOIs is greatly reduced by the high organic content of the shallow fill unit, which causes a relatively high degree of sorption.

Remediation Plan

A Brownfields proposal has been put forth in which a layer of processed dredged material up to 10 m thick would be placed as

structural fill across the entire site (Figure 1). In addition, a sheetpile and slurry wall containment structure would be placed along approximately one mile of shoreline and keyed into the underlying low-permeability strata. The remedial objective is to prevent discharge of DNAPL and dpCOIs to the river through the surficial fill unit. An important component of this program is to prevent discharge of dpCOIs above regulatory standards [71 ug/L for benzene; no standard for naphthalene] to the river south of the site, after the northward discharge is prevented by the containment system.

Comparison of Pre- and Post-Construction Conceptual Models

In the pre-construction conceptual model (Figure 3), shallow groundwater generally flows by the shortest path to the adjacent Hackensack River, from throughout the peninsula on which the site is located. The post-construction conceptual model indicates the substantial effect that the remediation plan will have on the local hydrogeologic regime. Installation of the containment wall along the entire on-site shoreline of the river eliminates direct shallow groundwater discharge from the site to the river. Placement of processed dredged material over the entire site decreases groundwater recharge from on-site infiltration to negligible amounts. However, in the short term, substantial influx of groundwater to the shallow fill unit occurs, due to consolidation of the underlying compressible

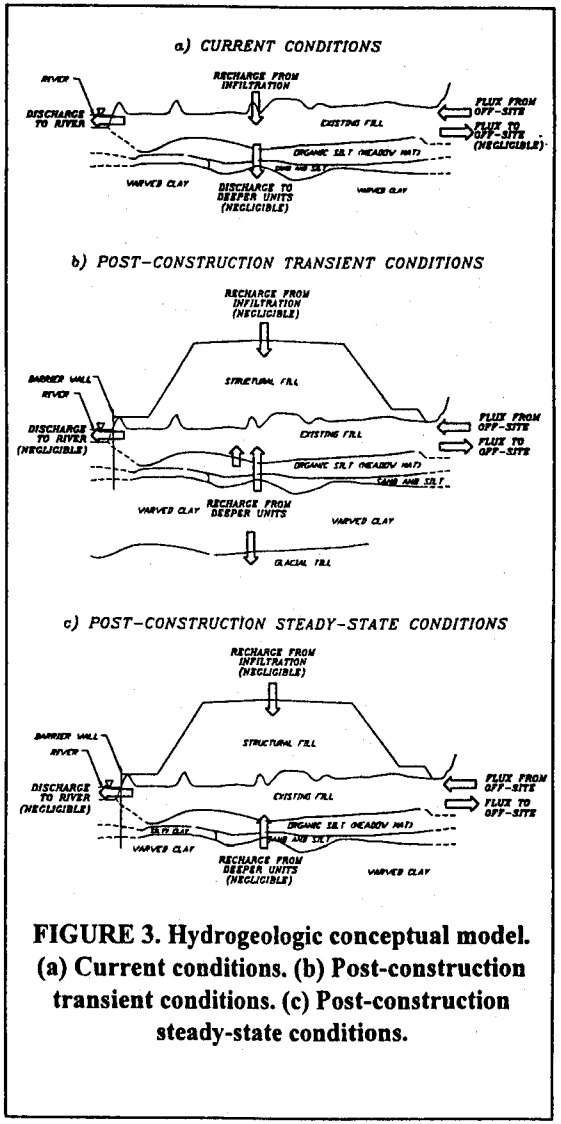

FIGURE 3. Hydrogeologic conceptual model. (a) Current conditions. (b) Post-construction transient conditions. (c) Post-construction steady-state conditions.

units. In the post-construction stage, the flow direction of on-site groundwater is generally away from the river, toward off-site areas to the south.

METHODS

Data Collection

Samples from each of the compressible units were subjected to geotechnical testing to determine the expected rate of consolidation and pore-water discharge, under the expected surcharge loading due to fill placement. Initial conditions for COI distribution were obtained through groundwater sampling and monitoring. Analysis of fill material showed a mean organic carbon content of 20%, indicating relatively high potential for sorption of dpCOIs. Site DNAPL was analyzed and results were used to estimate effective solubility for various coal tar constituents.

Numerical Model Design

The entire peninsula on which the site is located was chosen as the model domain (Figure 4), on the basis that it represented a discrete hydrologic unit. All boundaries corresponding to the river were represented as constant-head, zero-concentration boundaries. The inland boundary was represented as a no-flow boundary, on the assumption that the direction of shallow groundwater flow was similar to the topographical gradient (i.e. parallel to the boundary). DNAPL source areas were represented as constant-concentration nodes (infinite sources of dpCOIs) at the effective solubility of all coal tar constituents.

The compressible subsurface units were assumed to be either single-drained or double-drained, as follows: consolidation pore water derived from the uppermost compressible units was assumed to drain only to the shallow fill aquifer, while pore water discharge from the lower compressible units was assumed to be split equally between the shallow fill and the lower glacial till unit (underlying the compressible units). Pore water flux was modeled as an external flux into the fill unit, similar to the manner in which infiltration would be handled. The flux rate was estimated from consolidation

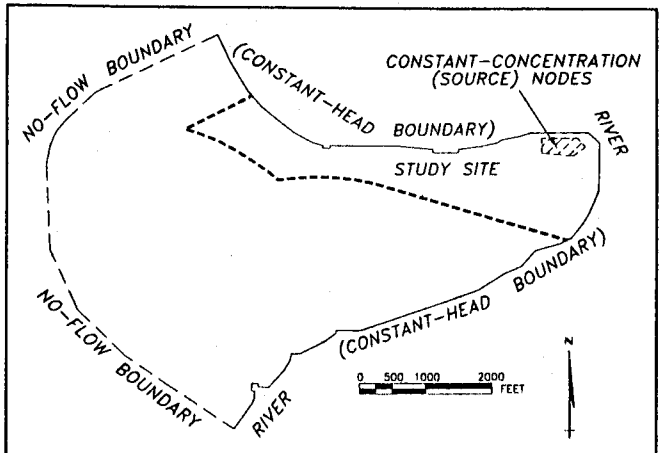

FIGURE 4. Model domain and boundary conditions.

testing.

The numerical modeling packages used to perform the simulation were the commercially available programs MODFLOW and MT3D, for simulation of groundwater flow and dpCOI transport, respectively. All simulations were executed under transient conditions for a period of fifty years.

RESULTS

Flow simulations indicated that the groundwater flow regime will approach steady-state in less than five years after construction (Figure 5). Results of the dpCOI transport simulation indicate that the most soluble and mobile dpCOIs, as represented by benzene and naphthalene, do not migrate substantially over this period (Figures 6 and 7), due to the highly sorptive character of the shallow fill. Long term migration continues to be negligible due to sorption and also because consolidation flux is minimal in the long term, and because long term infiltration is limited by placement of processed dredge material. A minimal biodegradation rate (half-life = 1000 days) was incorporated into the model for benzene, while no biodegradation was assumed for naphthalene, adding an additional degree of conservatism to the results.

A sensitivity analysis was performed as part of this evaluation to determine which parameters most strongly influence the behavior of the system, within the range of expected values. Values for hydraulic conductivity and storativity of the fill, off-site recharge, dispersivity, dpCOI decay rate, and sorption coefficients were varied individually. Results showed that none of the parameters influenced the system in a manner that would change the net conclusion: that MNA would meet the remedial objective of preventing dpCOI migration to the river south of the site.

Implementation of the site remedy is in progress. Preliminary groundwater monitoring

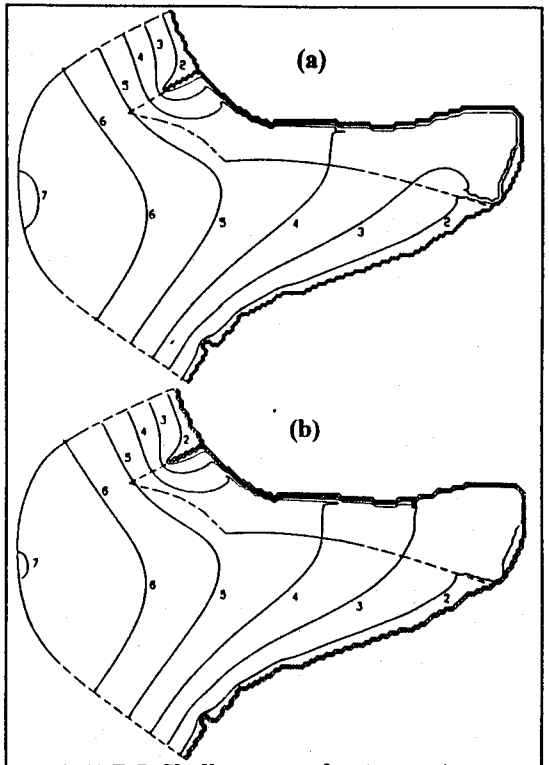

FIGURE 5. Shallow groundwater contours (ft-msl). (a) t = 5 years. (b) t = 50 years.

results suggest that the shallow aquifer is responding to surcharge loading as expected.

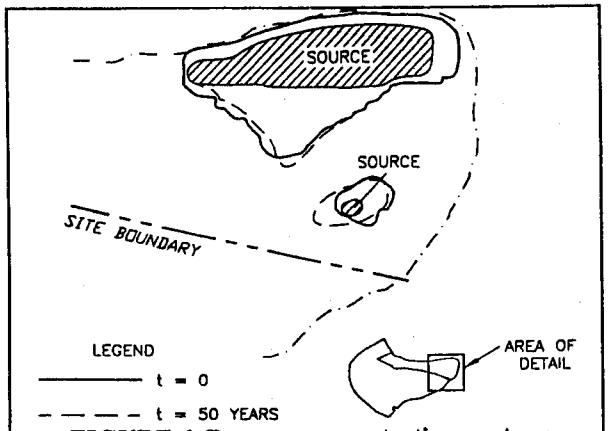

FIGURE 6. Benzene concentration contour (71 ug/L) at t = 0 and t = 50 years.

CONCLUSIONS

The evaluation presented herein used conventional modeling programs to simulate consolidation flux - a process that is not typically considered in fate and transport modeling. Results indicated that in the post-construction setting, MNA would achieve the remedial objective of preventing dpCOIs from migrating to the river south of the site, at concentrations in excess of remediation standards. The objective is met through the combination of existing site conditions, and substantial modifications to the hydrogeologic regime. In the early post-construction period, a relatively large quantity of groundwater flows off the site, but plume migration is limited by a high degree of sorption. In the long term, the tendency for off-site groundwater flow is minimal, as on-site consolidation flux subsides and on-site infiltration is limited due to a cover of processed dredge material.

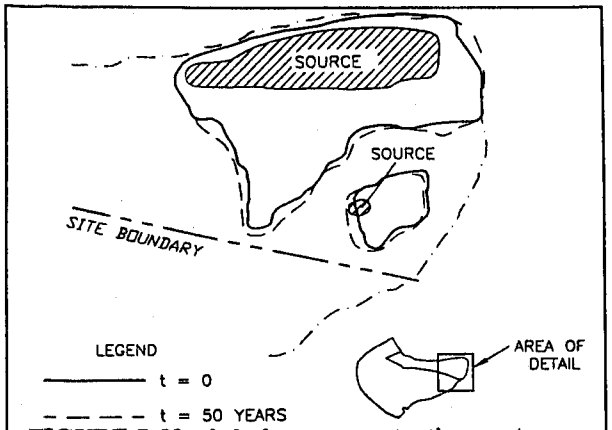

FIGURE 7. Naphthalene concentration contour (1 ug/L) at t = 0 and t = 50 years.

INCORPORATION OF IN SITU BIODEGRADATION INTO A COMPLEX REGULATORY CLOSURE

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ABSTRACT: A former manufactured gas plant (MGP) site in Baltimore, MD retains the legacy of over 100 years of manufacturing gas from coal and later oil. Faced with the technical impracticability of restoring groundwater to drinking water and/or background standards and extremely high costs just to provide containment, the best solution appeared to be a demonstration that source removal with natural attenuation would stabilize, and eventually reduce, the plume, recognizing that engineered remediation was technically impractical with current technology. The state agreed that a risk-based approach was appropriate, but retained the need to address the nondegradation policy. Using modeling as a tool and incorporating both field and laboratory data, we found that the plume is attenuating naturally, sufficient assimilative capacity exists in the aquifer to degrade the compounds present, and, except for removal of free phase source material on site, engineered remediation will not significantly enhance the process. The state concurred and approved a remedial plan consisting of monitored natural attenuation with on-site removal of free phase coal tar. We will reevaluate in five years to confirm that conditions have not changed. The economic benefits of this strategy were significant with no increased risk to human health or the environment.

INTRODUCTION

The site, located on approximately 70 acres in south Baltimore in a mixed industrial/residential area, operated as a manufactured gas plant (MGP) from 1855 until the early 1970's when the use of natural gas brought an end to the MGP industry nationwide. In terms of both production and site area, it is one of the largest former MGP sites of which there are estimated to be over 1,500 in the U.S. (EEI 1984). Coal tars containing both mono- and polycyclic aromatic hydrocarbons are among the primary constituents at this site. Contamination on site extends through three aquifer systems to the bedrock surface at 25-30 m below grade, with both residual and free phase dense non-aqueous phase liquids (DNAPL) present. Rough calculations, using interpolated isocontours of DNAPL occurrences and porosity of the soil media, result in an estimated DNAPL volume in excess of 3.5 $x10^6$ l. A plume of dissolved contamination has migrated approximately 1.2 km downgradient in the groundwater and, based on a "weight of evidence" analysis, DNAPL has also moved off site, providing an ample reservoir of constituents to propagate the dissolved phase plume for many decades. Although there is no unacceptable risk to human health or the environment