

# **Natural Attenuation Software (NAS): Assessing Remedial Strategies and Estimating Timeframes**

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# **Natural Attenuation Software (NAS): Assessing Remedial Strategies and Estimating Timeframes**

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## **Abstract**

Natural Attenuation Software (NAS) was developed as a screening tool to estimate remediation timeframes for monitored natural attenuation (MNA) to lower groundwater contaminant concentrations to regulatory limits, and to assist in decision-making on the level of source zone treatment in conjunction with MNA using site-specific remediation objectives. In addition, NAS facilitates the combined use of MNA with engineered remedial actions (ERAs) so that the benefits of each technology can be maximized while minimizing costs of remediation. The primary expected benefit of NAS is to increase regulatory acceptance of MNA, thereby decreasing overall remediation costs.

NAS is designed for application to ground-water systems consisting of porous, relatively homogeneous, saturated media, and assumes that groundwater flow is uniform and unidirectional. NAS consists of a combination of analytical and numerical solute transport models implemented in three main interactive modules to provide estimates for: (1) target source concentration required for a plume extent to contract to regulatory limits, (2) time required for NAPL contaminants in the source area to attenuate to a predetermined target source concentration, and (3) time required for a plume extent to contract to regulatory limits after source reduction. Natural attenuation processes that NAS models include advection, dispersion, sorption, non-aqueous phase liquid (NAPL) dissolution, and biodegradation. NAS determines redox zonation, and estimates and applies varied biodegradation rates from one redox zone to the next.

Recently, NAS was enhanced to include petroleum hydrocarbons, chlorinated ethenes, chlorinated ethanes, chlorinated methanes, and chlorinated benzenes, or any user-defined contaminants (e.g., heavy metals, radioisotopes), and has included the capability to model co-

mingled plumes. To enable comparison of remediation timeframe estimates between MNA and specific ERAs, NAS was modified to incorporate an estimation technique for timeframes associated with pump-and-treat remediation technology for comparison to, or in conjunction with, MNA. NAS also expanded analysis tools for improved performance assessment, as well as the assessment of sustainability of natural attenuation processes over time.

A Department of Defense (DoD) Environmental Security Technology Certification Program (ESTCP) demonstration was undertaken to evaluate the capability of the NAS software to provide reasonable estimates of MNA cleanup timeframes in a variety of environments and sites throughout the United States. Overall, results suggest that NAS was satisfactory in meeting performance objectives set forth in the demonstration, and that because NAS is based on sound science, it can serve as an effective tool for decision-making and data analysis at a wide range of contaminated sites and is not limited to a small subset of “simple sites” because of its simplicity. At some sites, NAS-estimated timeframes were crucial for winning regulatory acceptance of MNA, with cost-benefit analyses providing estimates of savings associated with using MNA as a final remediation strategy.

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Prof. Mark A. Widdowson - Ph.D. (Department of Civil and Environmental Engineering - CEE, Virginia Tech) is the primary Advisor and Committee Chair. Dr. Widdowson provided the resources and guidance required to achieve the goals of the research objectives of this dissertation.

### **Chapter 3 through Chapter 6, and Appendix A**

Dr. Mark A. Widdowson and Francis H. Chapelle - Ph.D. (United States Geological Survey) served as Co-Principal Investigators, developing essential written products, generating models, altering code, assessing model performance, and overseeing improvements to the NAS software and capabilities.

Clifton Casey (Navy Facilities Engineering Command - NAVFAC, Southern Division) served as the NAVFAC liaison, compiling site data, assisting with technology evaluation, and was responsible for transferring the technology throughout the Navy.

### **Chapter 3**

J. Steven Brauner - Ph.D (Parsons Engineering and formerly, CEE, Virginia Tech) was also a co-author of NAS, and assisted with the initial design, development, testing, and application of NAS.

### **Chapter 6**

Mark Kram - Ph.D (Naval Facilities Engineering Service Center - NFESC) served as Principal Investigator being the primary point of contact for the project, and was responsible for data compilation, modeling logistics, and helped to prepare essential documents.

Cristhian Quezada (formerly, CEE, Virginia Tech) was a research associate and contributed to the site applications and helped to prepare essential documents.

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# **1 Executive Summary**

## ***1.1 Introduction***

Monitored Natural Attenuation (MNA) is a remedial alternative recognized by the United States Environmental Protection Agency (USEPA) that relies on naturally occurring processes to achieve site-specific remediation objectives within a time frame that is reasonable when compared to other alternatives (USEPA 1999). The cleanup timeframe is defined as a period of time during which the quality of ground water will achieve a certain level at a specific location (USEPA 2001). A precursor, therefore, to selection of MNA as a viable remedy requires a quantitative estimate of the time to reach remediation objectives. Estimating the cleanup time associated with MNA requires evaluation of a variety of physical, chemical, and biological attenuation mechanisms. To estimate cleanup timeframes based on these processes, a screening level tool is needed that can be used by project scientists and engineers to make informed decisions during remedy selection.

Natural Attenuation Software (NAS) was developed with the objective of addressing the need for (1) guidelines to help engineers select appropriate methods for estimating remediation timeframes, (2) step-by-step procedures for applying these methods, and (3) decision criteria for selecting or rejecting MNA, either as a stand-alone remediation strategy or in conjunction with source zone engineered remedial actions (ERAs). The main goal of NAS was to be an applicable and useful remediation tool and methodology. If NAS could be demonstrated to be successful, the primary expected benefit would be increased regulatory acceptance of MNA and improved remediation efforts. Ideally, as well, this would lead to decreased overall remediation costs for applicable sites.

At sites where simplifying assumptions related to ground water flow and transport can be made, a computational model can be used to estimate the behavior of plumes and source zones where MNA is being considered. The Naval Facilities Engineering Command (NAVFAC), Southern Division partnered with the United States Geological Survey (USGS, South Carolina District)



and Virginia Polytechnic Institute and State University (Virginia Tech) to develop a screening level modeling tool to estimate the site-specific cleanup time for MNA. The result of that collaboration was the development of NAS, funded by NAVFAC. This tool was designed to evaluate plume dynamics such as the projected plume length, the time for the plume to stabilize, the time required for the plume to attenuate, as well as estimates of the cleanup timeframes following an engineered remedial application (ERA) to remove the contaminant source, including non-aqueous phase liquids (NAPL). When used in conjunction with ERAs of source zones, MNA may be considered as a part of a combined remedy. Under these circumstances, the NAS software can be used to establish nonzero cleanup thresholds for actively engineered remedies in the source area that will meet time, distance, and exposure constraints of the project. Recently NAS was enhanced to allow for assessment of MNA in comparison with engineered remediation solutions, namely, pump-and-treat systems.

Although NAS had previously been successfully applied to data from several field sites, there was a need to demonstrate and validate this enhanced NAS approach by comparing model predictions to field observations from sites representing a wide-range of conditions. A project was undertaken with the Department of Defense (DoD) Environmental Security Technology Certification Program (ESTCP) to demonstrate NAS. The tool was evaluated by using data from multiple sites with long-term monitoring data that encompass diverse geologic and hydrogeochemical environments and different remediation options.

### **1.1.1 Natural Attenuation Software (NAS): A computer program for estimating remediation times of contaminated groundwater - NAS Version 1.0.0 (Chapter 3)**

This paper describes the development and application of a modeling system called Natural Attenuation Software (NAS). NAS was designed as a screening tool to estimate times of remediation (TORs), associated with monitored natural attenuation (MNA), to lower groundwater contaminant concentrations to regulatory limits. Natural attenuation processes that

NAS models include advection, dispersion, sorption, biodegradation, and non-aqueous phase liquid (NAPL) dissolution. This paper discusses the three main interactive components of NAS: (1) estimation of the target source concentration required for a plume extent to contract to regulatory limits, (2) estimation of the time required for NAPL contaminants in the source area to attenuate to a predetermined target source concentration, and (3) estimation of the time required for a plume extent to contract to regulatory limits after source reduction. The model's capability is illustrated by results from a case study at a MNA site, where NAS time of remediation estimates compared well with observed monitoring data over multiple years.

### **1.1.2 Natural Attenuation Software (NAS): Assessing Remedial Strategies and Estimating Timeframes - NAS Version 2.0.0 (Chapter 4)**

With the successful development of the initial version of NAS and application of NAS to several contaminated sites, several critical needs had been identified. Software enhancements have been implemented to improve NAS and maximize its utility for site managers. Including general operational and functional revisions, NAS has expanded source contaminant specification options to include chlorinated ethanes, chlorinated methanes, and chlorinated benzenes, and to allow for the analysis of any other user-defined contaminants that may be subject to microbially-mediated transformations (e.g., heavy metals, radioisotopes). Included is the capability to model co-mingled plumes, with constituents from multiple contaminant categories. To enable comparison of remediation timeframe estimates between MNA and specific engineered remedial actions (ERAs), NAS was modified to incorporate an estimation technique for timeframes associated with pump-and-treat remediation technology for comparison to, or in conjunction with, MNA. NAS is now able to model sites with existing or proposed pumping wells, based on user-specified site hydrogeologic and source data. NAS also includes expanded analysis tools for improved performance assessment. Sustainability of natural attenuation processes over time may also be assessed. Users may analyze historically successive, site-measured, contaminant concentration and redox indicator data, to allow for comparisons of NAS-predicted versus observed trends, and to monitor changes in natural attenuation capacities and redox conditions over time. The model's capability is illustrated by application of NAS to a chlorinated ethene plume at a site near Niagara Falls, NY. NAS was able to satisfactorily simulate the remedial

action over multiple years, with NAS simulations using the pump-and-treat option providing a more favorable match with the observed data compared to the MNA option with no pumping well.

### **1.1.3 Time Estimates for Reaching Compliance Using Source Remediation Combined with Monitored Natural Attenuation (Chapter 5)**

An analytical solution is presented to estimate the time required to achieve a groundwater concentration-based remedial action objective (RAO) using a combined remedy of contaminant source reduction and monitored natural attenuation. The proposed method is consistent with a framework for evaluating the time of remediation proposed by Chapelle et al. (2003). Solutions are also presented for determining the decrease in the source zone groundwater concentration required to reach a site-specific RAO at a downgradient point of compliance (POC) and the time trend in the contaminant concentration following source concentration reduction. The method enables precise and approximate calculation for the time of stabilization (TOS); that is, the time between source reduction and when concentrations reach a new steady-state at a POC. The approximate solution corresponds to a concentration that is within a margin of error of 2% and 23% of the target concentration when the pretreatment contaminant concentration at the POC is one to two orders of magnitude greater than the target compliance concentration, respectively. The solutions show greatest sensitivity to the groundwater velocity, sorption parameters, and first-order decay coefficient. The approach is demonstrated at a chlorinated solvent-contaminated site where a six-year monitoring program was documented followed aggressive source treatment. Good agreement between observed data and simulated concentrations at downgradient monitoring wells is achieved when uncertainty in the groundwater velocity is reduced.

### **1.1.4 Evaluating the Capabilities of the Natural Attenuation Software (NAS) - Lessons Learned (Chapter 6)**

This paper reports the lessons learned from a Department of Defense (DoD), Environmental Security Technology Certification Program (ESTCP) demonstration and validation of the Natural Attenuation Software (NAS) and its methodology. The objective of the project was to validate

NAS using a consistent set of procedures for comparing predicted and observed time of remediation (TOR) results. This paper focused on the distance/time of stabilization (DOS/TOS) feature of NAS reported in the demonstration. Sites were selected to represent a range of different hydrologic settings and engineered remedial actions (ERAs). Overall, the DOS/TOS feature was satisfactory in meeting quantitative and qualitative performance objectives set forth in the demonstration. Factors affecting the degree of accuracy were reflected in the uncertainty associated with the contaminant velocity estimates and source characteristics (width and concentration) following remediation. The results of this demonstration strongly suggest that because NAS is based on sound science, it can serve as an effective tool for decision-making and data analysis at a wide range of contaminated sites and is not limited to a small subset of “simple sites” because of its simplicity.

## **1.2 References**

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## **2 Literature Review**

### ***2.1 Regulatory Considerations for Monitored Natural Attenuation***

Monitored natural attenuation (MNA) is the considered use of naturally occurring contaminant degradation, dispersion, and immobilization processes to reach site-specific remediation goals (USEPA 1996; USEPA 1998). In current engineering practice, the effectiveness of MNA is evaluated on a site-by-site basis by considering three lines of evidence: (1) historical monitoring data showing decreasing contaminant concentration and/or mass over time, (2) geochemical data showing that site conditions favor contaminant transformation or immobilization, or (3) site-specific laboratory studies documenting ongoing biodegradation processes (USEPA 1998). A variety of field and laboratory methods for assessing these three lines of evidence have been developed and are currently in use (Wiedemeier et al. 1999).

More recently, it has been pointed out that these “lines of evidence” reflect the more general principle of mass balance (USDOE 2003). If, for example, the capacity of a ground-water system to attenuate contaminants exceeds the mass loading of contaminants to that system, then the efficiency of MNA is considered relatively high (Line of evidence #1). Conversely, if the delivery of contaminants exceeds this natural attenuation capacity, then the efficiency of MNA is proportionally lower. In either case, this contaminant loading/attenuation balance is affected by ambient geochemical conditions (Line of evidence #2) and can be assessed by laboratory studies as well as field studies (Line of evidence #3). The successful implementation of MNA requires a quantitative assessment of how contaminant mass loading is balanced by the natural attenuation capacity of a given system relative to site-specific remediation objectives.

### ***2.2 Time of Remediation Associated with Natural Attenuation***

In concept, estimating the length of time required for natural processes to remove a particular contaminant from a ground-water system is a simple mass balance problem, and is described by Chapelle et al. (2003). If the initial mass of contaminant,  $M_0$ , (units of mass) present in a ground-water system is known, and if the rate that the contaminant is transformed or destroyed

by natural attenuation processes,  $R_{NA}$ , (units of mass removed per unit time) is known, a mass balance equation can be written

$$M(t) = M_o - \int_0^t R_{NA} dt \quad (2-1)$$

in which  $t$  is time and  $M(t)$  is the contaminant mass remaining at any time  $t$ . It follows that a time of remediation can be defined as the time required to lower contaminant mass below a given threshold ( $M^*$ ):

$$M^* = M_o - \int_0^{t^*} R_{NA} dt \quad (2-2)$$

where  $t^*$  is the time of remediation (TOR) and is defined explicitly as given in Equation (2-2), and refers to the length of time needed for a given mass of initial contaminant ( $M_o$ ) to be lowered below a given regulatory threshold ( $M^*$ ), by the rate of natural attenuation processes ( $R_{NA}$ ) occurring in a ground-water system.

In addition to providing a working definition of TOR, Equation (2-2) also indicates the kinds of information necessary to make remediation time estimates. This information includes an estimate of the mass of contaminant present, and an estimate of the rate of ongoing natural attenuation processes acting on the contaminant. The principal technical problem, therefore, is to obtain reliable estimates of these parameters. Clearly, the reliability of any remediation time estimates will be directly linked to the reliability of the parameter estimates. In addition, Equation (2-2) shows that determining remediation times requires the definition of an acceptable contaminant mass threshold. This threshold must be predetermined in order to make remediation time estimates.

In practice, however, the problem is much more complex than indicated by Equation (2-2), primarily because the term  $R_{NA}$  is the sum of several processes that include advection, hydrodynamic dispersion, biodegradation, and dissolution from non-aqueous phase liquid (NAPL) or diffused/sorbed contaminant sources. Widdowson (2004) expressed the mass balance equation of an aqueous-phase constituent in the form:

$$-v_i \frac{\partial C_l}{\partial x_i} + \frac{\partial}{\partial x} \left( D_{ij} \frac{\partial C_l}{\partial x_j} \right) + \frac{q_s}{\theta} C_l^* - R_{\text{sink},l}^{\text{bio}} + R_{\text{source},l}^{\text{bio}} + R_{\text{source},l}^{\text{NAPL}} = R_l \frac{\partial C_l}{\partial t} \quad (2-3)$$

where  $C_l$  is the aqueous phase contaminant concentration [ $\text{M L}^{-3}$ ];  $x_i$  is distance [ $\text{L}$ ];  $t$  is time [ $\text{T}$ ];  $v_i$  is the average linear ground water velocity [ $\text{L T}^{-1}$ ];  $D_{ij}$  is the tensor for the hydrodynamic dispersion coefficient [ $\text{L}^2 \text{T}^{-1}$ ];  $C_l^*$  is the contaminant point source concentration [ $\text{M L}^{-3}$ ];  $q_s$  is the volumetric flux of water per unit volume of aquifer [ $\text{T}^{-1}$ ];  $\theta$  is the effective porosity [ $\text{L}^0$ ];  $R_l$  is the contaminant retardation factor [ $\text{L}^0$ ];  $R_{\text{sink},l}^{\text{bio}}$  is a biodegradation mass loss term dependent on the mode of respiration [ $\text{M L}^{-3} \text{T}^{-1}$ ];  $R_{\text{source},l}^{\text{bio}}$  is a source term for the biogenic mass production [ $\text{M L}^{-3} \text{T}^{-1}$ ];  $R_{\text{source},l}^{\text{NAPL}}$  is a source term due to NAPL dissolution [ $\text{M L}^{-3} \text{T}^{-1}$ ].

The NAPL source term for petroleum hydrocarbons and chlorinated compounds utilizes first-order kinetics for dissolution from a multiple-component mixture:

$$R_{\text{source},l}^{\text{NAPL}} = k^{\text{NAPL}} (C_l^{\text{eq}} - C_l) \quad (2-4)$$

where  $k^{\text{NAPL}}$  is the NAPL dissolution rate constant [ $\text{T}^{-1}$ ]; and  $C_l^{\text{eq}}$  is the equilibrium contaminant concentration [ $\text{M L}^{-3}$ ], represented as the product of the solubility of the constituent in water and the mole fraction,  $f_l$ , of NAPL constituent  $l$ . The mole fraction is a function of the mass fractions of the NAPL constituents:

$$f_l = \frac{C_l^{\text{NAPL}} / \omega_l}{I^{\text{NAPL}} / \omega_l + \sum_{l=1}^{\text{NS}} C_l^{\text{NAPL}} / \omega_l} \quad (2-5)$$

where  $C_l^{\text{NAPL}}$  is the NAPL mass of constituent  $l$  per unit mass dry soil [ $\text{M M}_{\text{solid}}^{-1}$ ]; and  $\omega_l$  is the molecular weight of NAPL constituent  $l$ ; and  $I^{\text{NAPL}}$  is the NAPL concentration of the inert (i.e., relatively insoluble) fraction [ $\text{M M}_{\text{solid}}^{-1}$ ]. The mass balance equation for the NAPL phase is expressed as:

$$\frac{dC_l^{\text{NAPL}}}{dt} = -\frac{\theta}{\rho_b} R_{\text{source},l}^{\text{NAPL}} \quad (2-6)$$

where  $\rho_b$  is the bulk density of the porous medium [ $\text{M}_{\text{solid}} \text{L}^{-3}$ ].

For the multi-component NAPL problems, solutions to quantify TOR using Equation (2-3) through Equation (2-6) are achieved using numerical models. SEAM3D (Sequential Electron Acceptor Model, 3D transport) is a code designed to simulate the transport and attenuation of contaminants subject to aerobic and anaerobic biotransformations (Waddill and Widdowson 2000). SEAM3D includes mass balance equations for a multi-component NAPL. The rate of release for each NAPL constituent is calculated at each time step using the SEAM3D code and is a function of mass transport and mass transfer parameters ( $v_i$  and  $k^{NAPL}$ ), NAPL parameters (mass, mole fraction, and geometry), and chemical properties (molecular weight and solubility) of the NAPL components.

Using Equation (2-3), Chapelle et al. (2003) divided the time of remediation problem into three parts: (1) distance of plume stabilization (DOS), (2) time of plume stabilization (TOS), and (3) time of NAPL dissolution (TOD). Each of these issues can be addressed using particular solutions of Equation (2-3), which can be developed according to specific needs. Natural Attenuation Software (NAS) was developed to make use of solutions to Equation (2-3) in order to address these three classes of TOR problems. This software was designed to aid the user in assembling and organizing the data needed to make TOR estimates, to obtain appropriate and useful solutions of the TOR equation, and to illustrate the various uncertainties inherent in TOR estimates. No attempt has been made to make NAS applicable to all, or even most, TOR problems. Rather, NAS is designed around numerous simplifications of hydrologic, microbial, and geochemical processes that, while convenient, may introduce unacceptable error to some problems.

### **2.3 Existing Modeling Technology**

Deterministic modeling tools are useful in supporting the MNA methodology and its implementation at contaminated sites (McGuire et al. 2004). This modeling approach uses available site data as initial conditions to be applied to mathematical representations of various groundwater transport and remediation processes, to predict contaminant fate over time. These



technologies are commonly based on the mass balance concept, and range in sophistication from simple spreadsheet-based analytical solutions, to complex numerical models with extensive graphical interfaces, to integrated decision support tools.

A variety of analytical models have been developed based on relatively simple initial and boundary conditions and may provide approximate or exact analytical solutions for concentration estimates at different locations and times within the model domain. With this simplicity comes limitation, in that analytical models require the simplified initial and boundary conditions, source characteristics, and attenuation processes to be a satisfactory approximation of the site being modeled. Numerical models, on the other hand, though entailing increased complexity and data requirement, allow greater control over specifying conditions, processes, and spatial or temporal data heterogeneity.

Table 2-1 displays various types, and examples, of technologies currently available (Looney et al. 2006, ITRC 2007). The source box model approach has been used since the mid-1990s to estimate source attenuation over time. These simple models use basic mathematical functions (e.g., exponential decay) instead of simulating complex or multiple processes that may be occurring (e.g., BIOSCREEN (Newell et al. 1996), BIOCHLOR (Aziz et al. 2000), SourceDK (Farhat et al. 2004)). Deterministic source models are more sophisticated and may simulate multiple source phases through source geometry, contaminant mass fractions, and NAPL dissolution (e.g., SEAM3D, NAS (Widdowson et al. 2005)). Models that simulate plume dynamics through the transport and fate of dissolved contaminants after leaving the source (e.g., by advection, dispersion, sorption, and biodegradation), are available in both analytical (e.g., BIOSCREEN, BIOCHLOR) and numerical (e.g., RT3D (Clement 1997), BIOPLUME (Rafai et al. 1998), SEAM3D) models. Some models calculate maximum plume size and estimate time required for plume stabilization (e.g., NAS, BIOBALANCE (Kamath et al. 2006)). Additional attenuation mechanisms are being recognized as relevant processes and being incorporated into existing models, such as the recent ability to model abiotic degradation pathways (e.g., BIOPLUME, NAS). Some models include a mass balance of available electron donors and

electron acceptors, and also consider competing sequential electron acceptors (e.g., SEAM3D, BIOBALANCE). Newer flux calculation tools (e.g., Mass Flux Toolkit (Farhat et al., 2006)) estimate an important metric, the mass flux, or flow rate, of contaminant throughout the model domain. Most recently, technologies have been developed that combine source and plume models into a single integrated tool, allowing for the mass balance concept to be applied to the entire area of contamination (e.g., NAS, BIOBALANCE). MNA sustainability is also being evaluated through comparing the contaminant mass flux from a source with the system's assimilative capacity (e.g., BIOBALANCE).

Effective use of available technologies requires applying the appropriate tool(s) to each site. Modeling objectives, site specific conditions, and available data determine which technologies may be the best match for each site. Table 2-2 summarizes some of the key modeling issues associated with matching a technology with a site.

**Table 2-1. Modeling features available in technology.**

<b>Technology</b>	<b>Source Box Model</b>	<b>Deterministic Source Model</b>	<b>Plume Mass Balance</b>	<b>Mass Flux Estimates</b>
<b>SourceDK</b>	Yes			
<b>BIOSCREEN</b>	Yes		Yes	
<b>BIOCHLOR</b>	Yes		Yes	
<b>BIOBALANCE</b>	Yes	Yes	Yes	Yes
<b>BIOPLUME</b>			Yes	
<b>RT3D</b>			Yes	
<b>SEAM3D / NAS</b>		Yes	Yes	
<b>Mass Flux Toolkit</b>				Yes

**Table 2-2. Modeling issues addressed by technology.**

<b>Technology</b>	<b>DOS</b>	<b>TOS</b>	<b>TOD</b>	<b>Sustainability</b>
<b>SourceDK</b>	No	No	Yes	No
<b>BIOSCREEN</b>	Yes	Yes	Yes	No
<b>BIOCHLOR</b>	Yes	Yes	Yes	No
<b>BIOBALANCE</b>	Yes	Yes	Yes	Yes
<b>BIOPLUME</b>	Yes	Yes	No	No
<b>RT3D</b>	Yes	Yes	No	No
<b>SEAM3D / NAS</b>	Yes	Yes	Yes	Indirectly
<b>Mass Flux Toolkit</b>	No	No	Indirectly	Indirectly

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### **3 Natural Attenuation Software (NAS): A computer program for estimating remediation times of contaminated groundwater - NAS Version 1.0.0**

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*Mendez, E., M. Widdowson, S. Brauner, F. Chapelle and C. Casey. 2004. Natural Attenuation Software (NAS): A computer program for estimating remediation times of contaminated groundwater, In Envirosoft X, ed. G. Latini, G. Passerini, and C. Brebbia, 185-194, Billerica MA, Computational Mechanics.*

#### **3.1 Abstract**

This paper describes the development and application of a modeling system called Natural Attenuation Software (NAS). NAS was designed as a screening tool to estimate times of remediation (TORs), associated with monitored natural attenuation (MNA), to lower groundwater contaminant concentrations to regulatory limits. Natural attenuation processes that NAS models include advection, dispersion, sorption, biodegradation, and non-aqueous phase liquid (NAPL) dissolution. This paper discusses the three main interactive components of NAS: (1) estimation of the target source concentration required for a plume extent to contract to regulatory limits, (2) estimation of the time required for NAPL contaminants in the source area to attenuate to a predetermined target source concentration, and (3) estimation of the time required for a plume extent to contract to regulatory limits after source reduction. The model's capability is illustrated by results from a case study at a MNA site, where NAS time of remediation estimates compared well with observed monitoring data over multiple years.

#### **3.2 Introduction**

MNA is the use of naturally occurring contaminant-reducing processes, with environmental monitoring, to remediate contaminated groundwater. The time required for these processes to lower contaminant concentrations to acceptable levels may vary greatly between sites and is a function of the hydrogeology, contaminant concentrations, and redox conditions of the particular

groundwater system. In the U.S., environmental regulations mandate that groundwaters shall be returned to their beneficial uses wherever practicable, within a timeframe that is reasonable given the particular site circumstances. MNA is an appropriate remediation strategy if it meets site remediation objectives within a reasonable timeframe compared to other methods (USEPA 1997; USEPA 1999). This report describes a methodology for estimating TORs associated with MNA. NAS consists of a combination of analytical and numerical models and is designed for systems consisting of a relatively homogeneous, porous, saturated media layer. Simulated contaminants are currently limited to petroleum hydrocarbons and chlorinated ethenes, but application to generic contaminants is also possible. The report describes the processes that contribute to natural attenuation, quantifies these processes into mass-balance equations, incorporates solutions to these equations in NAS, and applies NAS at a field site to make TOR estimates.

### **3.3 Natural Attenuation Processes**

#### **3.3.1 Natural Attenuation Capacity**

Time of remediation (TOR) can be defined as the time required to lower contaminant mass below a given threshold. Estimation of the time required for natural attenuation processes to remove contaminants from groundwater requires a mass-balance approach. The natural attenuation processes can be summed mathematically in the following solute-transport, mass-balance equation to give overall contaminant concentration changes over time:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \frac{\rho_b K_d}{n} \frac{\partial C}{\partial t} - kC \quad (3-1)$$

When a contaminant plume has reached approximate steady-state conditions, the sorption term becomes negligible and Equation (3-1) simplifies to:

$$D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - kC = 0 \quad (3-2)$$

For generalized conditions that treat contaminants as a point source of constant concentration, Equation (3-2) has the particular solution:

$$C(x) = C_o \exp\left[-\frac{-v + \sqrt{v^2 + 4Dk}}{2D}\right]x \quad (3-3)$$

Equation (3-3) may be expressed in terms of the one-dimensional natural attenuation capacity (NAC) model (Chapelle and Bradley 1998). NAC is the contaminant-lowering capacity of an aquifer per unit length of flowpath, and is proportional to the slope of the solute concentration profile along the flowpath where:

$$NAC = \frac{-v + \sqrt{v^2 + 4Dk}}{2D} \quad (3-4)$$

### 3.3.2 Redox Processes in Groundwater Systems

The most common terminal electron-accepting processes (TEAPs) in groundwater systems are O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, Mn(IV), Fe(III), SO<sub>4</sub><sup>2-</sup>, and CO<sub>2</sub> reduction (methanogenesis). Microorganisms use the most energetically efficient electron acceptor available, with each sequential process becoming predominant only in the absence of another more efficient electron acceptor. The zonation of predominant microbial processes can be determined by the distribution of electron acceptors consumed and final products produced (Chapelle et al. 1995). Dissolved H<sub>2</sub> may also be an effective indicator of ambient redox processes. Under anaerobic conditions, H<sub>2</sub> is produced by fermentive microorganisms metabolizing organic matter and then utilized by respirative microorganisms in TEAPs, with each process having a different affinity for H<sub>2</sub> uptake (Lovley and Goodwin 1988). See Figure 3-1 for a flowchart for determining TEAP zonation in groundwater systems.

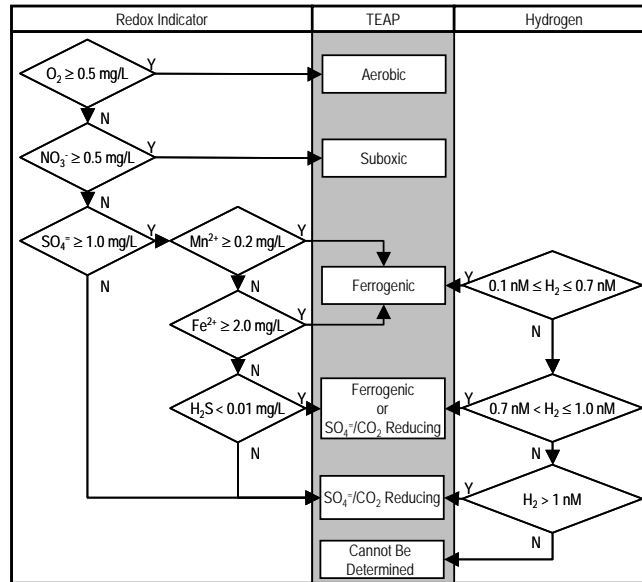


Figure 3-1. Flowchart showing how NAS determines redox condition.

### 3.3.3 Advection and Dispersion

Advection is the transport of solutes resulting from the movement of the fluid in which the solutes are dissolved. Heterogeneity of groundwater systems causes variations in the solute transport speed. Hydrodynamic dispersion accounts for these variations within advective transport. The mechanical process of dispersion, transport along concentration gradients, causes a solute to occupy a larger volume than by advection alone.

### 3.3.4 Sorption

Sorption is the distribution of solute between the aqueous and solid phases. Solute may be sorbed to the surface or to the interior of aquifer media. The sorptive capacity of media is greatest when the plume first develops from a contaminant source, and is gradually reduced as the solute is transported and sorbed to the media. This results in retardation initially having a greater impact on contaminant transport velocity relative to groundwater velocity, and then having less of an impact as the capacity of the media is approached.



### 3.3.5 Petroleum Hydrocarbon Biodegradation

Biodegradation of petroleum hydrocarbons occurs in both aerobic and anaerobic aquifer systems. The ability of microorganisms to degrade petroleum hydrocarbons and their associated biochemical pathways have been widely studied (Barker et al. 1987). Hydrocarbon contaminants are simulated as electron donors (i.e., substrates) for microbial growth. Inhibition functions allow any TEAP to inhibit utilization of all other TEAPs that provide less energy to the microbes. The hydrocarbon biodegradation sink term for the solute-transport, mass-balance equation is the sum of all applicable TEAPs:

$$R_{\text{sink},ls}^{\text{bio}} = \sum_x \sum_{le} \frac{M_x}{\theta} v_{x,ls,le}^{\text{max}} \left[ \frac{\bar{S}_{ls}}{\bar{K}_{x,ls,le}^s + \bar{S}_{ls}} \right] \left[ \frac{\bar{E}_{le}}{\bar{K}_{x,le}^e + \bar{E}_{le}} \right] I_{le,li} \quad (3-5)$$

### 3.3.6 Chlorinated Ethene Reductive Dechlorination

Chlorinated ethenes are relatively oxidized compounds and can act as electron acceptors in microbial metabolism. Reductive dechlorination is a microbially catalyzed process in which a hydrogen can replace a chlorine on a chlorinated ethene molecule. The tendency of chlorinated ethenes to undergo reductive dechlorination decreases with decreasing number of chlorine substituents (Vogel et al. 1987). The reductive dechlorination sink term for the solute-transport, mass-balance equation, represented by Monod kinetics is a series of inter-related microbial sink reactions:

$$R_{\text{sink},lc}^{\text{bio,EA}} = \frac{M_y}{\theta} v_{lc}^{\text{max,EA}} \left[ \frac{\bar{C}_{lc}}{\bar{K}_{lc}^e + \bar{C}_{lc}} \right] I_{lc,li} \quad (3-6)$$

### 3.3.7 NAPL Dissolution

When groundwater contacts a NAPL, components of the NAPL will dissolve into the aqueous phase until equilibrium is reached or NAPL mass is depleted. For each substrate, the driving force for dissolution is the difference between the actual aqueous phase concentration, and the equilibrium concentration. The rate of NAPL dissolution depends on the interface between the NAPL and water, aquifer heterogeneity, NAPL geometry, and groundwater velocity (Imhoff et

al. 1993; Waddill and Widdowson 1998). The NAPL dissolution term for the solute-transport, mass-balance equation is:

$$R_{Source,ls}^{NAPL} = \max\left[0, k^{NAPL} \left(S_{ls}^{eq} - S_{ls}\right)\right] \quad (3-7)$$

### 3.4 Natural Attenuation Software

A flowchart describing how the NAS software can be used to address TOR questions is shown in Figure 3-2. NAS requires detailed site information about hydrogeology, contaminant concentrations, and redox conditions before the analysis can proceed. See Table 3-1 for required input and data generated by NAS. After initial site data entry, NAS utilizes either analytical or numerical solutions to the TOR equations. An analytical solution calculates the target source concentration (TSC) required for a plume extent to contract to regulatory limits. A numerical solution estimates the time of NAPL dissolution (TOD): the time required for NAPL contaminants in the source area to attenuate to a predetermined target source concentration. NAS then analytically estimates the time of stabilization (TOS): the time required for a plume extent to contract to regulatory limits after source reduction. When the TOD and the TOS are acceptable, MNA can become an integral component of site remediation.

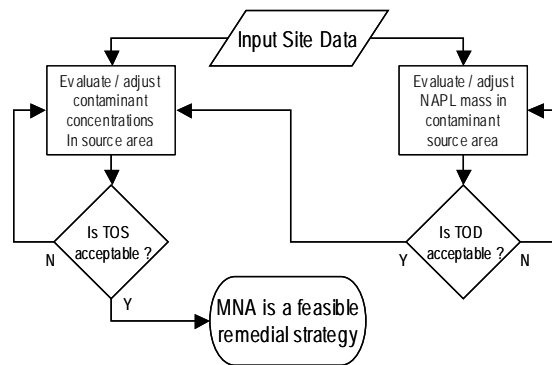


Figure 3-2. Flowchart showing how NAS can be applied to TOR problems.

**Table 3-1. NAS input requirements and generated data.**

Modules	Input Required	Data Generated
Hydrogeology	$K, i, n, n_e, f_{oc}, T_a$	$v, P, \alpha, R$
Contaminants	Concentration versus distance	NAC, $k$
Redox indicators	Concentration versus distance	Redox zones distribution
TSC	$L_{POC}, RCC$	TSC
TOD	$M_N, S_X, S_Y, S_Z, f_i^m, C_i^{EA}, SCC$	TOD, $S_N$
	NAPL mass removal options	
TOS	No additional data needed	TOS

### 3.5 Target Source Concentration

The distance a contaminant is transported in groundwater depends on the NAC and the contaminant concentration at the source area. If an NAC is sufficient to achieve plume containment without additional remediation procedures, MNA may be an acceptable stand-alone remediation strategy. However, if the NAC is not sufficient, source concentrations need to be lowered through natural or engineered processes. The target source concentration (TSC) is the maximum concentration allowable at the source for natural attenuation to lower contamination below the regulatory compliance concentrations (RCC) at a given downgradient point of compliance (POC). An analytical method for determining the TSC is presented in Chapelle and Bradley (1998). Employing the steady-state solution to Equation (3-1) on the plume centerline and expressing in terms of the one-dimensional NAC model yields:

$$C(x) = (C_o - \Delta C_o) \exp\{-(NAC)x\} \quad (3-8)$$

If the concentration at the POC is to be less than or equal to the RCC, Equation (3-8) may be rewritten to find the maximum TSC:

$$TSC = (RCC) \exp\{-(NAC)L_{POC}\}^{-1} \quad (3-9)$$

### 3.6 Time of NAPL Dissolution

Time of NAPL dissolution (TOD) is the time required to lower aqueous phase contaminants below a given threshold, immediately downgradient of the NAPL source. Since realistic estimates of TOD depend on the NAPL dissolution rate and how rapidly the dissolved

constituents are attenuated, the dissolution and biodegradation of NAPL should not be modeled by simple analytical solutions to Equation (3-1), and instead require a quantitative, numerical approximation. NAS uses the numerical model SEAM3D (Sequential Electron Acceptor Model, 3 Dimensional) (Waddill and Widdowson 1998; Waddill and Widdowson 2002), to estimate the TOD. SEAM3D consists of a series of modules, including the parent code MT3DMS (Zheng and Wang 1999), for simulating the solute fate and transport, with aerobic and sequential anaerobic biodegradation and NAPL dissolution, of multiple constituents in a three-dimensional, anisotropic, heterogeneous domain.

### 3.7 Time of Stabilization

The previous NAS modules estimate maximum allowable source concentrations, and time for source concentration reduction by dissolution, but do not provide any indication of how long it takes for the plume to reach steady-state after source reduction. The time of plume stabilization (TOS) can be addressed using time-dependent solutions of Equation (3-1). For the case of a semi-infinite aquifer with a constant source, a time-dependent, two-dimensional solution is given by Domenico (1987):

$$C(x,0,t) = \exp\{-(NAC)x\} \left\{ \operatorname{erf} \left[ \frac{Y}{4(\alpha_y x)^{0.5}} \right] \right\} \left\{ C_o - \frac{\Delta C_o}{2} \operatorname{erfc} \left[ \frac{x - v_c t (1 + 4\lambda \alpha_x / v_c)^{0.5}}{2\sqrt{\alpha_x v_c t}} \right] \right\} \quad (3-10)$$

The impact of source reduction on the concentration at the POC will only be observed when the source groundwater reaches the POC and can be expressed mathematically by setting the complementary error function in Equation (3-10) equal to one. TOS may be solved for by setting the argument of the complementary error function equal to zero and solving in terms of the NAC:

$$TOS = \frac{L_{POC}}{v_c [2\alpha_x (NAC) + 1]} \quad (3-11)$$

### 3.8 Case Study

TOR estimations were performed for petroleum hydrocarbon releases at the Laurel Bay site, Marine Corps Air Station, Beaufort, South Carolina. In 1991, a leak was discovered in an underground storage tank (UST), and it was estimated that approximately 500 to 1000 pounds of gasoline leaked into the aquifer. The UST and surrounding contaminated soil were removed in 1993, with site monitoring beginning in 1994. NAS-estimated benzene concentrations were compared to measured concentration reductions in the plume. Figure 3-3 compares estimated concentration reduction at monitoring well MW-8, located in the central part of the plume, with measured concentration data taken between 1996 and 2001. Three concentration profiles were predicted, based on minimum, best estimate, and maximum groundwater velocities that were calculated by NAS from user-specified site data. Based on measured hydraulic conductivity and head values, the groundwater velocity in the area of MW-8 would be relatively high between the best and maximum plume estimates. Results indicate that benzene concentrations were initially high, but decreased rapidly over time and reached remediation levels by 2001. The data shows, therefore, that the TORs representing higher groundwater velocities correlate well with measured values over multiple years of site monitoring (Chapelle et al. 2003; Landmeyer et al. 1998).

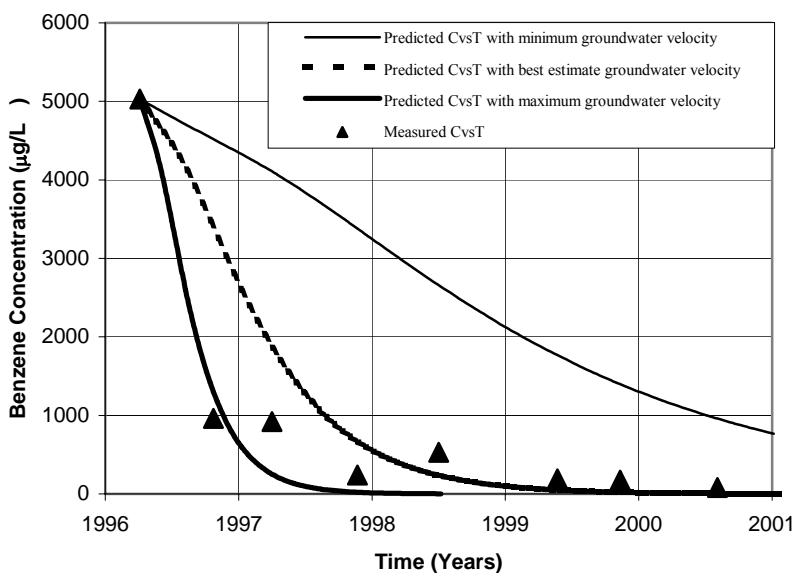


Figure 3-3. Measured versus NAS-predicted concentration changes at MW-8.

### **3.9 Summary**

To facilitate TOR estimates it is useful to divide the problem into three interactive components: TSC, TOD, and TOS. In general, NAS predictions compared well with monitoring data. One observation is that measured contaminant concentrations tended to initially decrease more rapidly than predicted by NAS. Over relatively short time periods, NAS predictions often differ considerably from measured data, however, comparison of predicted and measured data over longer time periods shows that the precision of TOR estimates does improve. These differences can be attributed to the simplifications required to model complex groundwater systems in NAS, and show that this procedure involves a level of uncertainty. For highly heterogeneous systems, this may introduce unacceptable errors, and more intensive numerical modeling may be required. Therefore, although TOR estimates can be useful for evaluating different remediation strategies, they are neither precise nor permanent predictions of contaminant behavior, and should always be reaffirmed with continued site monitoring.

### **3.10 Acknowledgement**

Software development was funded by Southern Division, Naval Facilities Engineering Command (NAVFAC) and the Naval Facilities Engineering Service Center (NFESC), and was a collaboration between Virginia Tech, United States Geological Survey (USGS), and NAVFAC. NAS can be downloaded from the Web site: <http://www.nas.cee.vt.edu>.

### 3.11 Notation

**Table 3-2. Symbols used in this paper.**

$D$ = hydrodynamic dispersion [ $L^2/T$ ]	$k^{NAPL}$ = NAPL dissolution rate
$\alpha$ = dispersivity of the porous media [L]	$C$ = aqueous concentration of contaminant [ $M/L^3$ ]
$v$ = average linear pore velocity of groundwater [L/T].	$t$ = time [T]
$R^{bio}$ = removal of contaminant due to biodegradation ?	$x$ = distance [L]
$R^{NAPL}$ = addition of contaminant dissolving from NAPL	$\rho_b$ = bulk density of the porous medium [-]
$M_x$ = microbial biomass concentration [ $M/L^3$ ]	$K_d$ = equilibrium sorption coefficient [-]
$\theta$ = effective porosity [-]	$n$ = porosity [-]
$v_{x,ls,le}^{max}$ = maximum specific rate of substrate utilization [1/T]	$k$ = first order decay rate [1/T] ?
$\bar{S}_{ls}$ = effective concentration [ $M/L^3$ ]	$L_{POC}$ = Distance to POC [L]
$\bar{K}_{x,ls,le}^s$ = effective half saturation constant [ $M/L^3$ ]	$v_c$ = velocity of contaminant in groundwater [L/T]
$\bar{E}_{le}$ = effective concentration of electron acceptor [ $M/L^3$ ]	$K$ = Hydraulic Conductivity [L/T]
$\bar{K}_{x,le}^e$ = effective half saturation constant for electron acceptor [ $M/L^3$ ]	$i$ = Hydraulic Gradient [L/L]
$I_{le,li}$ = inhibition function (defined by?)	$n_e$ = effective porosity [-]
$R_{sin k,lc}^{bio,EA}$ = biodegradation sink term to account for the reduction of a chlorinated ethene [ $M/L^3T$ ]	$f_{oc}$ = fraction organic carbon [-]
$M_y$ = microbial biomass concentration [ $M/L^3$ ]	$T_a$ = aquifer thickness [L]
$v_{lc}^{max,EA}$ = maximum rate of reductive dechlorination [1/T]	$P$ = Estimated plume length [L]
$\bar{C}_{lc}$ = effective concentration [ $M/L^3$ ]	$M_N$ = NAPL mass [M]
$\bar{K}_{lc}^e$ = effective half saturation constant [ $M/L^3$ ]	$S_x$ = Source length [L]
$I_{lc,li}$ = inhibition function (defined by?)	$S_y$ = Source width [L]
$R_{source,lc}^{DNAPL}$ = source term of a chlorinated ethene dissolving from a DNAPL [ $M/L^3T$ ]	$S_z$ = Source thickness [L]
$ls$ = NAPL substrate	$f_i^m$ = NAPL contaminant mass fractions
$S_{ls}$ = NAPL aqueous phase concentration	$C_i^{EA}$ = Background electron acceptor concentrations
$S_{ls}^{eq}$ = NAPL equilibrium concentration	$S_N$ = NAPL residual saturation

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## **4 Natural Attenuation Software (NAS): Assessing Remedial Strategies and Estimating Timeframes - NAS Version 2.0.0**

Authors: Eduardo Mendez III, Mark A. Widdowson, Francis H. Chapelle, Clifton C. Casey

### **4.1 Abstract**

With the successful development of the initial version of NAS and application of NAS to several contaminated sites, several critical needs had been identified. Software enhancements have been implemented to improve NAS and maximize its utility for site managers. Including general operational and functional revisions, NAS has expanded source contaminant specification options to include chlorinated ethanes, chlorinated methanes, and chlorinated benzenes, and to allow for the analysis of any other user-defined contaminants that may be subject to microbially-mediated transformations (e.g., heavy metals, radioisotopes). Included is the capability to model co-mingled plumes, with constituents from multiple contaminant categories. To enable comparison of remediation timeframe estimates between MNA and specific engineered remedial actions (ERAs), NAS was modified to incorporate an estimation technique for timeframes associated with pump-and-treat remediation technology for comparison to, or in conjunction with, MNA. NAS is now able to model sites with existing or proposed pumping wells, based on user-specified site hydrogeologic and source data. NAS also includes expanded analysis tools for improved performance assessment. Sustainability of natural attenuation processes over time may also be assessed. Users may analyze historically successive, site-measured, contaminant concentration and redox indicator data, to allow for comparisons of NAS-predicted versus observed trends, and to monitor changes in natural attenuation capacities and redox conditions over time. The model's capability is illustrated by application of NAS to a study site. The site is a well-delineated and characterized chlorinated ethene plume at the previous Bell Aerospace Textron facility in Wheatfield, New York. Due to the physical characteristics of the DNAPL, remediation of the source by pumping or other extraction methods was not technically feasible, therefore, on-site and off-site ground water extraction systems were installed as an alternative to control the dissolution of the DNAPL by hydraulically or physically containing the source

(Yager 2002). NAS was able to satisfactorily simulate the remedial action over multiple years, with NAS simulations using the pump-and-treat option providing a more favorable match with the observed data compared to the MNA option with no pumping well.

## **4.2 Introduction**

Natural Attenuation Software (NAS) (Chapelle et al. 2003; Mendez et al. 2004) is a screening tool to estimate remediation timeframes for monitored natural attenuation (MNA), to lower groundwater contaminant concentrations to regulatory limits, and to assist in decision-making on the level of source zone treatment in conjunction with MNA. NAS development is funded by Southern Division, Naval Facilities Engineering Command (NAVFAC) and Naval Facilities Engineering Service Center (NFESC), and has resulted from a continuing collaboration between Virginia Tech, United States Geological Survey (USGS), and NAVFAC. NAS consists of a combination of analytical and numerical models and is designed for systems consisting of a relatively homogeneous, porous, saturated media layer. Simulated contaminants of the previous version had been limited to either petroleum hydrocarbons or chlorinated ethenes. Natural attenuation processes that NAS models include advection, dispersion, sorption, biodegradation, and non-aqueous phase liquid (NAPL) dissolution. NAS incorporates three main interactive modules to provide estimates for:

1. target source concentration required for a plume extent to contract to regulatory limits (TSC),
2. time required for NAPL contaminants in the source area to attenuate to a predetermined target source concentration (TOD), and
3. time required for a plume extent to contract to regulatory limits after source reduction (TOS).

NAS was developed to address the need for (1) guidelines to help engineers select appropriate methods for estimating remediation timeframes, (2) step-by-step procedures for applying these methods, and (3) decision criteria for selecting or rejecting MNA, either as a stand-alone remediation strategy or in conjunction with source zone engineered remedial actions (ERAs).

With the successful development of the initial version of NAS and application of NAS to several contaminated sites, several critical needs have been identified. NAS was not previously configured for estimating and comparing remediation timeframes associated with remediation technologies other than MNA. It was recognized that there is a critical need for remediation timeframe estimates when incorporating specific ERAs in conjunction with MNA.

Software enhancements were implemented to improve NAS and maximize its utility for site managers. The general design was modified to enhance navigation within the software and to create a modularized structure to the code for future addition of new modules such as pump-and-treat, vegetable oil injection, and other in-situ treatment technologies. In this latest version specifically, NAS incorporates an estimation technique for cleanup times associated with pump-and-treat technology for comparison with, or in conjunction with, MNA. In addition, NAS has been revised to expand analysis tools for a wider variety of site conditions, contaminant source constituents, and remediation options. See Appendix A for the NAS User's Guide.

### ***4.3 Modified NAS Design***

General structural and navigational features of NAS have been redesigned. The layout of forms and functions was improved by redesigning to the Microsoft Windows standard (Microsoft 1995; Microsoft 1999) to provide a more familiar user interface and facilitate navigation between the separate NAS functions. A main project window allows separate module forms to be viewed simultaneously, enabling the modeler to interact with the different components of NAS at the same time. The users may easily navigate between data entry screens, modules and output forms. A major advantage over the initial NAS version, the user is now allowed to change previously entered site/source data (e.g., simulation units, source contaminants) without having to start a new simulation, and with other modules being automatically updated. This restructuring to a 'modularized' format makes NAS a more adaptable software system to easily incorporate and interact with additional components, as needed, in the future.

To further improve NAS, three objectives were incorporated into this new design:

1. Improved source specification options
2. Pump-and-treat module
3. Post-audit data analysis

#### **4.3.1 Improved Source Specification Options**

In the previous configuration of NAS, the user may have only selected either chlorinated ethenes or petroleum hydrocarbons as contaminants, with the contaminant properties required by NAS for simulation being hardwired in the software. The NAS user now has the ability to specify the contaminant source constituents, and the values for contaminant properties required by NAS for the analytical and numerical solutions. NAS has expanded the kinds and numbers of contaminants considered, to include chlorinated ethanes, chlorinated methanes, and chlorinated benzenes, and has enabled the user to add contaminant categories and/or individual contaminants. NAS now allows for the analysis of the natural attenuation capacity of any other user-generated contaminants that may represent source compounds (e.g., heavy metals, radioisotopes). NAS also has the capability to model co-mingled plumes, allowing the user to specify source constituents from different contaminant categories (e.g., allows for concurrent consideration of solvents (chlorinated ethenes) and petroleum hydrocarbons), including user-generated contaminants.

For data management and reporting purposes, NAS provides a contaminant information database that may be managed by the user. The user may manage the database, including editing existing contaminant source groups as well as creating new user-defined groups. When the user defines a new source, it may then be saved in the NAS database for use in future simulations. Figure 4-1 shows the list-tree in the NAS Site Data Form that displays the database of contaminants that the user can choose from to add to the source zone. From the list-tree, users will be able to edit contaminant data, create new contaminant data, and save to the NAS database for future use. For improved data management the contaminant database is importable / exportable as Microsoft Excel or standard text files.

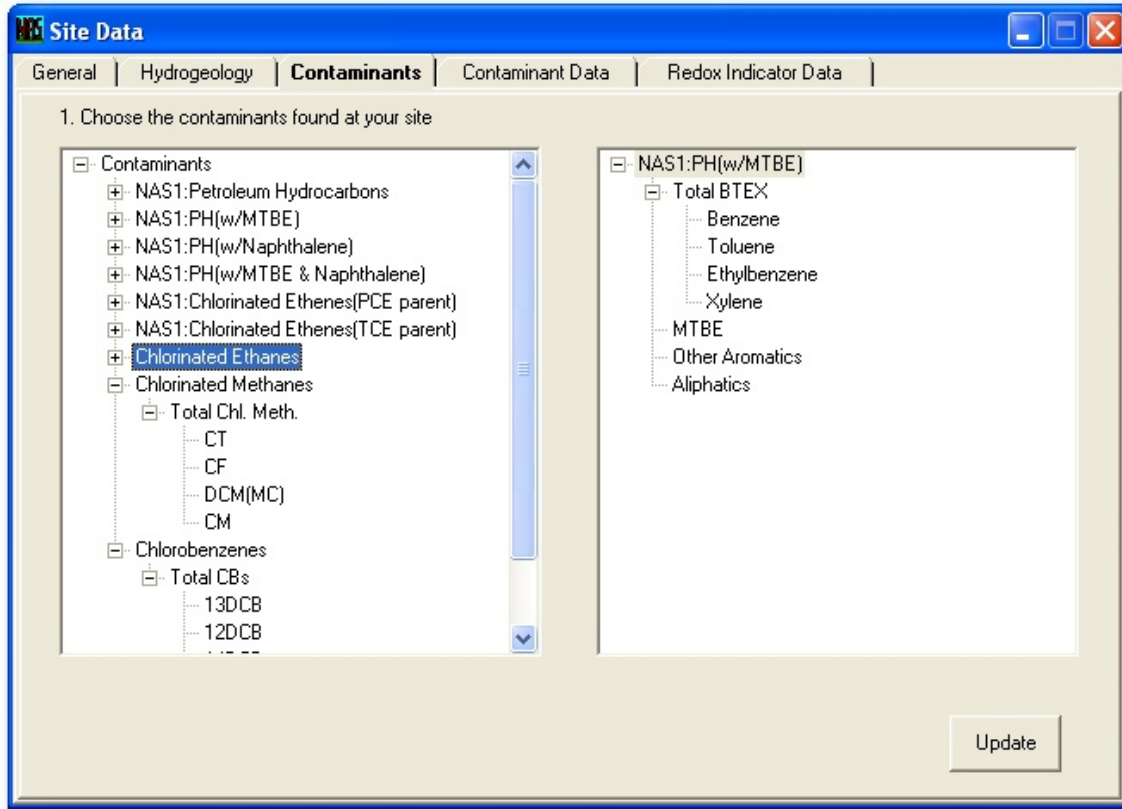


Figure 4-1. Site Data – Contaminants Tab

Three types of items are represented in the contaminant database, and may be edited or created: Contaminant Groups, Contaminant Totals, and Contaminants.

#### 4.3.1.1 Contaminant Group

The contaminant group item is a collection of individual contaminants. A group will be classified as a specific ‘Group Type’ with all contaminants within the group being classified as this type of contaminant. The list of group types is: Non-reactives, Electron Donors, Electron Acceptors, and Co-mingled. If a group is classified as ‘Co-mingled’, it may then have, at the most, one of each other group (i.e., Non-reactives, Electron Donors, Electron Acceptors) in it.

Group classification depends on the types and availability of electron donors and acceptors used in the microbial-mediated attenuation processes. For the Electron Donor Group, constituents are

simulated as electron donors for microbial growth (e.g., hydrocarbon compounds that serve as a carbon and energy source). Observed concentration distributions for all specified donor and acceptor species are required from the user. For the Electron Acceptor Group, constituents serve as electron acceptors (e.g., perchlorate and associated daughter products of reduction) with the electron donor (e.g., molecular hydrogen) availability not being explicitly simulated; that is, the observed electron donor concentration is not required from the user. For the Non-reactive Group, constituents (e.g., conservative, non-biodegradable tracers) are simulated as in the Electron Donor Group, though in SEAM3D, they are indirectly simulated through a first order decay term replacing the biodegradation sink term.

#### **4.3.1.2 Contaminant Total**

The contaminant total item is a collection of individual contaminants (e.g., ‘Total BTEX’ from the previous NAS version). Contaminant totals will not be explicitly simulated in NAS, in that the user will not be required to enter concentration profile data for the item. NAS will sum the concentrations of the individual contaminants listed within the contaminant total, and use those values for calculations.

#### **4.3.1.3 Contaminant**

The contaminant item is an individual contaminant. For each contaminant, the user may specify if a plume concentration versus distance profile will be supplied, and if the contaminant will be simulated as a NAPL source constituent in the TOD simulation. The required properties for a contaminant are:

If concentration profile data is specified, or it is simulated in NAPL source:

- Carbon Matter Partition Coefficient –  $K_{oc}$

If it is simulated in NAPL source:

- Mass Fraction
- Solubility
- Molecular Weight

If it is simulated in NAPL source, and ‘Group Type’ is ‘Electron Acceptors’:

- Stoichiometric Factor
- Alternate Pathway (see next section)

#### **4.3.1.4 Alternate Pathways**

The ‘Electron Acceptors’ group was initially developed for modeling chlorinated volatile organic compounds (CVOCs). The principally supported process in natural attenuation of CVOCs has been biologically-mediated sequential reductive dechlorination. This is the default pathway in the ‘Electron Acceptors’ group, and an example representation can be seen in Figure 4-2 where the reductive dechlorination pathway of 1,1,1-trichloroethane (1,1,1-TCA) produces 1,1-dichloroethane (1,1-DCA), chloroethane and ethane. However, degradation of CVOCs, and other NAS constituents for that matter, may be complex, with both biotic and abiotic processes acting as degradation pathways. The alternate pathway function allows the user to incorporate these additional pathways. For example, 1,1,1-TCA is also subject to non-reductive, abiotic degradation processes, as illustrated in Figure 4-2 by the conversion of 1,1,1-TCA into 1,1-dichloroethene (1,1-DCE) through dehydrohalogenation, and acetate through hydrolysis, neither of which involves electron transfer.

Alternate reduction pathways may be specified only in ‘Electron Acceptors’ groups. Additional data that is required when the user selects the ‘Alternate Pathway’ are:

- Alternate Pathway Parent
- Contaminant Percent from Parent
- Stoichiometric Factor



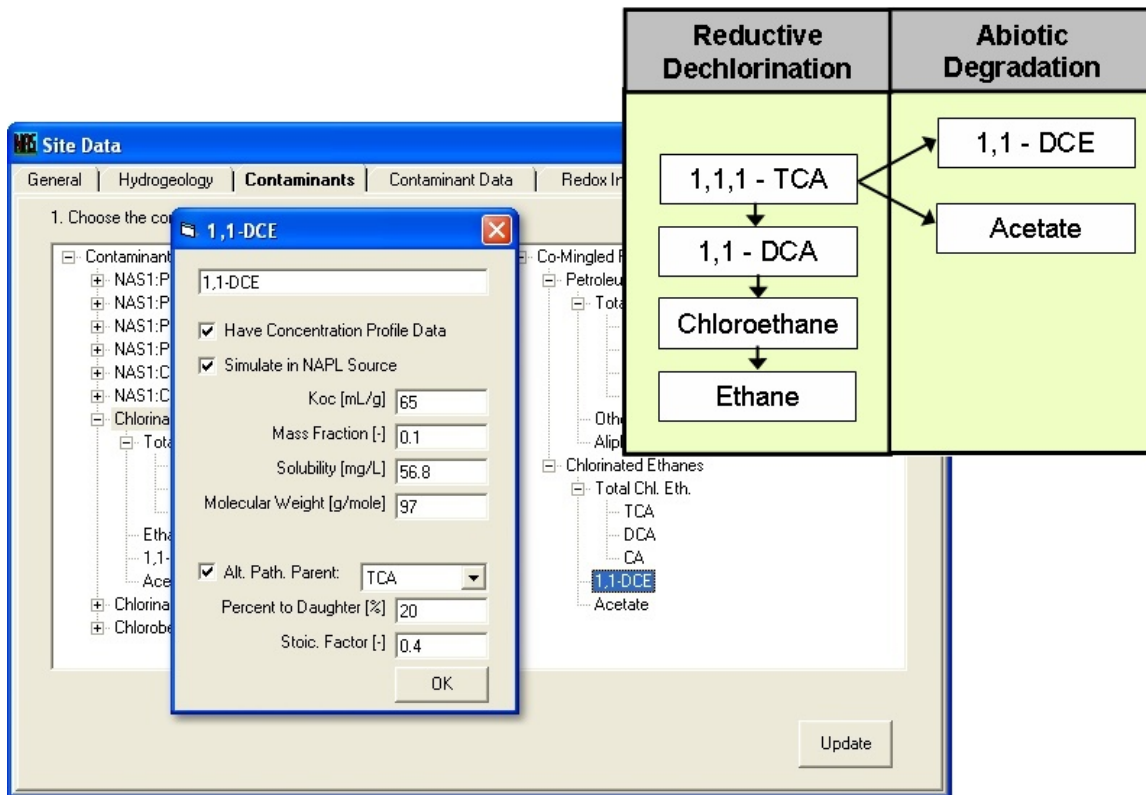


Figure 4-2. Example of Alternate Pathway Application

## 4.3.2 Pump-and-Treat Module

### 4.3.2.1 User Options

NAS has been modified for simulation of pump-and-treat remediation technology to provide expanded user options for estimating TOD. The Pump-and-Treat module allows the user to estimate TODs associated with pump-and-treat technology for comparison with, or in conjunction with, MNA. NAS can model sites with an existing (or proposed) pumping well, or optimally design a pumping well field. The two user options for estimating TOD for pump-and-treat (PnT) remediation using NAS may then be categorized as:

- A. TOD estimate for an existing (or proposed) PnT system: The NAS user will have the option to specify well location (distance from source) and pumping rate and duration.

This approach also allows the NAS user to estimate TOD using MNA if the pumping well is shut down at a specific date in the future.

- B. Automated comparison of PnT and MNA TODs: The pumping well rate is based on analytical solutions for hydraulic control using previously specified site hydrogeology and source delineation data.

#### **4.3.2.2 Conceptual Design**

The TOD estimate will be highly sensitive to a) the proximity of the pumping well to the source zone (i.e., the “x” distance of the well downgradient of the source) and b) to the pumping rate. The conceptual model for the NAS Pump and Treat (PnT) module will use a single pumping well located along the plume axis. The sole purpose of the single-well model is to allow NAS to estimate TOD using a centered source zone monitoring well. Although multiple wells for capture may be warranted at some sites, it is reasonable to assume that additional pumping wells (located adjacent to the pumping well and transverse to the plume axis) will not have any significant influence on the ground-water velocity in the center of the source. Therefore, TOD can be reasonably estimated using a single pumping well. The model grid design is dictated by where the pumping well is located along with the pumping rate and the associated capture width.

##### ***4.3.2.2.1 Approach to Well Location***

The location of pumping wells is highly site specific, based on site remediation objectives and access (e.g., well must be situated between buildings and utilities). Typically, pumping wells are located further downgradient to prevent off-site transport or to protect a Point of Compliance (POC). To enable a TOD comparison of PnT to MNA, the proposed approach is for NAS to have a default value for the well location (Option B) being the POC (or, if no POC has previously been specified, the distance to the furthest concentration well), or the NAS user may specify the well location (Option A).

##### ***4.3.2.2.2 Approach to Well Pumping Rate***

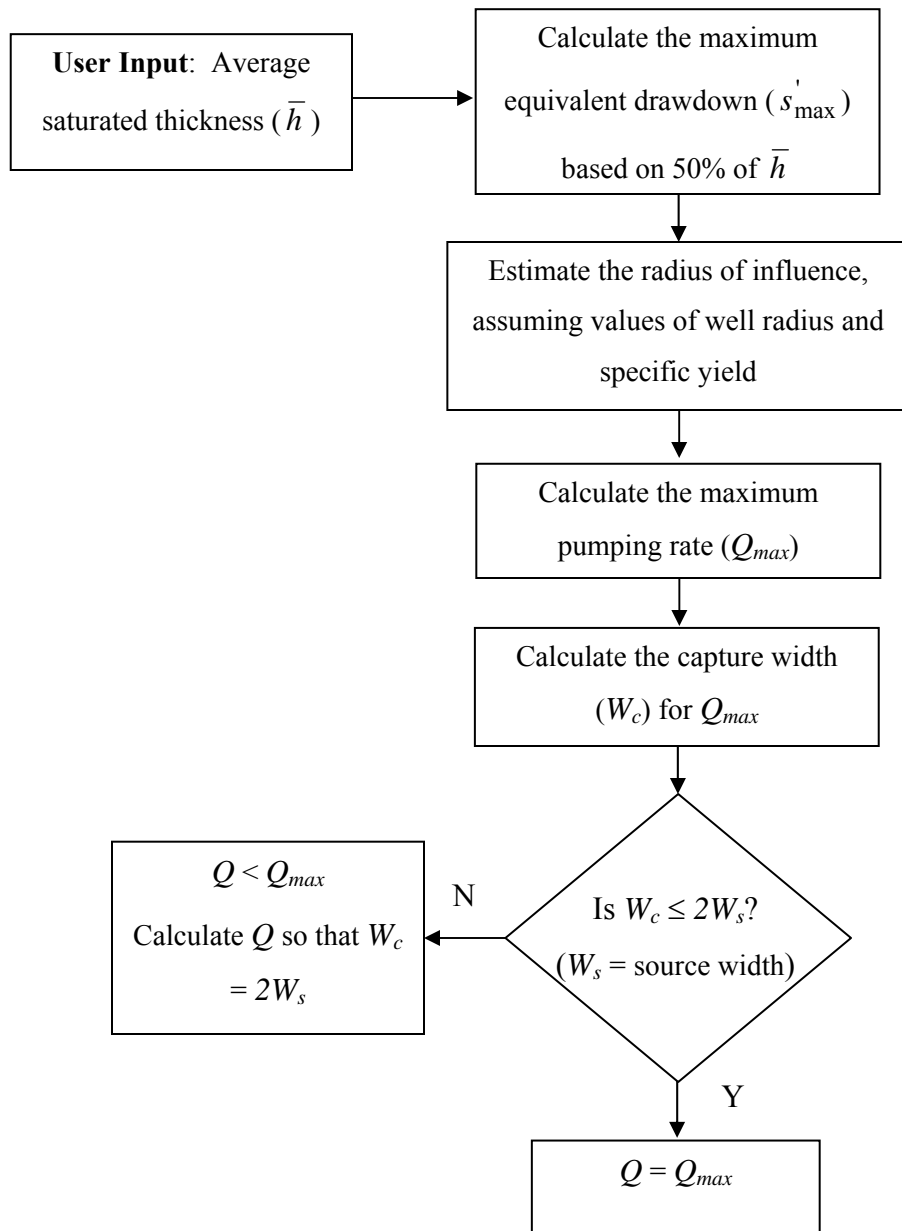
The user may specify the well pumping rate (Option A), or NAS may automatically determine to optimum rate (Option B). The following flowchart (Figure 4-3) outlines the process through which NAS determines the pumping rate of the single capture well under Option B. The pumping rate is a function of the required capture width and hydrogeologic parameters. The user will have already completed the “Site Data” section of NAS.

For an unconfined aquifer, the Dupuit equation for a pumping well at steady-state is expressed in terms of a corrected drawdown ( $s'$ ) at the pumping well (Dupuit 1857; Dupuit 1863; Jacob 1944):

$$s'_w \equiv \left( s_w - \frac{s_w^2}{2b} \right) = \frac{Q}{2\pi K b} \ln \left( \frac{R}{r_w} \right) \quad (4-1)$$

where  $b$  = initial saturated thickness,  $K$  = hydraulic conductivity,  $R$  = radius of influence, and  $r_w$  = the radius of the pumping well. NAS will solve for the maximum pumping rate using:

$$Q_{\max} = \frac{2\pi K b s'_{\max}}{\ln \left( \frac{R}{r_w} \right)} \quad (4-2)$$



**Figure 4-3. Flow chart showing the steps by which NAS will determine the pumping rate for a single capture well under Option B.**

The maximum corrected drawdown is calculated based on the assumption that the maximum acceptable drawdown ( $s_{max}$ ) in the pumping well will be 50% of the initial saturated thickness ( $b$ ) at the pumping well (i.e.,  $s_{max} = 0.5b$ ) (Viessman and Lewis 2003):

$$s'_{max} = s_{max} - \frac{s_{max}^2}{2b} = \frac{3b}{8} \quad (4-3)$$

This allows Equation (4-2) to be expressed as:

$$Q_{max} = \frac{0.75\pi K b^2}{\ln\left(\frac{R}{r_w}\right)} \quad (4-4)$$

Next, the radius of influence ( $R$ ) of the pumping well can be estimated from the equation (Bear 1979):

$$R = 1.5 \sqrt{\frac{K b t}{S_y}} \quad (4-5)$$

so that the term  $\ln\left(\frac{R}{r_w}\right)$  can be expressed as:

$$\ln\left(\frac{R}{r_w}\right) = \ln\left(\frac{1.5}{r_w} \sqrt{\frac{K b t}{S_y}}\right) \quad (4-6)$$

where  $t$  = time and  $S_y$  = specific yield. NAS will use conservative default values of time (365 days), specific yield (0.05), and pumping well radius (0.25 ft) that will prevent overestimation of  $Q_{max}$ .

NAS will next estimate the capture width ( $W_c$ ) from the equation (Grubb 1993):

$$W_c = \frac{Q_{max}}{K b i} \quad (4-7)$$

where  $i$  = best estimate of the horizontal hydraulic gradient. In the event that the capture width is much greater than the source width ( $W_s$ ), the maximum pumping rate may be significantly overestimated. If  $W_c > 2W_s$ , then the pumping rate ( $Q$ ) will be recalculated using:

$$Q = 2W_s Kbi \quad (4-8)$$

However, if  $W_c \leq 2W_s$ , then the pumping rate  $Q = Q_{max}$ .

#### 4.3.2.2.3 Approach to Well Pumping Duration

The NAS default value for pumping duration (Option B), is the ‘time of analysis’ the user has specified in the TOD module. NAS also provides the user with the option to specify a pumping duration (Option A) being a fraction of the total ‘time of analysis’, in which case the remaining fraction will be simulated as an MNA-only polish period.

See Figure 4-4 for the conceptual model for NAS PnT MODFLOW simulations.

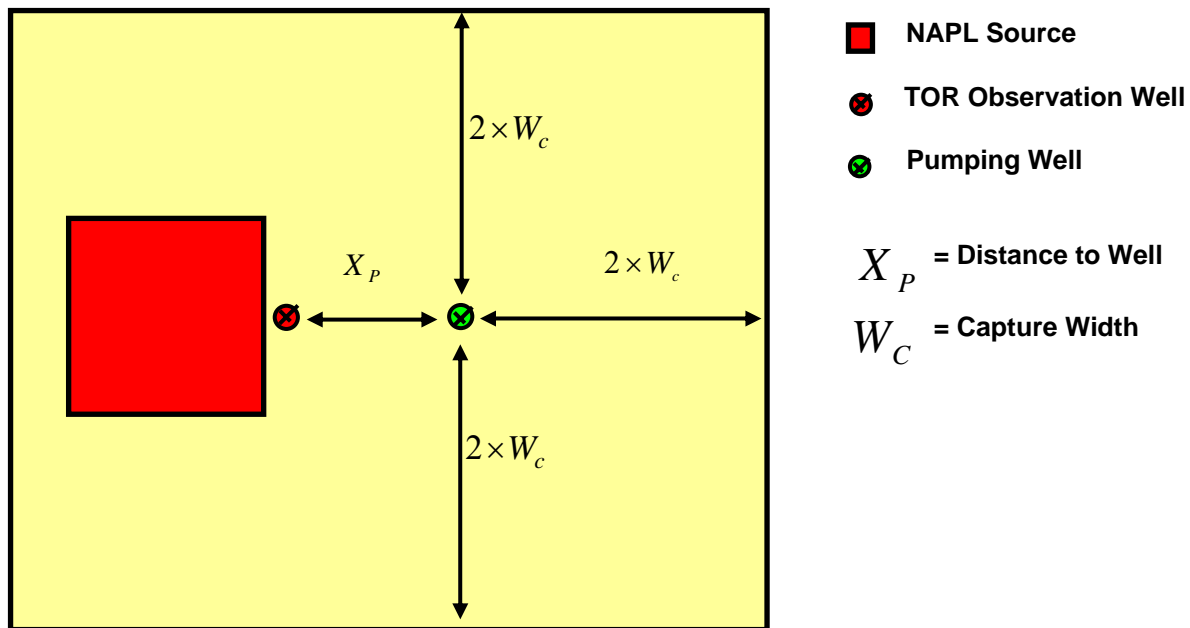


Figure 4-4. MODFLOW Pump-and-Treat Conceptual Model

#### 4.3.2.3 Computational Challenges

One of the challenges of simulating a capture well using SEAM3D with MODFLOW is setting numerical parameters so that the overall duration of SEAM3D simulation times are reasonable. In particular, high flow velocities in and around the pumping well result in relatively small transport time steps, which are required to minimize numerical error. This problem is

demonstrated in an example using the commercial software Groundwater Modeling System (GMS). In this example, a hypothetical aquifer is simulated using a 264-m wide by 216-m long model grid (99 columns by 81 rows). This model grid is wider and longer than what is used now in NAS version 1.x for simulating MNA-only scenarios. The larger grid is required for the pumping-well simulation so that the boundary conditions do not unduly influence the hydraulic head distribution. The same grid is used for both scenarios to allow a 1-to-1 comparison of results and simulation times between MNA-only and pump-and-treat (PnT).

The MODFLOW MNA model incorporates a uniform flow field in which ground water moves from the left boundary (constant flow) to the right boundary (constant head) at an average linear velocity of 2 cm/d (24 ft/yr). The NAPL source is centered in the grid. Because the goal of the simulation is to determine an estimate of the time of NAPL dissolution (TOD) for a monitoring well immediately down-gradient of the source (i.e., identical approach for MNA-only simulations using NAS version 1.x), the model grid was not extended to encompass the entire length of the plume.

The MODFLOW PnT model incorporates a pumping well operating at a constant rate (Q) of 1.0 L/min (~0.26 gpm) with the same uniform flow field used in the MNA scenario. For the hydrologic input parameters, the capture width of the pumping well (72 m) is over twice the width of the source. The well is located roughly 20 m (66 ft) downgradient of the source zone. Compared to the MNA scenario, the source zone concentrations are lower by a factor of 4 in the PnT scenario.

Table 4-1 summarizes the run times for the MNA and PnT scenarios for an 80-yr simulation period. TOD estimates are based on an MCL of 10 µg/L. These results illustrate the computational challenge of transport simulations with pumping wells. Compared to the MNA scenario, the PnT time step decreases by a factor of 10, and the simulation time increases proportionally. The longer run time is unacceptable given the constraints placed on NAS to limit simulation times to less than 10 minutes per run.

**Table 4-1. Comparison of MNA and PnT Time Step Size, Simulation Results and Run Times.**

<b>Simulation Scenario</b>	<b>Time Step (d)</b>	<b>TOD (yr)</b>	<b>Run Time</b>
MNA-only	15.19	80	2 min, 13 sec
Pump-and-Treat	1.46	65	23 min, 45 sec

#### **4.3.2.4 Approach to Computational Efficiency**

NAS initially sets the well location and pumping duration, and estimates a pumping rate. If the user wants NAS to make an estimate of TOD using PnT but doesn't have a specific design to input under Option A, then the NAS user will simply use the values that are automatically predetermine by NAS, otherwise the user enters user-specified values. The approach is to execute a two-step simulation of the ground-water flow problem. For the first simulation, NAS sets up a large domain, ground-water flow model (MODFLOW) that incorporates the pumping well (as shown in Figure 4-4). NAS uses the results of the steady-state solution of this first MODFLOW run to serve as the starting head values for a second simulation based on a smaller domain. This second simulation uses a grid that only encompasses the contaminant source zone area. Note now the pumping well is outside of the model grid, which reduces computational problems associated with high cell velocities. In this simulation the ground-water flow model (using the results from the first simulation) is then run with the contaminant transport model (SEAM3D). The periphery of the grid is comprised of constant-head cells. Identical cell dimensions are used in both steady-state models. NAS PnT simulation using this two-step approach produced TOD results identical to the GMS PnT scenario (65 yr). Furthermore, the NAS run time (43 sec) was even less than the GMS MNA-only run time, using the same 80-yr simulation period. This is due to the decreased number of model cells.

To summarize:

NAS performs the following 2 steps for comparison with MNA-only:



1. MODFLOW is run with the smaller domain under steady-state conditions with the user-defined uniform flow field, for the total simulation time (See Figure 4-5).
2. SEAM3D is run with the smaller domain, for the total simulation time, using the MODFLOW results of Step 1.

NAS will perform the following additional steps for each PnT simulation:

3. NAS generates a larger model grid to include the pumping well and to minimize the influence of boundary conditions on the MODFLOW results.
4. MODFLOW is run with the Well Package to simulate pumping and source capture under steady-state conditions (See Figure 4-6), for duration of pumping period. Hydraulic head values are retained for use in Step 5.
5. NAS creates a new model grid so that the pumping well is outside the boundaries of the domain (i.e., the domain used for MNA-only simulations). NAS assigns starting heads using the results from Step 4 (See Figure 4-7).
6. MODFLOW is run for the smaller domain under steady-state conditions, for duration of pumping period.
7. SEAM3D is run with the smaller domain and using the MODFLOW results of Step 6, for duration of pumping period.

If an MNA polishing period follows pumping:

8. Final contaminant concentrations from Step 7 are retained for use in Step 10.
9. MODFLOW is run for the smaller domain under steady-state conditions with the user-defined uniform flow field (i.e., the domain used for MNA-only simulations in Step 1), for the remainder of the total simulation time.
10. SEAM3D is run with the smaller domain, for the remainder of the total simulation time, using the MODFLOW results of Step 9. NAS assigns starting concentrations using the results from Step 7.

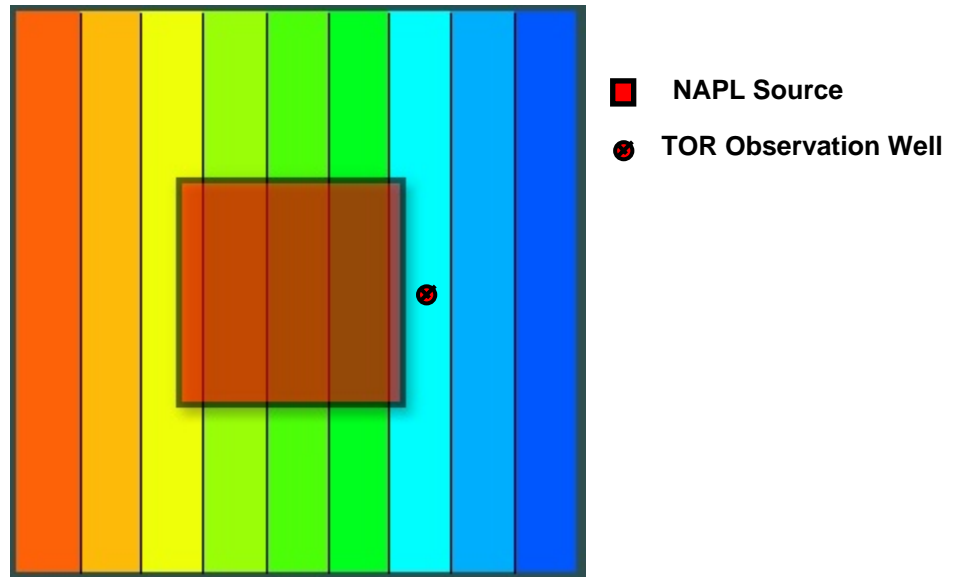


Figure 4-5. MODFLOW Heads: Small domain with uniform flow field – for MNA simulations

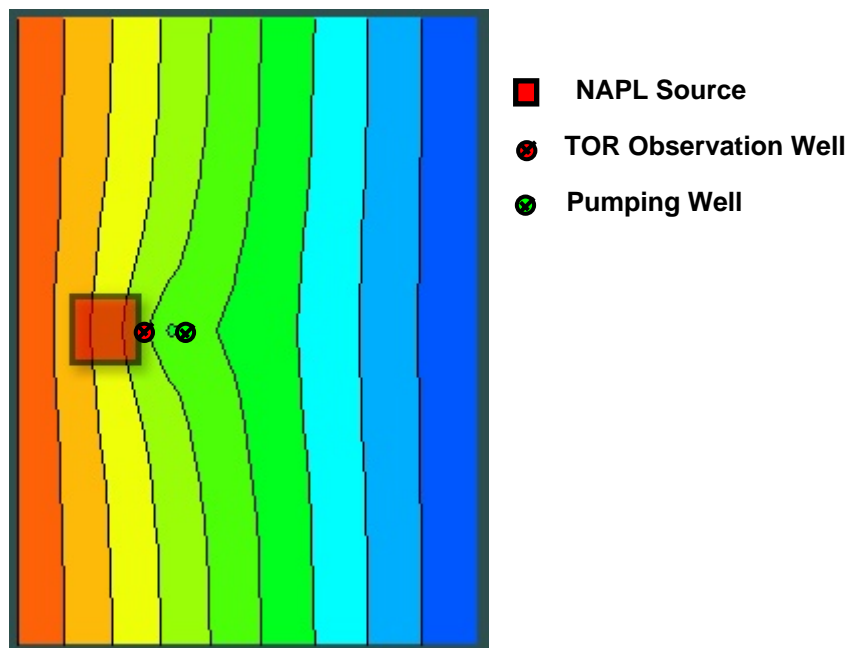


Figure 4-6. MODFLOW Heads: Large domain with Well Package

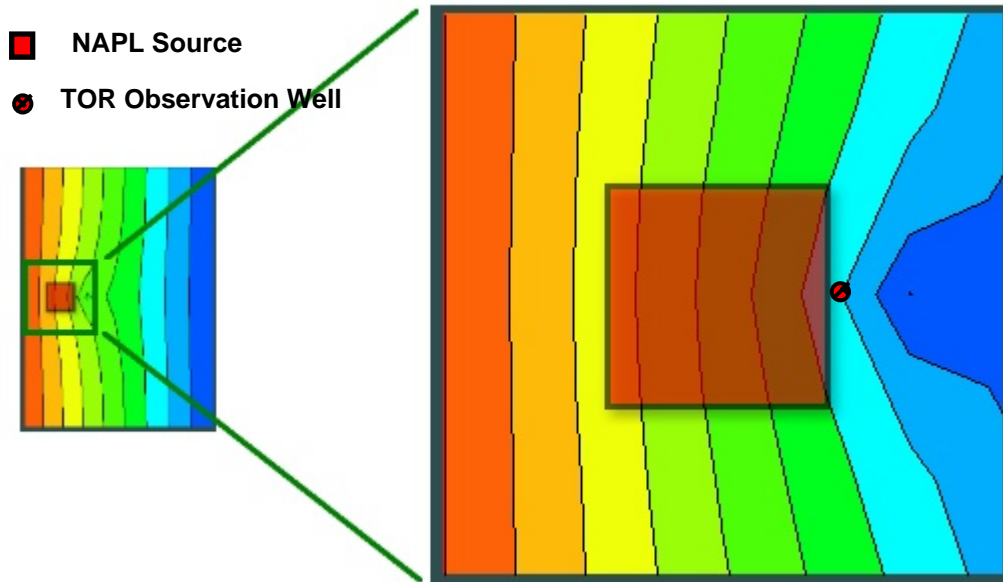


Figure 4-7. MODFLOW Heads: Final heads of large domain used as starting heads for small domain

### 4.3.3 Post-Audit Data Analysis

The goal of post audit data functions in NAS is to improve TOS/TOD estimates, and performance and sustainability assessment, with integration of long-term performance monitoring data. These functions allow the use of NAS for the post-audit of data collection at sites where remedial action has been employed, and aid in the chronologically comparative evaluation and dissemination of NAS data and results. Users are now able to combine chronologically successive, site-measured, concentration and redox indicator data for comparison of NAS-predicted versus observed trends. NAS has the ability to extract NAS-predicted contaminant concentrations at any user-specified distance downgradient. All user-specified contaminants may be analyzed. MNA sustainability assessment includes sustainability of reduction-oxidation zones and natural attenuation capacities (NACs). Transient datasets may be added to a NAS simulation either through importing additional '\*.nas', Microsoft Excel, or text files, or by progressively creating new data. Additional user-options are available in the NAS modules if NAS is in 'transient dataset mode'. Multiple-dataset NAS simulations may then be saved to one transient '\*.nas' file for user convenience in running future simulations. The

NAS user can fully document all data and results in tabular or graphical form, with the ability to print and save in multiple formats, to generate convenient, publication-quality reports.

#### **4.3.3.1 Site Data Module**

Users are able to cycle through each dataset to view/edit input data. New tables compare calculated data (e.g., groundwater velocity, estimated plume length, decay rates). The existing graphical summary can now show all datasets in one visual to easily compare changes in NAC-profile and redox zonation.

The multiple, transient ‘snap-shots’ of concentration profile data may be used to evaluate MNA sustainability over time (see Figure 4-8). In the Site Data Graphical Summary form, blue markers represent the first dataset in time, with green and purple marking subsequent datasets. Data points represent actual observed data with corresponding lines being the NAS-simulated NAC. Changes in line color (e.g., green and orange in this example) represent redox zonation.

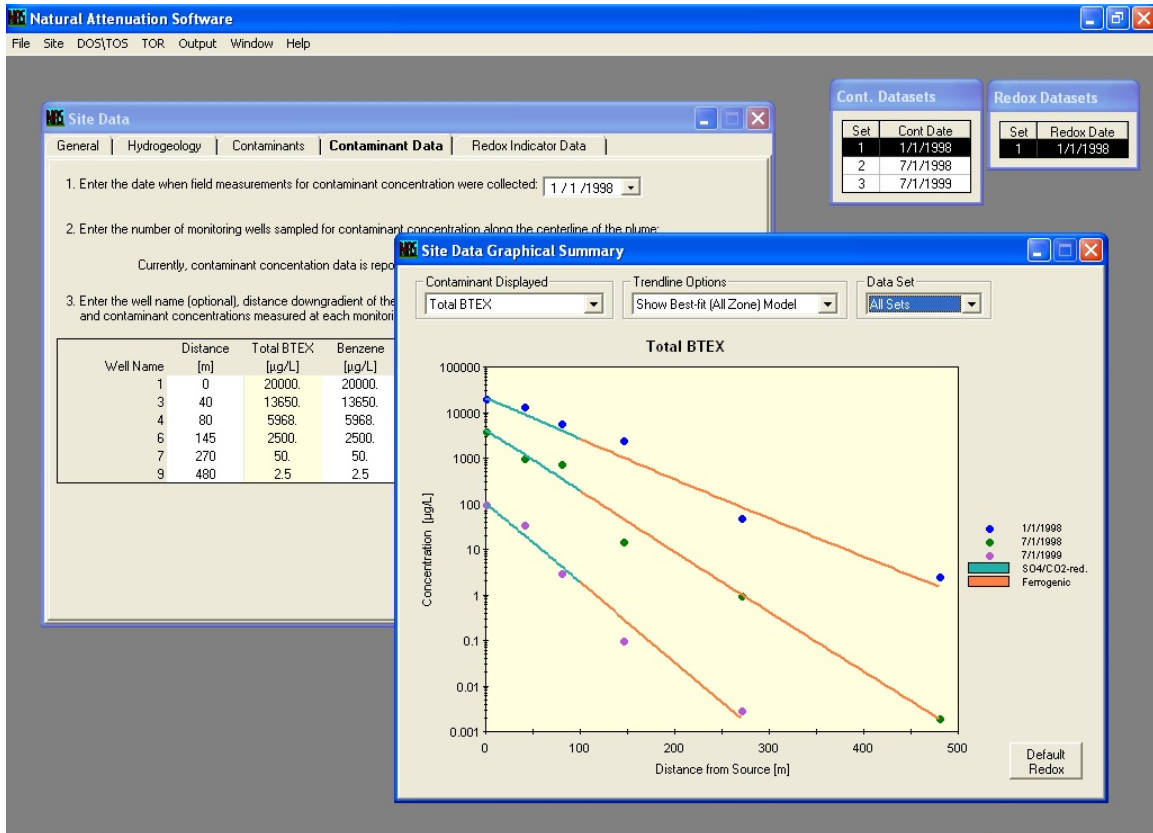


Figure 4-8. Transient concentration profile data from multiple NAS datasets.

### 4.3.3.2 Source Reduction / Time of Stabilization Module

Users are able to determine if future TOSs, based on previous source reduction actions, are in line with previous TOSs. This enables users to know if additional source reduction may be required based on plume instability, or if the regulatory compliance concentration will still be met at the point of compliance in a satisfactory time period. The steady-state and transient solution graphs have been modified to be able to display all datasets with any corresponding source reduction estimation plots.

Added to the module is the ability to plot transient source-reduction breakdown (C vs. T) curves at any user-defined point along the transient solution, spatial distribution (C vs. X) curve (see Figure 4-9). These graphs plot best estimate, maximum, and minimum solutions based on parameter range entered by the user in the Site Data module. Any monitoring data points

provided by the user for each specific location may be plotted on the graph for correlation with NAS-estimates. In Figure 4-9, the black solid line represents the best estimate NAS prediction, with the upper and lower dashed lines representing the maximum and minimum NAS prediction, respectively. Individual red points represent actual site monitoring data.

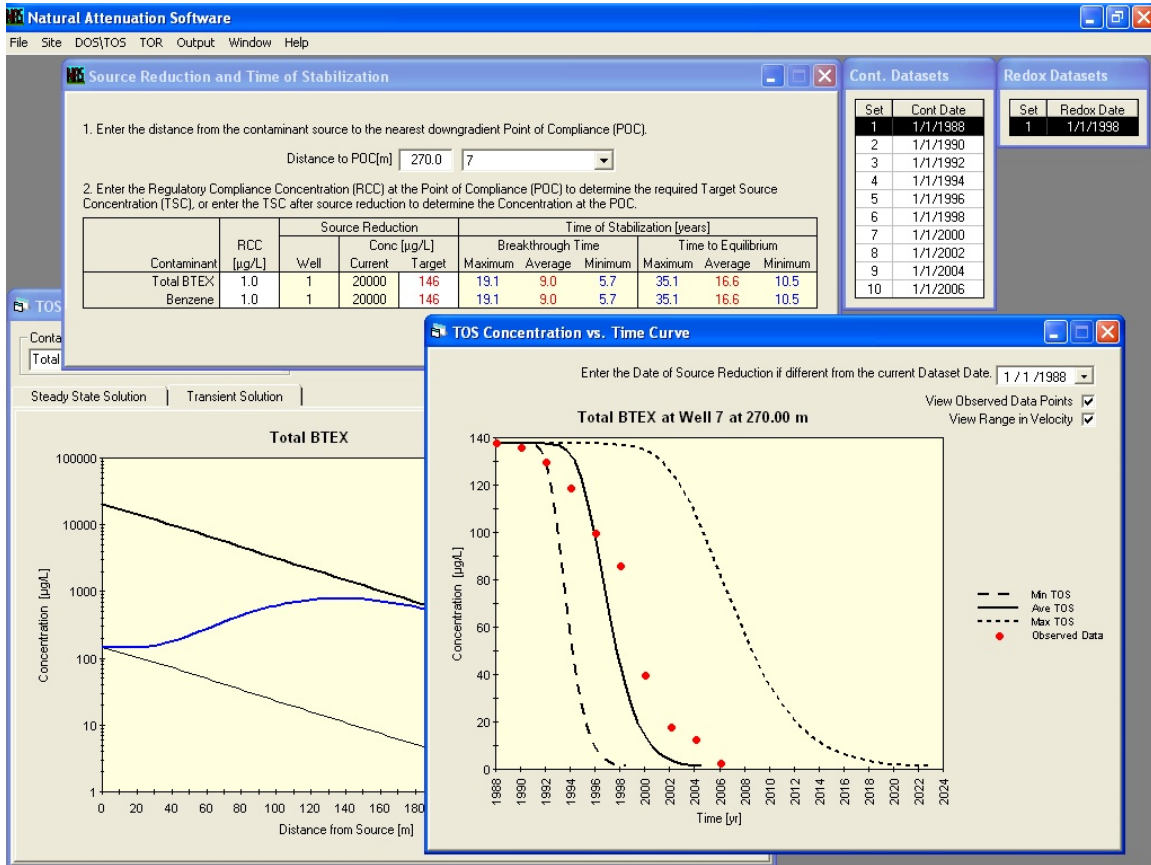


Figure 4-9. Transient source-reduction breakdown curve.

#### 4.3.3.3 Time of Remediation Module

Users are able to determine if future TODs, based on previous mass removal plans or continuing natural attenuation processes, are in line with previous TODs. This enables users to know if additional mass removal may be required based on plume instability, or if the source compliance concentration will still be met in a satisfactory time period. Statistical analysis of the TOD solution matrix, created from the NAPL mass range and removal plans, have been enhanced with improved user output options in both tabular and graphical form. Users also have the ability to simultaneously display results from transient datasets for comparison.

Added to the module is the ability to plot transient NAPL dissolution breakdown (C vs. T) curves (see Figure 4-10). These graphs plot a series of solutions based on user-selected options for range of NAPL mass and number of mass removal plans. Any monitoring data points provided by the user for each specific location may be plotted on the graph for correlation with NAS-estimates. In Figure 4-10, the black line represents the NAS prediction with no source mass removal, the blue line represents 50% source removal, and the green line represents 95% source removal. Individual red points represent actual site monitoring data.

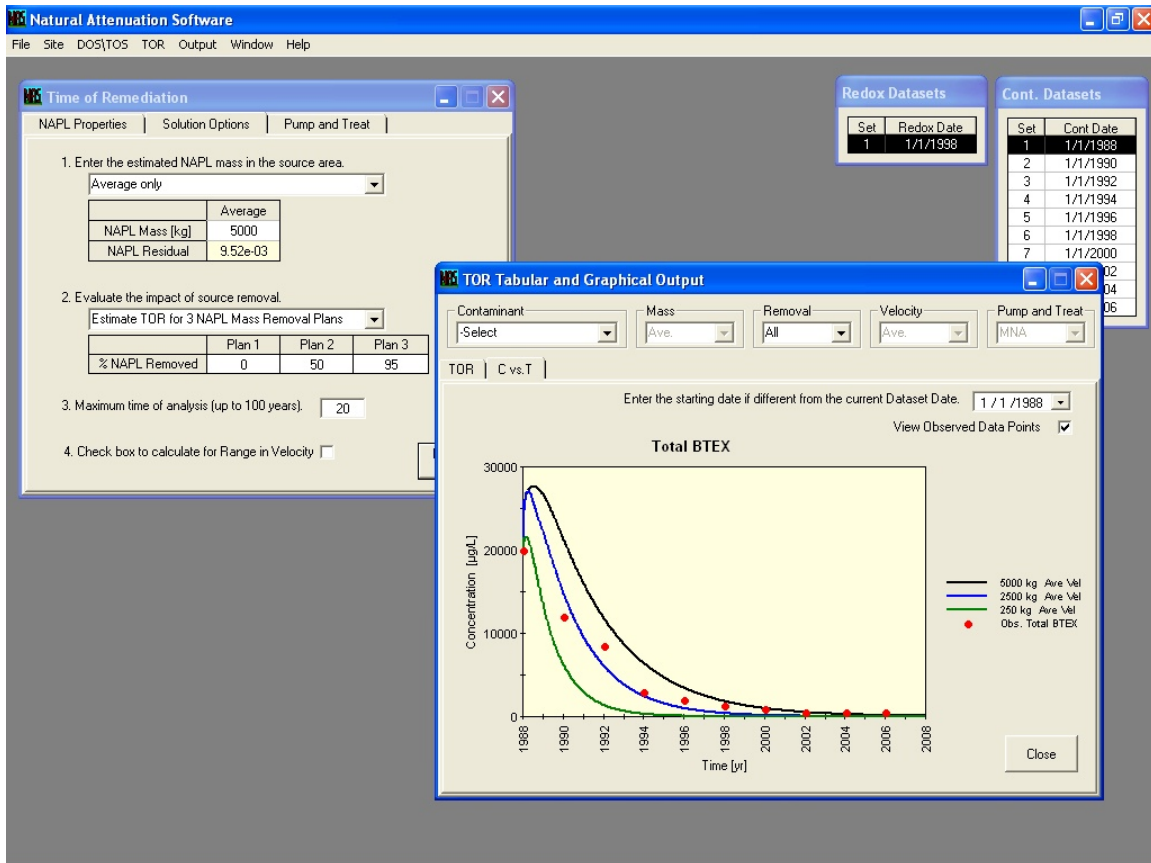


Figure 4-10. Transient NAPL dissolution breakdown curve (MNA only).

#### 4.3.3.4 Pump-and-Treat

These capabilities do not comprise a separate module but, rather, are incorporated into the TOD Module and become available when pump and treat is simulated. All auditing capabilities within the TOD Module are also available for comparing MNA with and without pump and treat.

When pump and treat is simulated, the transient NAPL dissolution breakdown (C vs. T) curves in the TOD Module may be plotted with the P-and-T (and MNA polish period if specified) solution breakdown curves for comparison with MNA-only. See Figure 4-11: Black represents the NAS prediction with no source mass removal, blue represents 50% source removal, and green represents 95% source removal. The thicker lines represent MNA only, while the thinner lines represent the NAS pump and treat predictions. Individual red points represent actual site monitoring data.

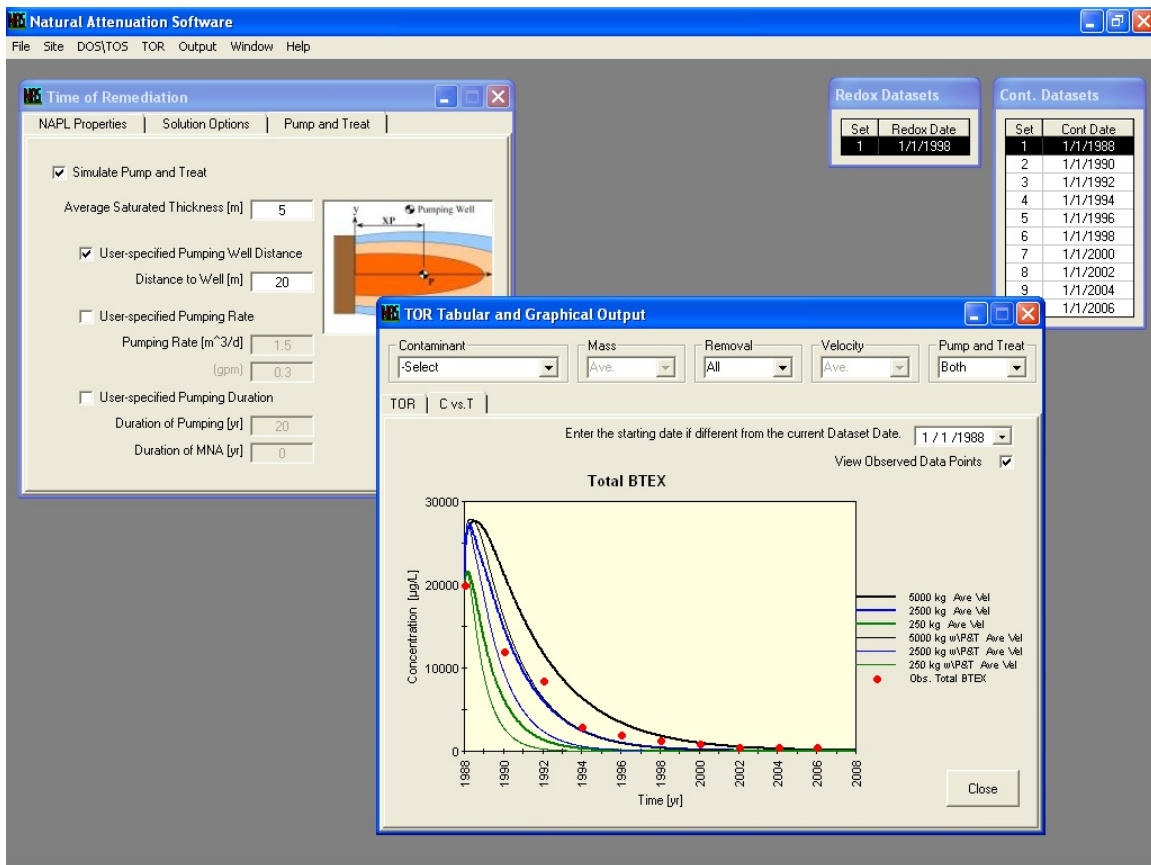


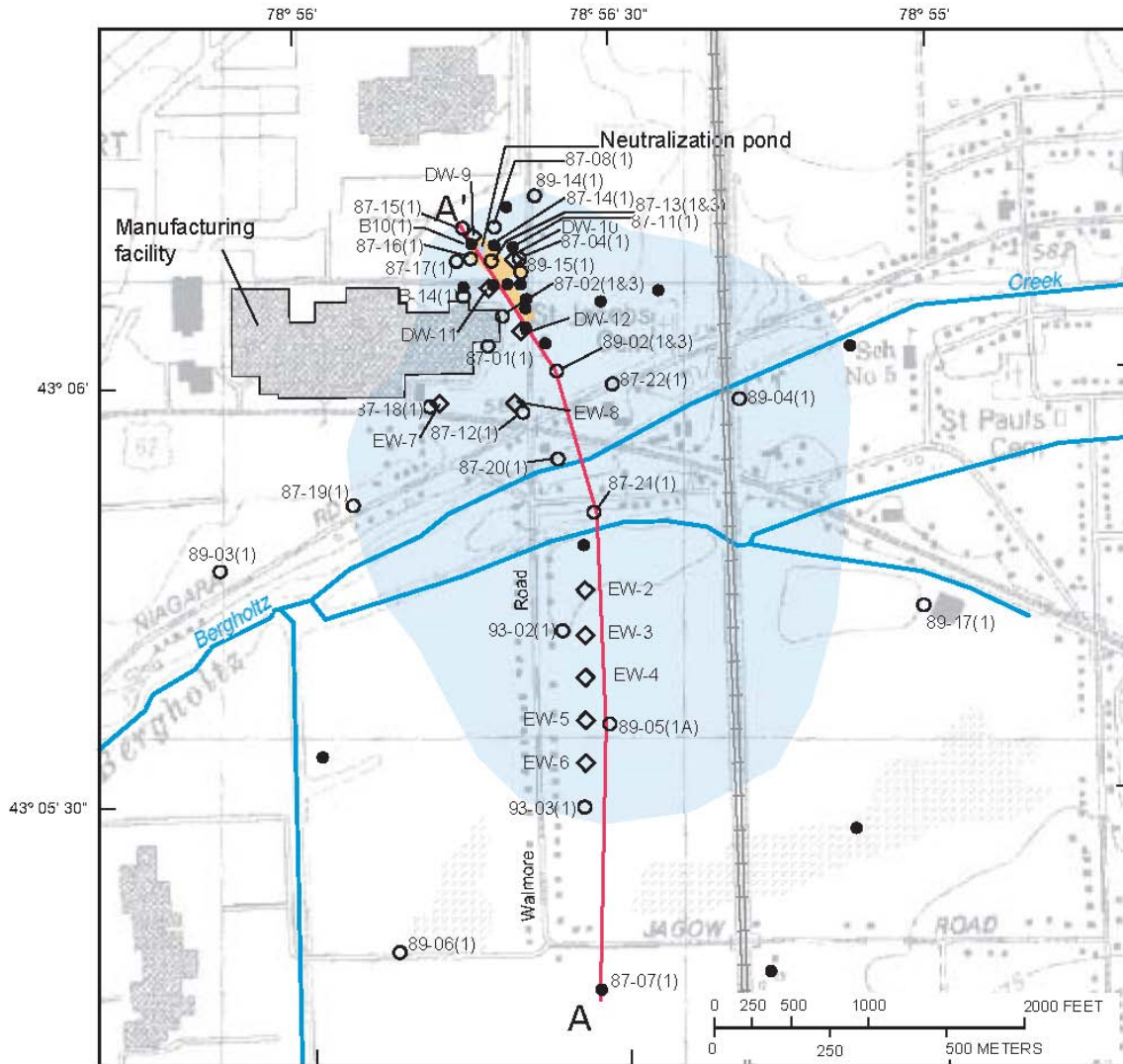
Figure 4-11. Transient NAPL dissolution breakdown curve (P-and-T versus MNA-only).



## **4.4 Site Application**







### **4.4.1 Site Background**

Textron Realty Operations Incorporated (formerly Bell Aerospace Textron) is located in Wheatfield, New York, near Niagara Falls. The facility's surface impoundment (SI), a rectangular basin measuring 60 feet by 100 feet by 10 feet, was used to collect wash water from rocket engine test firings from 1940 to 1984, and received storm runoff and cooling water for more than 30 years, and for a limited period, coal gasification wastes. The SI, closed in 1988, is a RCRA-regulated unit subject to both post-closure requirements and corrective action (Yager 2002). The site overlies 5-12 m of an unconsolidated overburden layer, which is then underlain by the Guelph Formation, a 3-6 m thick weathered dolomite bedrock layer that contains many open fractures, and also contains a water-bearing, horizontal-fracture zone near its lower bounds. The transmissivity of this formation was estimated at 6 m<sup>2</sup>/d. Ground water velocity was computed to range from 0.2-0.9 m/d, from an assumed effective porosity of 3% (Yager 2002). VOCs derived from the SI are present in the ground water as a DNAPL source and as an aqueous phase contaminant plume. Aqueous phase contamination (up to 100,000 parts per million VOCs) has been found in the soils, in the unconsolidated sediments above the bedrock and in the bedrock. The extent of the DNAPL source appears to be limited to the facility property but the extent of the aqueous phase bedrock plume is considerably greater (Figure 4-12), traveling beneath residential and commercial areas (USEPA 2004). The facility installed off-site (5 wells) and on-site (7 wells) ground water extraction systems, started in 1993 and 1995 respectively. Monitoring data indicate that both systems are achieving their design objectives, which are to control the further migration of contaminated ground water, remove contamination from the ground water, and eventually attain the New York State ground water standards (USEPA 2004; Yager 2002).



Base from U. S. Geological Survey, Tonawanda West, N.Y., 1:25,000, 1980

#### EXPLANATION

- |  |  |
|--|--|
|  Plume of dense nonaqueous-phase liquids in 1990                                |  Monitoring well                                |
|  Area in which concentration of chlorinated ethenes exceed 1 micromolar in 1990 |  87-19(1) Monitoring well sampled in this study |
|  Geologic section A-A'  |  EW-6 Pumped well                               |
|  | Number in parentheses is zone designated by Golder Associates (1991b)  |

**Figure 4-12. Map of USGS study site near Niagara Falls, NY (Yager 2002).**

#### **4.4.2 NAS Application**

For the purpose of this application, NAS was modified to allow the user some flexibility in specifying which well is simulated as the observation point at which the TOD concentration versus time estimates are evaluated (originally always set to the first/source concentration well), thereby allowing the position of the TOD observation well to be moved to a user-defined well located further downgradient of the source. This change was implemented to enable simulation of a downgradient monitoring well where concentration trends showed steady declines following the initiation of the system of pumping wells in 1993.

The approach taken for the NAS application was to vary input parameters (NAPL Mass and average saturated thickness) to find the best correlation between NAS-estimated TCE concentration-versus-time curves and observed data. NAPL Mass ranged from 1,000 to 100,000 kg and the average saturated thickness ranged from 3.5 to 10 ft (approximated from Yager 2002). Figure 4-13 and Figure 4-14 provide a comparison of the sensitivity of the average saturated thickness on the NAS-simulated TCE concentration versus time at Well 87-20(1). NAS simulations using the pump-and-treat option provided a more favorable match with the observed data compared to the MNA option with no pumping well.

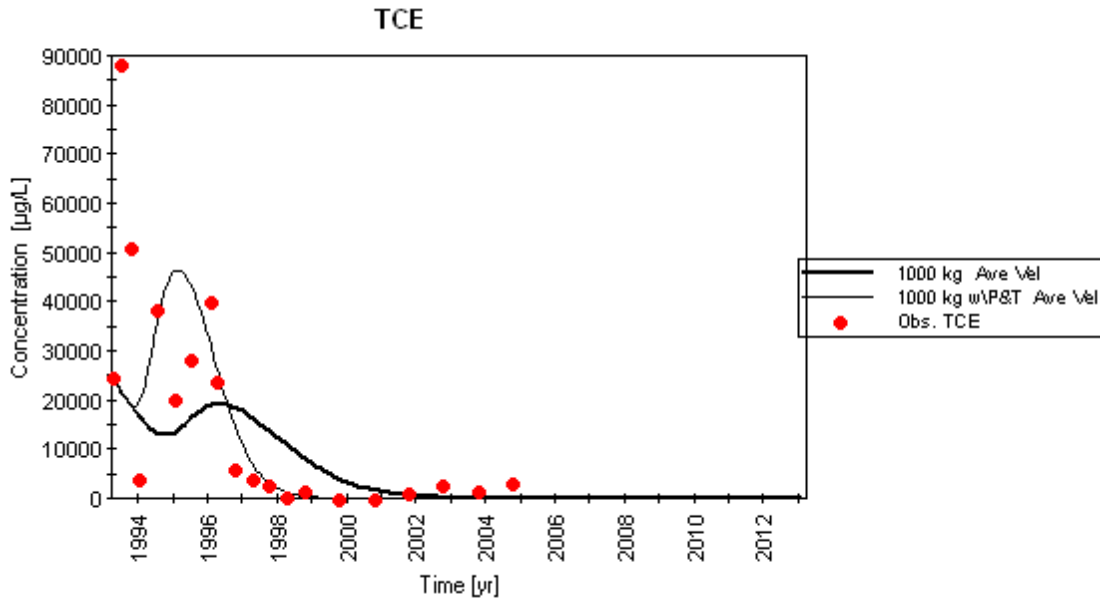


Figure 4-13. NAS-calculated vs. observed TCE - Average saturated thickness =6.75 ft.

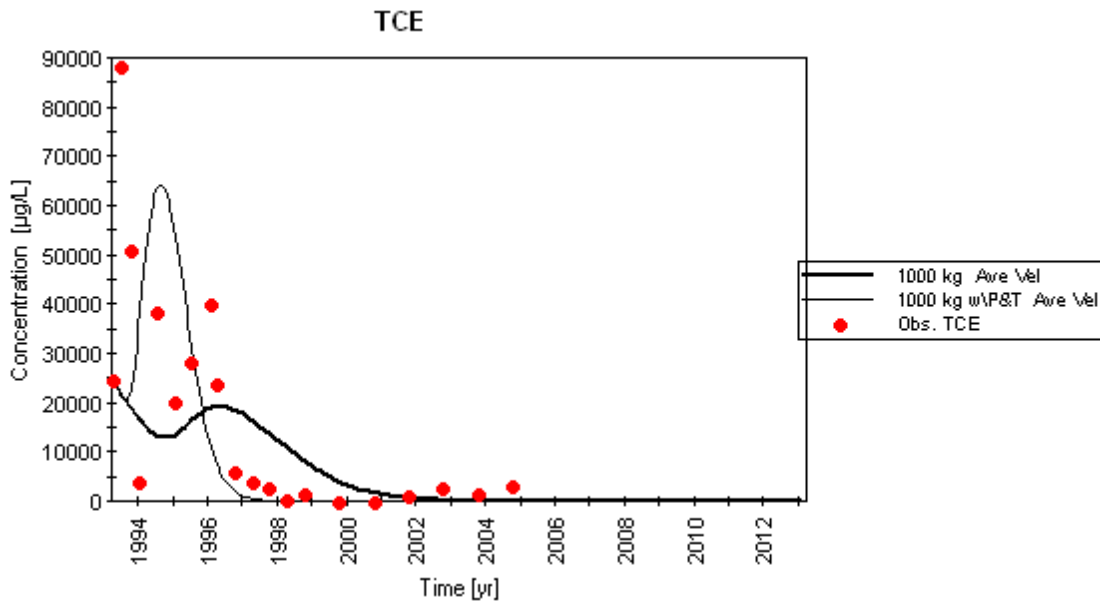


Figure 4-14. NAS-calculated vs. observed TCE - Average saturated thickness =3.50 ft.

## **4.5 Conclusions**

Results of the simulations show that NAS was effective in capturing concentration time trends of natural source depletion, through dissolution and dissipation, of a multi-component NAPL. A match between observed and simulated concentrations at observation wells was achieved based on observed pumping well parameters and reasonable estimates of the mass and dimensions of the source zone along with composition of the NAPL. This finding suggests that at some sites, knowledge of NAPL source complexities (e.g., interfacial area) is not required for a reasonably accurate estimate of TOD. However, the dependency of concentration versus time results on source zone mass and geometry along with NAPL composition suggests that source characterization methods have the potential to reduce the uncertainty associated with source depletion calculations using NAS. The NAS simulation results also demonstrate the value and efficiency of refining TOD predictions using post-audit data analysis.

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## **5 Time Estimates for Reaching Compliance Using Source Remediation Combined with Monitored Natural Attenuation**

Authors: Mark A. Widdowson, Eduardo Mendez III, Francis H. Chapelle, Clifton C. Casey

### **5.1 Abstract**

An analytical solution is presented to estimate the time required to achieve a groundwater concentration-based remedial action objective (RAO) using a combined remedy of contaminant source reduction and monitored natural attenuation. The proposed method is consistent with a framework for evaluating the time of remediation proposed by Chapelle et al. (2003). Solutions are also presented for determining the decrease in the source zone groundwater concentration required to reach a site-specific RAO at a downgradient point of compliance (POC) and the time trend in the contaminant concentration following source concentration reduction. The method enables precise and approximate calculation for the time of stabilization; that is, the time between source reduction and when concentrations reach a new steady-state at a POC. The approximate solution corresponds to a concentration that is within a margin of error of 2% and 23% of the target concentration when the pretreatment contaminant concentration at the POC is one to two orders of magnitude greater than the target compliance concentration, respectively. The solutions show greatest sensitivity to the groundwater velocity, sorption parameters, and first-order decay coefficient. The approach is demonstrated at a chlorinated solvent-contaminated site where a six-year monitoring program was documented followed aggressive source treatment. Good agreement between observed data and simulated concentrations at downgradient monitoring wells is achieved when uncertainty in the groundwater velocity is reduced.

### **5.2 Introduction**

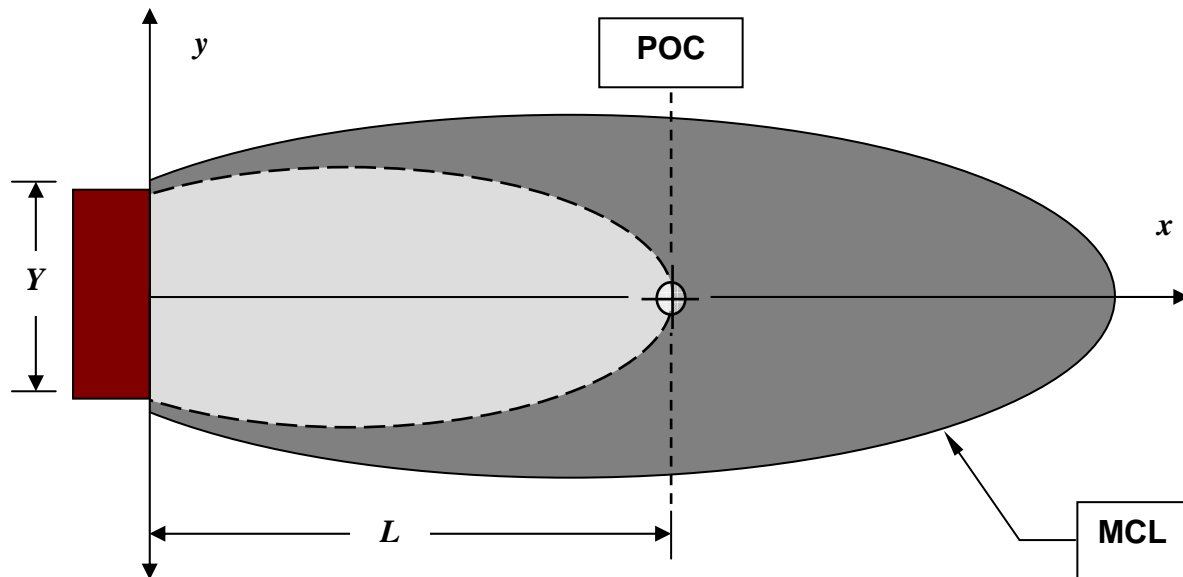
Source zone remediation combined with monitored natural attenuation (MNA) is one strategy for reaching regulatory closure at contaminated sites. Data from Superfund Records of Decision

show that source control treatment has been selected as a remedy at approximately 50% of sites with an increasing use of *in situ* technologies (USEPA 2004a). Innovative technologies are also being used more frequently, particularly at sites with dense nonaqueous-phase liquids (DNAPL), to remove or destroy contaminant mass and reduce aqueous-phase concentrations in groundwater (USEPA 2004b). Engineered remedial actions (ERAs) considered innovative include several *in situ* technologies (thermal treatment, chemical oxidation, zero-valent iron, and bioremediation) and surfactant flushing.

The potential benefits of DNAPL source zone remediation, technological challenges to implementing innovative methods, and strategies for performance assessment have been described in several recent publications (USEPA 2003; USEPA 2004b; Stroo 2003; ITRC 2004). Although reduction in the groundwater concentrations of site-specific contaminants of concern (COCs) to maximum contaminant levels (MCLs) may be impossible to achieve purely from source remediation, a number of DNAPL sites have reached regulatory closure following treatment (USEPA 2004b). In these cases, regulatory closure was facilitated using risk-based cleanup goals, and COC concentrations were not required to reach MCLs.

A related remediation strategy at contaminated sites is to couple partial source removal using an appropriate ERA, including combined remedies, with a reduction in the size and concentration of the contaminant plume. This approach is illustrated conceptually in Figure 5-1 in which a stable aqueous-phase plume is reduced in length by decreasing the mass flux at the source area as a result of the ERA. The length ( $L$ ) and the COC compliance concentration (e.g., MCL) is determined by site-specific remedial action objectives. This strategy is based on the assumption that following partial source removal, the plume will restabilize at concentrations that are lower than the pretreatment COC concentrations. Although COC concentrations in the post-treatment plume between the source and the POC will be above MCLs once the plume restabilizes, the COC concentration will not exceed the MCL beyond the POC.





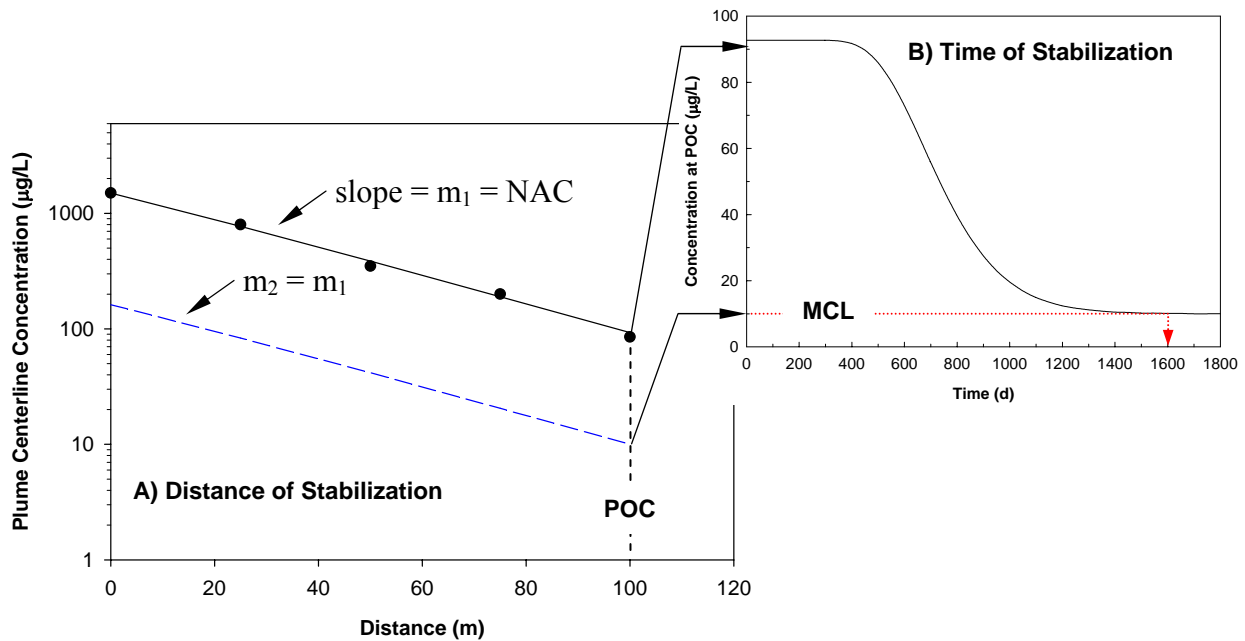
**Figure 5-1. Conceptual illustration of combining partial source area removal with monitored natural attenuation to achieve a remedial action objective which is designed to shrink a stable plume to a specified distance ( $L$ ) at a point of compliance (POC) and a specified compliance concentration (e.g., maximum contaminant level, MCL).**

Chapelle and Bradley (1998) present a method to calculate the level of source zone reduction combined with MNA in the aqueous-phase plume to achieve a site-specific remedial action objective at a POC downgradient of the source. This method assumes that the pretreatment plume is stable and utilizes a one-dimensional steady-state analytical solution in which the decline in concentration along the centerline of the plume can be mathematically described in terms of the natural attenuation capacity (NAC) of the aquifer. The target concentration in the source zone groundwater required to shrink the aqueous-phase plume to a prescribed compliance distance and compliance concentration of a COC is calculated.

The method of Chapelle and Bradley (1998) is consistent with EPA policy which states that source control is expected in conjunction with MNA and recommends the rare use of MNA as a stand-alone remediation technology (USEPA 1999). The OSWER Directive on the use of MNA also advises that the time frame for achieving remediation goals using MNA should not be excessive compared to other appropriate technologies (USEPA 1999). Thus, in order to properly

utilize the combined use of source remediation with MNA as a remediation strategy, it is prudent to determine (1) level of source zone concentration reduction required to meet site-specific remedial action objectives, and (2) time required for the plume to restabilize and reach the equilibrium COC concentration at a downgradient POC.

Chapelle et al. (2003) present a framework for evaluating time of remediation (TOR) estimates for reaching regulatory compliance using source remediation combined with MNA that is independent of the method of solution. Techniques to predict the COC concentrations in the plume and at the POC over time following partial source removal include both analytical solutions and numerical methods that encompass a range of complexity. Chapelle et al. (2003) divide the TOR problem into related components that include the distance of stabilization (DOS) and time of stabilization (TOS), which are illustrated in Figure 5-2. The DOS component (Figure 5-2A) is designed to determine the target source concentration in groundwater and extends the method proposed by Chapelle and Bradley (1998) by considering more robust methods of solution. The TOS component (Figure 5-2B) addresses the time required for a plume to shrink to the distance specified by site-specific remedial action objectives using the target source concentration calculated in the DOS solution.



**Figure 5-2. Illustration of the method to combine source zone treatment with monitored natural attenuation consisting of two components: (A) distance of stabilization and (B) time of stabilization. Prior to source remediation, contaminant concentration at the point of compliance (POC) exceeds the maximum contaminant level (MCL) in the stable plume. A steady-state model for the pretreatment plume (solid line) is fit to the monitoring well data. The predicted post-treatment plume (dashed line) is designed to meet the MCL at the POC. Time of stabilization is illustrated in the concentration versus time curve at the POC.**

The purpose of this paper is to present a method to determine a time estimate for reaching a remedial action objective using partial contaminant source removal combined with MNA in a groundwater system. A two-dimensional analytical solution of the solute transport equation is employed to simulate the transient response in a plume following source reduction and determine the time to reach a new steady-state concentration. The method is demonstrated at a chlorinated solvent-contaminated site in the U.S. Atlantic Coast Plain in Georgia where groundwater contaminant data at monitoring wells in the source area and at the point of compliance before and after partial source removal are documented over a 6-year period (Chappelle et al. 2005).

### 5.3 Mathematical Model

To illustrate the method a widely-used two-dimensional analytical solution for a reactive solute is utilized (Domenico 1987). Physical mass transport in the aquifer is governed by advection and hydrodynamic dispersion. Mass loss due to natural attenuation is expressed in terms of a lumped-parameter first-order model. Sorption is described using a linear equilibrium isotherm. The governing equation of mass balance for the aqueous-phase COC is

$$D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} - v_x \frac{\partial C}{\partial x} - \lambda C = R \frac{\partial C}{\partial t} \quad (5-1)$$

where  $C$  is the solute concentration [ $M/L^3$ ];  $x$  is distance in the longitudinal direction [ $L$ ];  $y$  is distance in the transverse direction [ $L$ ];  $t$  is time [ $T$ ];  $D_x$  and  $D_y$  are the longitudinal and transverse hydrodynamic dispersion coefficients [ $L^2/T$ ], respectively;  $v_x$  is the groundwater velocity [ $L/T$ ];  $\lambda$  is the first-order decay rate [ $T^{-1}$ ]; and  $R$  is the retardation factor [-].

A number of simplifying assumptions are evident in the mathematical model and analytical solution selected to illustrate the method. While these assumptions are not necessary to implement the method, it is prudent to describe the limitations of the solution. Groundwater flow is uniform, steady, and unidirectional. Molecular diffusion is assumed negligible relative to hydrodynamic dispersion so that  $D_x = \alpha_x v_x$  and  $D_y = \alpha_y v_x$  where  $\alpha_x$  and  $\alpha_y$  are longitudinal and transverse dispersivities [ $L$ ], respectively. The two-dimensional geometry of the problem implies that vertical dispersion is negligible or that the solute concentration is uniformly distributed with depth. In cases where microbial processes primarily control attenuation of a plume, the first-order model suggests that biodegradation is not limited by a second species (i.e., an electron donor in the case of reductive dechlorination of chlorinated solvents) and that the half-saturation constant  $\gg C$ . The biodegradation rate constant ( $\lambda$ ) does not vary along the flow path between the contaminant source and the POC, and other input parameters are constant over space and time.

The Domenico (1987) solution applies to a semi-infinite domain (Figure 5-1) with a uniform zero concentration as the initial condition. A finite source of width  $Y$  and uniform concentration

$(C_o)$  is fixed along the  $y$  axis at the influent boundary and is assumed to be constant with time before remediation. The source and remaining boundary conditions are

$$\begin{aligned}
 C(0, y, t) &= C_o & -Y/2 \leq y \leq Y/2 \\
 &= 0 & \text{otherwise} \\
 \frac{\partial C}{\partial x} \Big|_{x \rightarrow \infty} &= 0 \\
 \frac{\partial C}{\partial y} \Big|_{y \rightarrow \pm\infty} &= 0
 \end{aligned} \tag{5-2}$$

### 5.3.1 Transient Solution

The solution to Equation (5-1) subject to the specified boundary conditions and a uniform zero concentration initial condition is

$$\begin{aligned}
 C(x, y, t) &= \frac{C_o}{4} \left( \exp \left\{ \left( \frac{x}{2\alpha_x} \right) \left[ 1 - \left( 1 + \frac{4\lambda\alpha_x}{v_x} \right)^{0.5} \right] \right\} \operatorname{erfc} \left[ \frac{x - v_c t (1 + 4\lambda\alpha_x / v_x)^{0.5}}{2(\alpha_x v_c t)^{0.5}} \right] \right. \\
 &\quad \left. + \exp \left\{ \left( \frac{x}{2\alpha_x} \right) \left[ 1 + \left( 1 + \frac{4\lambda\alpha_x}{v_x} \right)^{0.5} \right] \right\} \operatorname{erfc} \left[ \frac{x + v_c t (1 + 4\lambda\alpha_x / v_x)^{0.5}}{2(\alpha_x v_c t)^{0.5}} \right] \right) \\
 &\quad \left\{ \operatorname{erf} \left[ \frac{y + Y/2}{2(\alpha_y x)^{0.5}} \right] - \operatorname{erf} \left[ \frac{y - Y/2}{2(\alpha_y x)^{0.5}} \right] \right\}
 \end{aligned} \tag{5-3}$$

where  $v_c$  is the contaminant velocity  $[L/T] = v/R$ . Equation (5-4) describes the contaminant concentration profile along the plume centerline

$$C(x,0,t) = \frac{C_o}{2} \left( \begin{aligned} &\exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_x}\right)^{0.5}\right]\right\} \operatorname{erfc}\left[\frac{x - v_c t \left(1 + 4\lambda\alpha_x/v_x\right)^{0.5}}{2(\alpha_x v_c t)^{0.5}}\right] \\ &+ \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 + \left(1 + \frac{4\lambda\alpha_x}{v_x}\right)^{0.5}\right]\right\} \operatorname{erfc}\left[\frac{x + v_c t \left(1 + 4\lambda\alpha_x/v_x\right)^{0.5}}{2(\alpha_x v_c t)^{0.5}}\right] \end{aligned} \right) \left\{ \operatorname{erf}\left[\frac{Y}{4(\alpha_y x)^{0.5}}\right] \right\} \quad (5-4)$$

### 5.3.2 Steady-State Solution

When the contaminant plume reaches stability or as  $t \rightarrow \infty$ ,  $\partial C/\partial t = 0$  in Equation (5-1) and the steady-state solution is applicable so that Equation (5-3) and Equation (5-4), respectively, may be written as

$$C(x,y) = \frac{C_o}{2} \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_x}\right)^{0.5}\right]\right\} \left\{ \operatorname{erf}\left[\frac{y + Y/2}{2(\alpha_y x)^{0.5}}\right] - \operatorname{erf}\left[\frac{y - Y/2}{2(\alpha_y x)^{0.5}}\right] \right\} \quad (5-5)$$

$$C(x,0) = C_o \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_x}\right)^{0.5}\right]\right\} \left\{ \operatorname{erf}\left[\frac{Y}{4(\alpha_y x)^{0.5}}\right] \right\} \quad (5-6)$$

Equation (5-6) may be expressed in terms of the natural attenuation capacity (NAC) presented in Chapelle and Bradley (1998)

$$C(x,0) = C_o \exp\left\{- (NAC)x\right\} \left\{ \operatorname{erf}\left[\frac{Y}{4(\alpha_y x)^{0.5}}\right] \right\} \quad (5-7)$$

$$\text{where } NAC = \frac{-v_x + \sqrt{v_x^2 + 4D_x\lambda}}{2D_x} \quad [L^{-1}].$$

### 5.4 Solution for Source-Area Engineered Remedial Action

The method of superposition (Van Genuchten 1981) may be employed to simulate the effects of concentration reduction at the source due to an ERA. The superposition approach is not

dependent on the plume first reaching stability, but for simplicity in illustrating the method, the steady-state solution is assumed to be applicable to describe concentrations in the pretreatment plume. The total decrease in the source concentration ( $\Delta C_o$ ) may be implemented over time using a series of sequential steps or may be implemented as an instantaneous decrease which occurs at time  $t = t_o$ . The solution for  $t > t_o$  is written using the latter approach as

$$\begin{aligned}
C(x, y, t) = & \frac{C_o}{2} \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_x}\right)^{0.5}\right]\right\} \left\{ \operatorname{erf}\left[\frac{y + Y/2}{2(\alpha_{yx})^{0.5}}\right] - \operatorname{erf}\left[\frac{y - Y/2}{2(\alpha_{yx})^{0.5}}\right] \right\} \\
- \frac{\Delta C_o}{4} & \left( \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v_x}\right)^{0.5}\right]\right\} \operatorname{erfc}\left[\frac{x - v_c(t - t_o)(1 + 4\lambda\alpha_x/v_x)^{0.5}}{2\sqrt{\alpha_x v_c(t - t_o)}}\right] \right. \\
& \left. + \exp\left\{\left(\frac{x}{2\alpha_x}\right)\left[1 + \left(1 + \frac{4\lambda\alpha_x}{v_x}\right)^{0.5}\right]\right\} \operatorname{erfc}\left[\frac{x + v_c(t - t_o)(1 + 4\lambda\alpha_x/v_x)^{0.5}}{2\sqrt{\alpha_x v_c(t - t_o)}}\right] \right) \\
& \left\{ \operatorname{erf}\left[\frac{y + Y/2}{2(\alpha_{yx})^{0.5}}\right] - \operatorname{erf}\left[\frac{y - Y/2}{2(\alpha_{yx})^{0.5}}\right] \right\} \tag{5-8}
\end{aligned}$$

where  $t$  is the time measured from the point in time when contaminant mass first enters the aquifer.

Equation (5-8) is the difference between the steady-state solution (Equation (5-5)) and the general solution (Equation (5-3)) evaluated at  $t \geq t_o$ . Because it is practical to measure time relative to completion of the ERA, the term  $(t - t_o)$  is replaced with a single term  $(t^*)$  which is time measured from the instantaneous decrease in the source concentration. An inherent assumption in this solution is that the *NAC*, source dimensions, and transverse dispersivity do not significantly change following the source area ERA. Equation (5-9) describes the transient concentration profile along the plume centerline for  $t^* > 0$  (i.e.,  $t > t_o$ )

$$\begin{aligned}
C(x,0,t^*) = C_o \exp\{-(NAC)x\} & \left\{ \operatorname{erf} \left[ \frac{Y}{4(\alpha_y x)^{0.5}} \right] \right\} \\
- \frac{\Delta C_o}{2} & \left( \exp \left\{ \left( \frac{x}{2\alpha_x} \right) \left[ 1 - \left( 1 + \frac{4\lambda\alpha_x}{v_x} \right)^{0.5} \right] \right\} \operatorname{erfc} \left[ \frac{x - v_c t^* (1 + 4\lambda\alpha_x / v_x)^{0.5}}{2\sqrt{\alpha_x v_c t^*}} \right] \right. \\
& \left. + \exp \left\{ \left( \frac{x}{2\alpha_x} \right) \left[ 1 + \left( 1 + \frac{4\lambda\alpha_x}{v_x} \right)^{0.5} \right] \right\} \operatorname{erfc} \left[ \frac{x + v_c t^* (1 + 4\lambda\alpha_x / v_x)^{0.5}}{2\sqrt{\alpha_x v_c t^*}} \right] \right) \\
& \left\{ \operatorname{erf} \left[ \frac{Y}{4(\alpha_y x)^{0.5}} \right] \right\}
\end{aligned} \tag{5-9}$$

#### 5.4.1 Reduction in Source-Area Concentration

The objective of the DOS component of the time of remediation framework presented in Chapelle et al. (2003) is to determine the target source area concentration ( $C_o^{\text{Rem}}$ ) to meet the regulatory-required concentration at a prescribed distance ( $L$ ) downgradient of the source along the plume centerline. The steady-state solution (Equation (5-6)) at  $x = L$  is set equal to the compliance concentration (e.g., MCL)

$$C(L,0) = C_o^{\text{Rem}} f(L) = MCL \tag{5-10}$$

$$\text{where } f(L) = \exp\{-(NAC)L\} \left\{ \operatorname{erf} \left[ \frac{Y}{4(\alpha_y L)^{0.5}} \right] \right\}$$

The target  $\Delta C_o$  is found by replacing  $C_o^{\text{Rem}}$  with  $(C_o - \Delta C_o)$  in Equation (5-10), so that

$$\Delta C_o = C_o - (MCL)f(L)^{-1} \tag{5-11}$$

By solving Equation (5-7) for the case where  $x = L$  and substituting  $C_o/C(L,0)$  for the term  $f(L)$  in Equation (5-11), a simplified expression for the target decrease in the source concentration ( $\Delta C_o$ ) is



$$\Delta C_o = C_o \left( 1 - \frac{MCL}{C_L^{ss}} \right) \quad (5-12)$$

where  $C_L^{ss}$  is the steady-state concentration at the POC prior to the ERA. This result suggests that the target  $\Delta C_o$  is independent of the dimensionality of the problem and that it is directly proportional to the regulatory-required concentration at the POC.

### 5.4.2 Time of Stabilization

Because the objective of the TOS component is to determine the time required to reach the compliance concentration at  $x = L$  after the ERA is completed and the source concentration is reduced, it is useful to derive a general expression for time. Equation (5-9) is simplified by noting that as  $t$  increases, the term

$$\exp \left\{ \left( \frac{x}{2\alpha_x} \right) \left[ 1 + \left( 1 + \frac{4\lambda\alpha_x}{v_x} \right)^{0.5} \right] \right\} \operatorname{erfc} \left[ \frac{x + v_c t^* (1 + 4\lambda\alpha_x / v_x)^{0.5}}{2\sqrt{\alpha_x v_c t^*}} \right] \rightarrow 0$$

and rearranged in the following form

$$\operatorname{erfc} \left[ \frac{L - v_c t^* (1 + 4\lambda\alpha_x / v_x)^{0.5}}{2\sqrt{\alpha_x v_c t^*}} \right] = \operatorname{erfc} \left[ \frac{1 - T \sqrt{1 + \frac{4\lambda\tau\alpha_x}{R L}}}{\sqrt{4T \frac{\alpha_x}{L}}} \right] = 2(1 - C^*) \quad (5-13)$$

where  $T = \text{dimensionless time} = t^* / \tau$ , in which  $\tau$  is the travel time from source to POC;  $C^* = \text{dimensionless concentration at the POC} = (C_L(t^*) - MCL) / (C_L^{ss} - MCL)$ . Immediately after the ERA is completed (i.e.,  $T \approx 0$ ), the downgradient plume remains at the initial steady-state concentration distribution and the COC concentration at the POC is  $C_L(t^*) = C_L^{ss}$  so that  $C^* = 1$ . One metric to establish when the effect of the source zone treatment will reach the prescribed distance ( $x = L$ ) is when 50% of the predicted decrease in concentration at POC is observed, so that  $C_L(t^*) = \frac{1}{2}(C_L^{ss} + MCL)$  and  $C^* = 0.5$ .

The time of stabilization ( $t_s$ ) occurs when the compliance concentration is reached at the POC; mathematically when  $C^* = 0$  and the  $erfc$  term = 2. However, the accuracy of the  $t_s$  estimate is dependent on the desired maximum relative error between the approximation concentration and the compliance concentration. Solving Equation (5-13) for  $C^*$ , substituting into the expression for  $C^*$ , and rearranging the expression to solve for  $(C_L(t^*)/MCL)-1$  yields

$$\left(\frac{C_L(t_s^*)}{MCL}-1\right)=\left(1-\frac{erfc(Z)}{2}\right)\left(\frac{C_L^{ss}}{MCL}-1\right) \quad (5-14)$$

$$\text{where } Z = \frac{1-T_s \sqrt{1+\frac{4\lambda\tau\alpha_x}{R L}}}{\sqrt{4T_s \frac{\alpha_x}{L}}} \quad (5-15)$$

An estimate of the time of stabilization in dimensionless form ( $T_s$ ) is found by direct solution of Equation (5-15)

$$T_s = \frac{(2\beta_1 + Z^2\beta_2) + \sqrt{(2\beta_1 + Z^2\beta_2)^2 - 4\beta_1^2}}{2\beta_1^2} \quad (5-16)$$

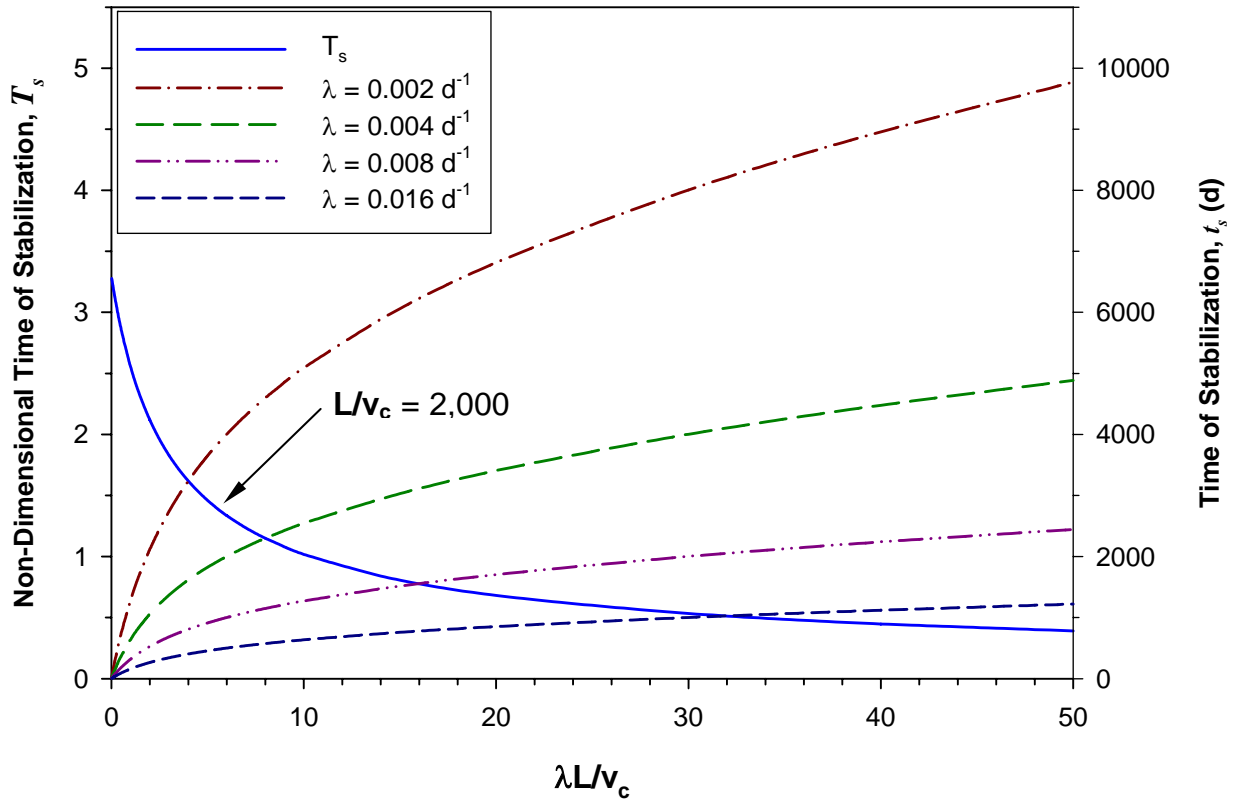
$$\text{where } \beta_1 = \sqrt{1 + \frac{4\lambda\tau\alpha_x}{R L}} \quad \text{and} \quad \beta_2 = \sqrt{4\frac{\alpha_x}{L}}$$

The time of stabilization ( $t_s$ ) is calculated as the product of the dimensionless time of stabilization and the travel time

$$t_s = T_s \tau = T_s \left(\frac{L}{v_c}\right) \quad (5-17)$$

Figure 5-3 shows a plot of  $T_s$  versus the Damköhler number ( $\lambda\tau/R$ ) using Equation (5-16) and time of stabilization ( $t_s$ ) using Equation (5-17) for the case where  $\alpha_x/L = 0.05$ . A reasonable approximation of  $t_s$  occurs when  $C^* = 0.005455$  and  $erfc$  term = 1.989, which corresponds with  $Z = -1.8$ . For a given Damköhler number larger estimates of the time of stabilization are expected for decreasing values of the degradation constant. Variability in the estimated time of stabilization with travel time is represented in the plot of  $T_s$ , which corresponds to a travel time

of 2,000 d when  $R = 1.0$ . Curves for travel times  $< 2,000$  d would fall below the solid curve, and curves for larger travel times would fall above and to the upper right-hand corner of the plot.



**Figure 5-3. Non-dimensional time of stabilization ( $T_s$ ) as a function of the Damköhler number ( $\lambda L/v_c$ ) and time of stabilization ( $t_s$ ) calculated for four first-order decay coefficients.**

The accuracy of this approximation is dependent on the magnitude of the starting steady-state concentration at the POC ( $C_L^{ss}$ ) prior to the ERA. Setting the expression for  $C^*$  equal to 0.005455 and rearranging the expression to solve for  $C_L(t^*)/MCL$  yields

$$\frac{C_L(t_s^*)}{MCL} = 1 + 0.005455 \left( \frac{C_L^{ss}}{MCL} - 1 \right) \quad (5-18)$$

where  $C_L(t_s^*)/MCL$  represents the ratio of the approximation to the compliance concentration. For example, using the concentration values shown in Figure 5-2 where  $MCL = 10 \mu\text{g/L}$  and  $C_L^{ss} = 93 \mu\text{g/L}$ , Equation (5-18) predicts a value of  $10.5 \mu\text{g/L}$  for  $C_L(t_s^*)$ . The difference between the

target compliance concentration and approximate value  $C_L(t_s^*)$  is easily within the margin of error for the laboratory analysis of many COCs (0.5  $\mu\text{g/L}$  or 5%). However, if the initial steady-state concentration at the POC is much larger than the target compliance concentration, larger disagreement between the target and predicted concentration using the approximation can be expected (e.g., for  $100 \leq C_L^{ss} / MCL \leq 1,000$ , then  $1.54 \leq C_L(t_s^*) / MCL \leq 6.45$ ).

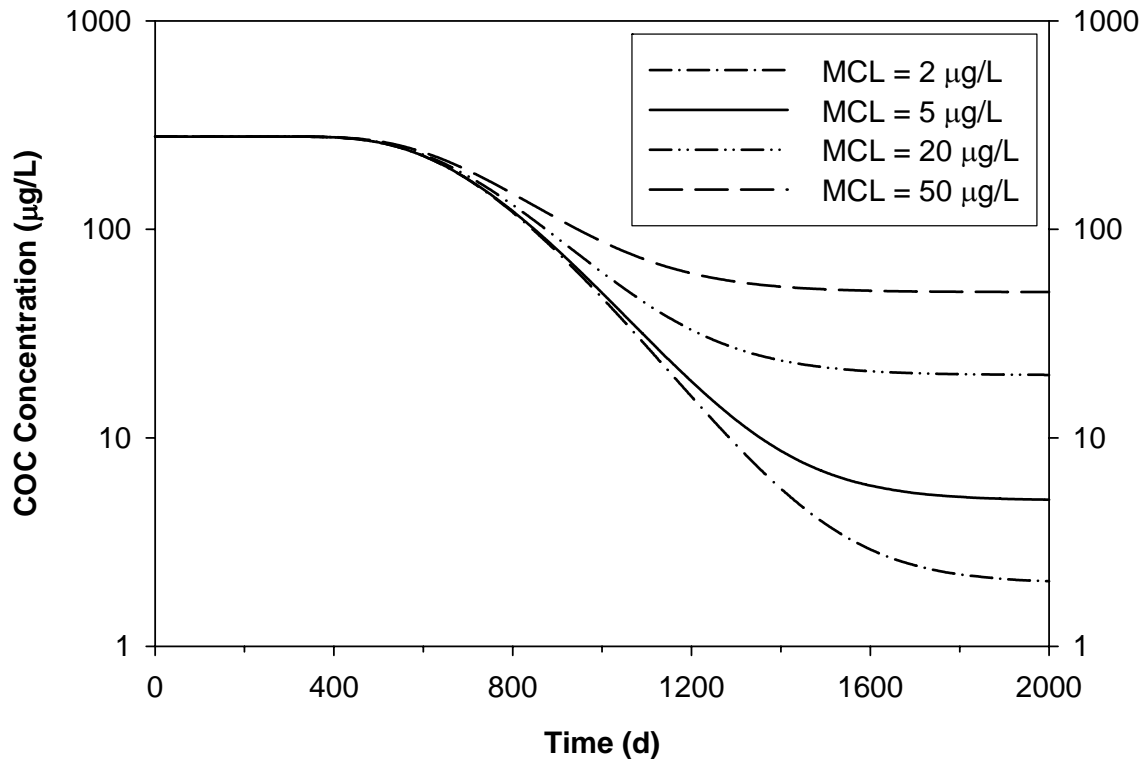
## 5.5 Results and Discussion

### 5.5.1 Example Application and Parameter Sensitivity

To illustrate the method a hypothetical problem is presented using parameters listed in Table 5-1. A stable plume is 270-m long, as defined by a COC concentration of 5  $\mu\text{g/L}$ . The source is 25-m wide with a pre-remediation concentration of 5,000  $\mu\text{g/L}$ . The groundwater velocity is 0.15 m/d, and the contaminant velocity is 0.10 m/d. The first-order decay coefficient is 0.0045  $\text{d}^{-1}$ , and longitudinal and transverse dispersivities are 5.0 and 0.5 m, respectively. At the POC ( $L = 100$  m), the COC concentration is 280  $\mu\text{g/L}$ . The required decrease in the source concentration is shown in Table 5-1 for four specified values (MCL) of the COC compliance concentration. The concentration at the POC at the estimated time of stabilization ( $t_s = 1,527$  d) is also listed. Figure 5-4 shows the predicted COC concentration versus time at the POC for the four target compliance concentrations (MCL = 2, 5, 20, and 50  $\mu\text{g/L}$ ).

**Table 5-1. Summary of Results for the Hypothetical Example**

MCL ( $\mu\text{g/L}$ )	$\Delta C_o$ ( $\mu\text{g/L}$ ) <sup>a</sup>	$C_L(t_s)$ ( $\mu\text{g/L}$ ) <sup>b</sup>
2	36	2.7
5	90	5.7
20	359	20.6
50	897	50.6
Calculated using Equations (5-11) <sup>a</sup> and (5-9) <sup>b</sup>		



**Figure 5-4. Predicted concentration versus time following partial source area removal at a specified distance ( $L = 100$  m) downgradient for four compliance concentrations (e.g., maximum contaminant level, MCL).**

The example illustrates that the time of stabilization calculation is independent of the specified MCL and the source concentration reduction. For the chosen parameters and for all four target MCLs, the concentrations at the POC calculated at the estimated the time of stabilization resulted in reasonable estimates for the MCL (Table 5-1). However, an increasing level of  $\Delta C_o$  is required with increasingly stringent concentration-based remedial action objectives at the POC.

An elementary analysis of parameter sensitivity reveals that the contaminant velocity has the greatest impact on the time of stabilization. This is illustrated by applying the method to the example above beginning with the pretreatment steady-state contaminant plume. Prior to source remediation, the first-order decay coefficient may be determined using the method of Zhang and Heathcote (2003) which is based on calculated or estimated values of the groundwater velocity and the longitudinal dispersivity. Table 5-2 shows the range in results for the first-order decay

coefficient and the time of stabilization, using Equation (5-16) and Equation (5-17) for the latter, for a range of groundwater velocity values ( $0.050 \leq v \leq 0.45$  m/d) and a retardation factor of 1.5. These results show that the estimate for the time of stabilization is indirectly proportional to the contaminant velocity when the ratio of the first-order decay coefficient to the groundwater velocity is held constant. The implication of this result suggests that detailed field characterization of groundwater velocity and sorption parameters will reduce uncertainty in the outcome for the time required to meet site remedial action objectives at the downgradient POC.

**Table 5-2. Sensitivity of Time of Stabilization to Velocity**

$v$ (m/d)	$\lambda$ (d <sup>-1</sup> )	$t_s$ (d)
0.050	0.0015	4582
0.075	0.0023	3055
0.15	0.0045	1527
0.30	0.0090	764
0.45	0.0135	509

### 5.5.2 Site Application

Application of the method using the 2D analytical solution is presented at a documented site where source zone treatment combined with MNA resulted in the reduction in the length and concentrations of a chlorinated ethene plume. The modeling objective is to simulate the transient response in the concentration of the total chlorinated ethenes at two downgradient monitoring wells (KBA-13A and USGS-5) following source zone treatment and address model uncertainty. In each case, results using the initial estimated contaminant velocities are shown along with results where the groundwater velocity was determined through analysis of a tracer (sulfate) breakthrough curve at the two monitoring wells. Calibration to the field data is assessed using the root mean of squared residual errors (*RMS*) defined in Zheng and Bennett (2002).

Chapelle et al. (2005) describe a 6-yr post-treatment monitoring program at a former 25-acre landfill located at a U.S. Navy facility in the Atlantic Coastal Plain adjacent to the Atlantic Ocean. Additional monitoring data is presented for the eight sampling events in 2005-2007. Beginning in the mid-1970s, municipal waste from the local community and the base were disposed of in the landfill along with the unregulated disposal of tetrachloroethene (PCE). A detailed description of the site hydrogeology is described previously in Chapelle and Bradley (1998) and Chapelle et al. (2005). Monitoring wells (Figure 5-5) were installed in a permeable sand layer of the surficial aquifer located 10-13 m below land surface. Groundwater flow in the northwest direction resulted in a 190-m-long plume of PCE and degradation products including trichloroethene (TCE), dichloroethene (DCE), and vinyl chloride (VC). Microbially-mediated degradation in the organic-rich, anaerobic aquifer is attributed to reductive dechlorination of PCE and TCE and reductive dechlorination combined with direct oxidation of *cis*-DCE and VC (Chapelle and Bradley 1998). Because concentrations of VC and *cis*-DCE exceeded MCLs at and beyond the facility boundary, an investigation of an ERA was implemented in the mid-1990s with pumping wells as an interim measure for hydraulic control of the plume.

Direct-push sampling in the suspected source zone detected two adjacent sources of PCE in the vicinity of well KBA-34 where the historically-highest concentrations of PCE (3,500 – 9074 µg/L) were detected (Chapelle and Bradley 1998). A remediation strategy was implemented to shrink the size of the chlorinated ethane plume to achieve regulatory compliance at the facility boundary by combining partial source removal with MNA. A target concentration of 100 µg/L (total chlorinated ethenes) at the source zone monitoring well was determined based on the NAC of the aquifer (Chapelle and Bradley 1998). Chemical oxidation using Fenton's reagent was implemented in the source area between December 1998 to November 2001 to reduce the contaminant concentration below the target level, and emulsified vegetable oil was injected to promote microbial activity and subsequent reductive dechlorination of the remaining chlorinated ethenes.

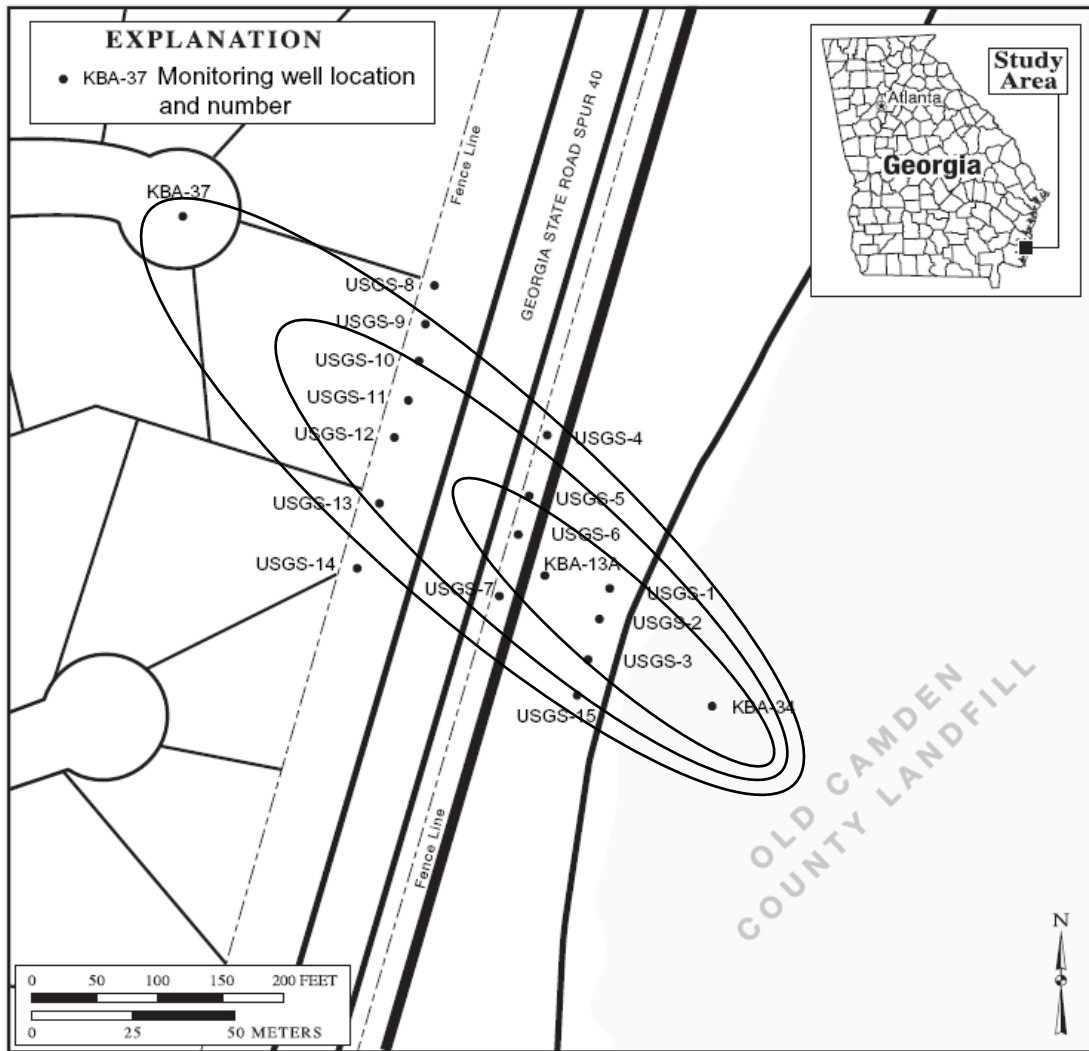


Figure 5-5. Location of monitoring wells and approximate extent of the pretreatment chlorinated ethane plume at Naval Submarine Base Kings Bay, Site 11, Camden County, Georgia.

### 5.5.3 Initial Parameter Estimation

Prior to source treatment, Chapelle and Bradley (1998) estimate the range in the groundwater velocity (0.072 to 0.23 m/d) using Darcy's Law and using the range in field-measured hydraulic conductivity, horizontal hydraulic gradient (0.006), and an estimate of effective porosity (0.25). Retardation factors for PCE, TCE, *cis*-DCE, and VC (6.50, 2.90, 1.98, and 1.86, respectively) are calculated based on the fraction of organic carbon (0.0019) and published values of the organic



carbon partition coefficients (364, 126, 65.0, and 57.0 L/kg, respectively). Because PCE rapidly depleted along the groundwater flow path and was absent from the downgradient monitoring wells (KBA-13A and USGS-5) in the pretreatment plume, the range in the estimated composite retardation factor for total chlorinated ethenes is 1.86 to 2.90. The resulting range in the contaminant velocity (0.025 to 0.12 m/d) shows that the maximum and minimum values vary by a factor of 5.

The other parameters are based on the results of the site investigation and the pre-treatment plume. By fitting Equation (5-4) to the pre-treatment steady-state plume, the initial conditions for the simulated results at each well (KBA-13A and USGS-5) are known. The longitudinal dispersivity (7.0 m) is estimated using the method of Xu and Eckstein (1995) and the length of the chlorinated ethene plume. Monitoring data are insufficient to accurately determine the transverse dispersivity, requiring an estimate (0.35 m) assuming  $\alpha_x/\alpha_y = 20:1$ . The range in the first-order decay coefficient (0.0052-0.0165 d<sup>-1</sup>) is calculated using the method of Zhang and Heathcote (2003) for two-dimensional plumes and is found based on the range in the groundwater velocity. The source width (20 m) is based on the results of the source zone investigation.

#### **5.5.4 Well KBA-13A**

Figure 5-6 shows a comparison of observed data at KBA-13A ( $L = 49$  m) with two sets of solutions for the reduction in the total chlorinated ethene concentration versus time; one solution set represents the maximum estimated groundwater velocity (0.23 m/d) using the range of retardation factors (1.89-2.90) and the other represents the initial minimum estimated contaminant velocity range. Results using the initial estimated input parameters show an underestimate of the actual concentration time trend and the time of stabilization (Table 5-3).

A tracer-based value of the groundwater velocity is obtained from the breakthrough curve in the sulfate concentration at KBA-13A presented in Chapelle et al. (2005). A pulse of sulfate was observed in several observation wells resulting from the use of ferrous sulfate with the Fenton's

reagent in the source zone and subsequent transport with the natural gradient. The resulting velocity (0.055 m/d) is simply the travel distance between KBA-34 and KBA-13A divided by the travel time (895 d) to the peak sulfate concentration. The results using the tracer-based velocity estimate in Figure 5-7 and Table 5-3 show improved agreement between the observed and calculated concentration trend when compared to the initial estimates. However, an improved velocity estimate is only available approximately 30 months into the post-source remediation monitoring program because the sulfate breakthrough at KBA-13A was not sufficiently ahead of the decrease in the concentration of total chlorinated ethenes to allow an earlier updated prediction. For the tracer-based velocity a minimum value of RMS is achieved for a contaminant velocity 0.0304; however there is only a slight difference in the results compared to the estimates using  $R = 1.86$ . Using Equation (5-16) and Equation (5-17), the time of stabilization estimate (2,590 d) is consistent with observed concentration data between the source and KBA-13A.

**Table 5-3. Input Parameter and Time of Stabilization for Well KBA-13A**

$v$ (m/d)	$\lambda$ (d <sup>-1</sup> )	$R$	$v_c$ (m/d)	$t_s$ (d)	$RMS$
Initial Max. Est.					
0.23	0.0165	1.86	0.124	610	56
		1.98	0.116	650	53
		2.90	0.079	960	55
Initial Min. Est.					
0.072	0.0052	1.86	0.039	1960	138
		1.98	0.036	2090	135
		2.90	0.025	3060	112
Tracer-based					
0.055	0.0039	1.86	0.029	2590	47
		1.98	0.028	2760	49
		2.90	0.019	4040	86

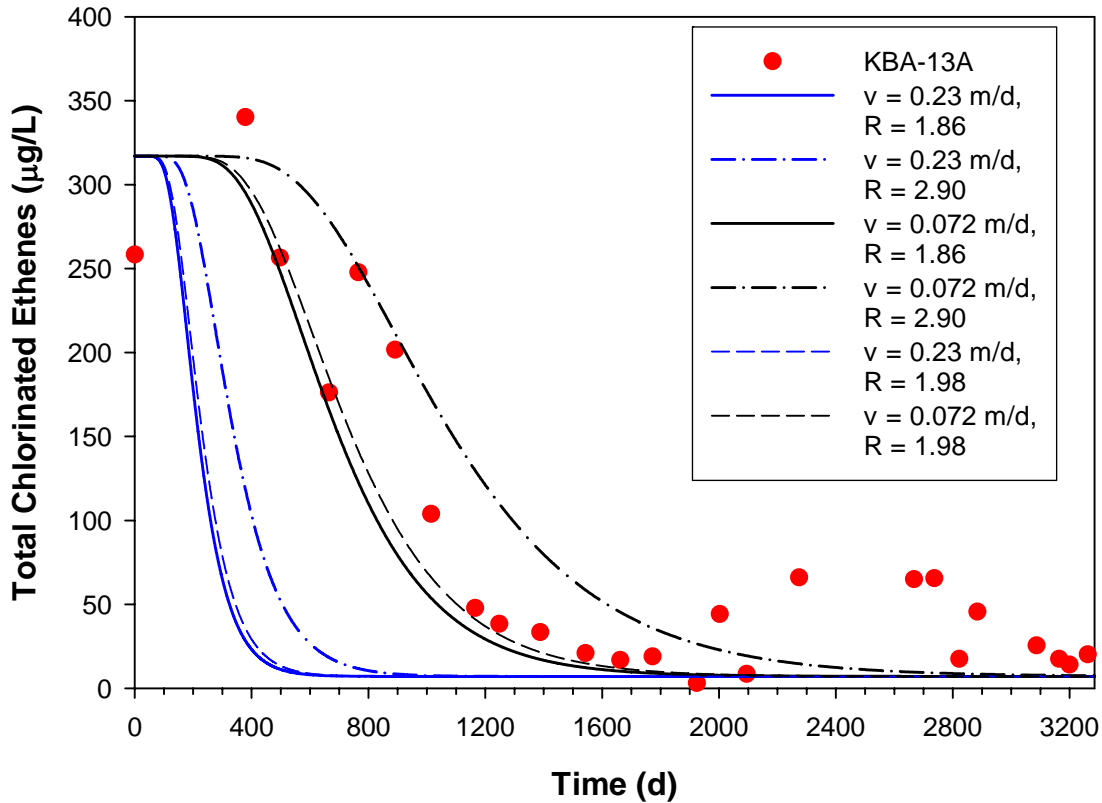
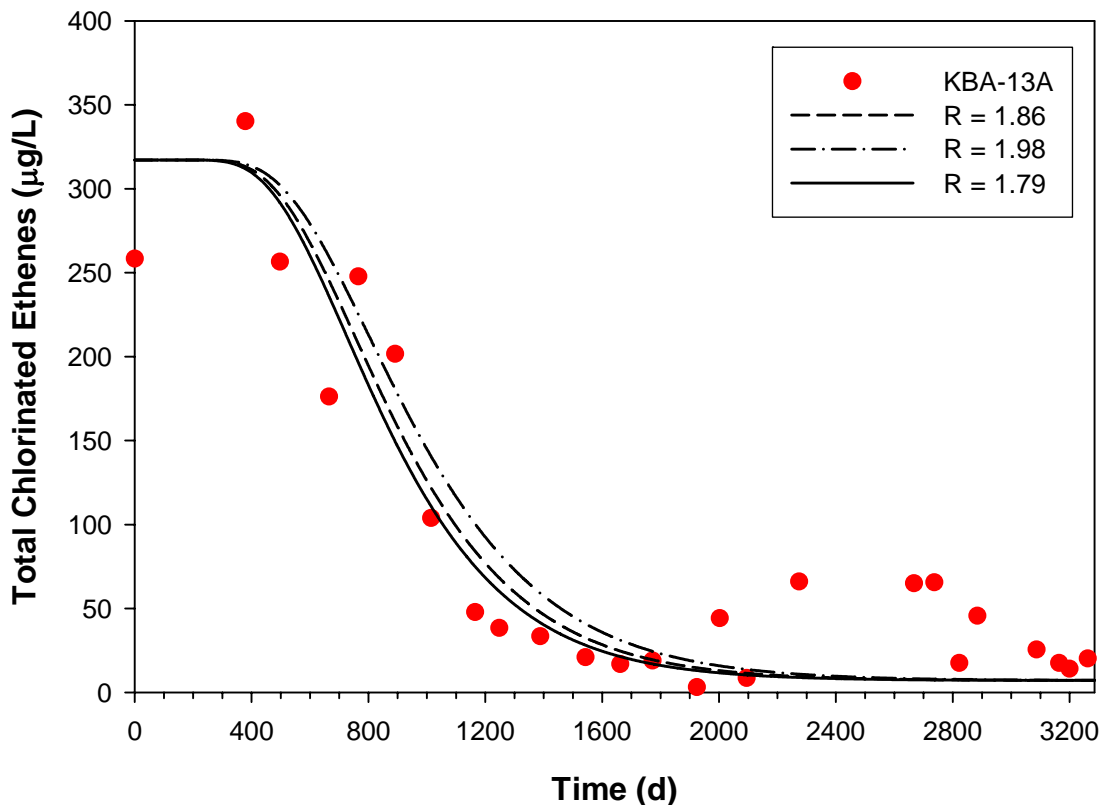


Figure 5-6. Observed (circles) and predicted total chlorinated ethene concentrations at well KBA-13A showing the full range of groundwater velocity and retardation factor values based on initial estimates made prior to the source zone treatment.

### 5.5.5 Well USGS-5

Figure 5-8 shows a comparison of observed data at well USGS-5, which is located further downgradient from the source ( $L = 67$  m), with predicted total chlorinated ethenes concentration for four input parameter sets. Chapelle et al. (2005) note a rapid drop in VC concentrations at well USGS-5 but also a gradual rise over time in *cis*-DCE concentrations, possibly due to the mobilization of contaminants following the source zone ERA. Chapelle et al. (2005) also note that a shift in the chlorinated ethene plume to the south when the pumping wells were turned off in August 1998. Therefore, a change in the magnitude and direction of the groundwater velocity may also be a contributing factor in the rapid initial decrease in the observed VC concentrations at well USGS-5. Regardless of the cause, the concentration of total chlorinated ethenes remains

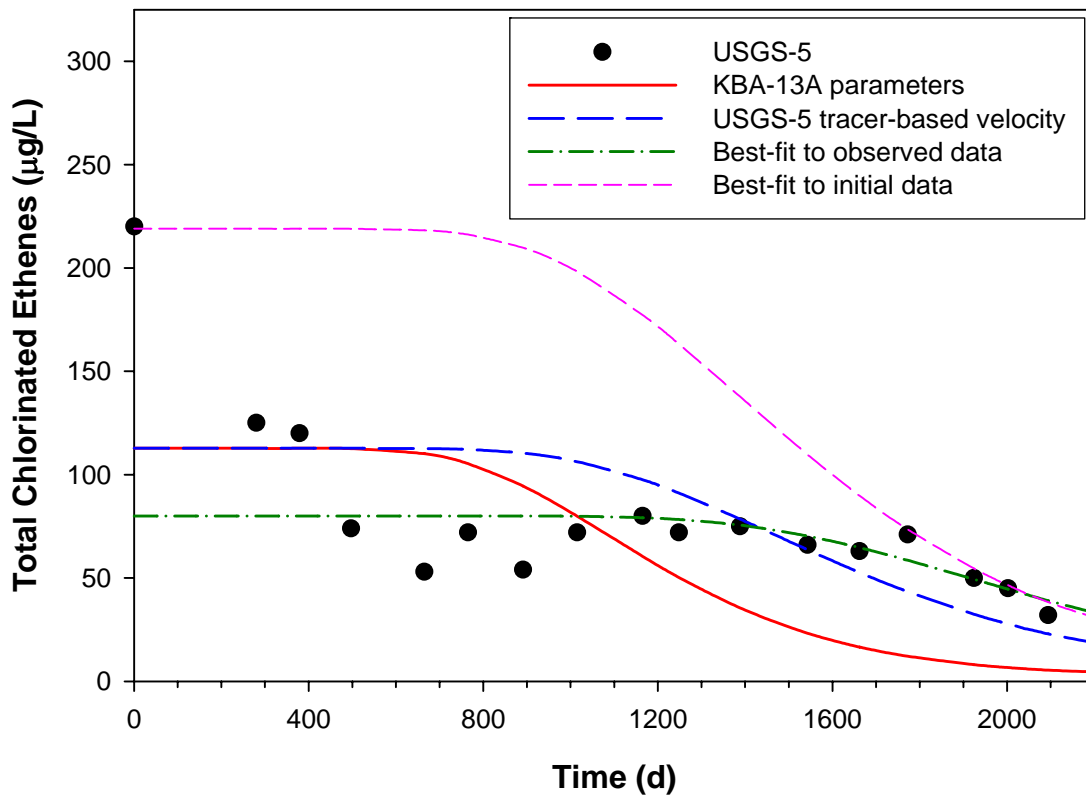
constant after the initial decrease and then begins a sustained decline in concentration beginning approximately 1,400 days following source treatment, reaching 11  $\mu\text{g/L}$  at the end of the 9-year monitoring period.



**Figure 5-7. Observed (circles) and predicted total chlorinated ethene concentrations at well KBA-13A using groundwater velocity ( $v = 0.055$  m/d) determined from the breakthrough of sulfate and the range of retardation factors, including the case ( $R = 2.28$ ) where the residual error is minimized.**

Concentration versus time at USGS-5 simulated with the input parameter set for well KBA-13A clearly fails to represent the observed monitoring data (Figure 5-8). Specifically, the simulated decrease in concentrations begins at  $t \approx 600$  d, well before the start of the observed decline ( $t \approx 1,400$  days), indicating that the simulated contaminant velocity is too large. Analysis of the sulfate breakthrough curve at well USGS-5 resulted in a groundwater velocity of 0.040 m/d. The discrepancy in this result and the tracer-based groundwater velocity at well KBA-13A (0.055 m/d) may reflect the proximity of wells USGS-5 and KBA-13A to the extraction wells and source-area injection wells, respectively. The impact of a reduction in groundwater velocity

caused by cessation of pumping is more likely to impact observations at well USGS-5 relative to well KBA-13A, whereas the impact of a temporal increase in velocity induced by injection of Fenten’s reagent is more likely to be observed at well KBA-13A. An improved match between the observed and simulated concentration reduction over time is noted using lower values of the groundwater velocity (0.040 m/d) and the decay coefficient (0.0029 d<sup>-1</sup>). The latter parameter is modified to maintain the same initial condition (120 µg/L) as the previous case. Time of stabilization estimates are 3,100 and 4,200 days, respectively.



**Figure 5-8. Observed (circles) and predicted total chlorinated ethene concentrations at well USGS-5 for four input parameter sets: (1) best-fit input parameters from Figure 5-7; (2) velocity using tracer breakthrough at USGS-5 (0.040 m/d); (3) best-fit to the complete data set; (4) best-fit to the initial concentration data.**

An additional simulation is presented in Figure 5-8 using the tracer-based groundwater velocity at USGS-5. In this case, the observed concentration at well USGS-5 immediately prior to source treatment (as opposed to a best-fit match of the pretreatment plume) is exactly matched by decreasing the decay coefficient (0.0022 d<sup>-1</sup>) relative to the other simulations. Although the

simulated result does not match the observed concentration data for  $t < 2,600$  days, the latter part of the concentration decline is captured by the solution with the least error relative to other parameter sets. The resulting estimate for time of stabilization is 4,700 days.

## **5.6 Summary and Conclusions**

The time of stabilization solution consists of three components for evaluating remedial action decisions at sites where a combined remedy of source zone reduction and MNA is proposed:

1. An approximate two-dimensional solution for simulating contaminant concentrations in the plume as a function of time at a point of compliance along the plume centerline (Equation (5-9)) or at any monitoring location (Equation (5-8)) following a reduction (either observed or calculated using an exact solution) in the source zone concentration,
2. An exact solution (Equation (5-11) or Equation (5-12)) for calculating the level of reduction in the source zone aqueous-phase contaminant concentration required to achieve a groundwater-based remedial action objective at a downgradient point of compliance when the plume returns to a steady-state condition, and
3. An approximate solution (Equation (5-16) and Equation (5-17)) for estimating the time required to achieve a RAO at a downgradient point of compliance following source zone treatment.

Application of the method to simulate post-treatment data from monitoring wells located downgradient of a chlorinated solvent source zone provides evidence that reasonable results can be expected when uncertainty associated with contaminant velocity and attenuation rates is reduced. Results based on tracer-based velocity estimates show significant improvement and reduction of error compared to estimates derived from hydrogeologic parameters. The best agreement between observed and simulated data occurs at well KBA-13A, which is the closest monitoring well to the source zone, but the solution is much less effective in simulating the temporal fluctuations in the total chlorinated ethene concentrations observed at well USGS-5. The difference in agreement is believed to be related to the changes in the groundwater velocity

field and mobilization of contaminants following source zone treatment, but may also be influenced by differences in redox conditions observed at the wells. Specifically, Chapelle and Bradley (1998) note a transition between sulfate- and iron-reducing conditions along the groundwater flow path that occurs between wells KBA-13A and USGS-5.

The advantage of this approach is the simplicity of implementation, which is facilitated through a recently-developed screening/simulation tool – Natural Attenuation Software (Chapelle et al. 2003; Mendez et al. 2004). Application of the method to sites in a predictive mode can enable site decision-makers to assess the sensitivity of model input parameters on time of stabilization estimates and assist in directing the collection of additional data to determine parameters and reduce model uncertainty *a priori*. However, the solution does not determine the outcome of any specific remediation technology on the source concentration. Numerical models that incorporate more detailed mathematical expressions for microbially-based attenuation of chlorinated ethenes (Widdowson 2004) and non-uniform velocity fields caused by variability in hydrogeologic parameters may be warranted to simulate the complexities in natural attenuation.

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## **6 Evaluating the Capabilities of the Natural Attenuation Software (NAS) - Lessons Learned**

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### **6.1 Abstract**

This paper reports the lessons learned from a Department of Defense (DoD), Environmental Security Technology Certification Program (ESTCP) demonstration and validation of the Natural Attenuation Software (NAS) and its methodology (Chapelle et al. 2003; Mendez et al. 2004; Widdowson et al. 2007). The objective of the demonstration was to evaluate the NAS software capability to provide reasonable estimates of MNA cleanup timeframes in a variety of environments and sites throughout the United States. This paper will focus on the distance/time of stabilization (DOS/TOS) feature of NAS reported in the demonstration. The DOS/TOS feature was evaluated by using data from four sites with long-term monitoring data that encompass diverse geologic and hydrogeochemical environments and various engineered remedial actions (ERA). Results were judged based on accuracy, versatility, reliability, and applicability. Overall, the DOS/TOS feature was satisfactory in meeting quantitative and qualitative performance objectives based on the match between NAS and the data inflection points and concentration versus time slopes, respectively. NAS was effective in predicting the time of stabilization of concentrations at monitoring wells located relatively close to the source (up to 700 ft downgradient) following source remediation and a subsequent reduction in groundwater contaminant concentrations in the source zone. Factors affecting the degree of accuracy were reflected in the uncertainty associated with the contaminant velocity estimates and source characteristics (width and concentration) following remediation.

### **6.2 Introduction**

Remedial actions at Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sites must be protective of human health and the environment and comply with

applicable or relevant and appropriate requirements (ARAR) (USEPA 1988). Drinking water standards provide relevant and appropriate cleanup levels for ground waters that are a current or potential source of drinking water. Drinking water standards include federal maximum contaminant levels (MCL) and/or non-zero maximum contaminant level goals (MCLG) established under the Safe Drinking Water Act (SDWA), or more stringent state drinking water standards. Under suitable conditions, monitored natural attenuation (MNA) can be a cost-effective strategy for restoring contaminated aquifer systems either as a stand-alone technology or in combination with other engineered remedial actions. However, USEPA guidance specifically requires MNA to achieve site-specific cleanup objectives within a reasonable time frame (USEPA 1999). Thus, selection of MNA as a remedy for cleanup of hazardous substances requires that estimates of time of cleanup be made to assess its feasibility as a remedy.

In response, the Natural Attenuation Software (NAS) was co-developed by the Naval Facilities Engineering Command (NAVFAC), U.S. Geological Survey (USGS), and Virginia Tech. NAS is a screening tool designed for estimating time of remediation (TOR) for MNA with varying degrees of source area remediation. Conventional screening tools for MNA are not designed to address source zone remediation options or simulation of plume reduction. NAS consists of a combination of computational tools implemented in three main interactive modules to provide estimates for: (1) target source concentration required for a plume extent to contract to regulatory limits, (2) time required for contaminants in the source area to attenuate to a predetermined target source concentration, and (3) time required for a plume extent to contract to regulatory limits after source reduction. Natural attenuation processes that NAS models include advection, dispersion, sorption, non-aqueous phase liquid (NAPL) dissolution, and biodegradation of petroleum hydrocarbons, chlorinated solvents, or any user-specified contaminants or mixtures.

The objective of the DoD ESTCP demonstration was to evaluate the capability of the NAS software to provide reasonable estimates of MNA cleanup timeframes in a variety of environments and sites throughout the United States. The tool is evaluated by using data from multiple sites with long-term monitoring data that encompass diverse geologic and

hydrogeochemical environments and different remediation options. Criteria for site selection included (1) high-quality, long-term ground-water monitoring data and (2) long-term decline in contaminant concentrations in source-area monitoring wells following source remediation. An evaluation of predictions based on pre-remediation site data is used to make assessments of the utility of the estimates. This paper focuses on the distance/time of stabilization (DOS/TOS) feature of NAS reported in the demonstration.

## **6.3 Demonstration Design**

### **6.3.1 Selection of Test Sites**

Extensive verification testing of NAS was performed using data from sites with (1) differing hydrogeologic conditions and (2) various methods of source remediation. The criteria and requirements for site selection reflect these two needs. In addition, sites were screened to eliminate sites that do not include (1) high-quality data sets and (2) long-term decline in contaminant ground water concentrations following source remediation.

Although NAS is ideally suited for sites that have wells near the source and along the center line of the plume coupled with relatively simple hydrogeologic conditions, it was viewed as useful to select some sites with non-ideal conditions. The notion was not to set up the demonstration for failure but to test the limits of the software and assess how robust the solutions are in relation to the performance objectives. For example, at some sites the monitoring infrastructure and sample data resulting from characterization efforts were not specifically aimed at demonstrating MNA lines of evidence or lacked the detail for a comprehensive modeling effort. The conceptual models at some sites were not based on a simple homogeneous unconsolidated aquifer as the site data was indicative of more complex hydrogeologic conditions. Therefore, some of the sites selected for the demonstration exhibited a few non-ideal characteristics.

Desired site characteristics included:

- Five years of annual monitoring data that includes both the geochemical and contaminant chemistry, and water levels

- Appropriate geochemical data that allows for assessment of the plume status in an electron acceptor distribution framework
- Ground water velocities exceeding 5 ft/year
- Darcy flow (i.e., not conduit flow such as Karst)
- Unidirectional ground water flow fields and boundary conditions that can be reasonably simulated by the analytical code

Site data sets were screened so that sites where contaminant concentrations did not decline were removed from consideration. Specifically, data from the demonstration sites exhibited either natural depletion of source zones over times or a declining trend in contaminant concentration at downgradient wells following a source-area ERA. Allowance was made for noise in the data and/or variation indicative of sampling or other issues that cannot be sufficiently incorporated into the solution.

Candidate sites were screened based on the availability of redox indicator data collected in accordance with EPA/DoD protocols for MNA (USEPA 1998). Ideal sites included annually-collected geochemical data that enabled determination of predominate terminal electron accepting processes and the spatial distribution of dominating redox conditions using NAS. Minimally, dissolved oxygen (DO), sulfate, and ferrous iron data were necessary. The geochemical data were examined for potential errors associated with sample collection that may have inadvertently altered the chemistry. For example, DO that exceeds the solubility of ground water in the aquifer may have been aerated during sample collection.

Ground water velocities and travel times must be sufficient to measure changes over time relative to the period of time for which monitoring data has been collected. Lower contaminant velocities and travel times were acceptable where monitoring data has been accumulated over longer periods of time. Because the software is not designed to handle conduit flow, sites with hydrogeologic conditions that can best be described as complex fractured bedrock and/or Karst

with solution channels were not considered.

The local ground water flow pattern along the length of the contaminant plume should not be significantly impacted by pumping wells or natural sources and sinks. For example, if the site was situated in a ground water recharge area where ground water mounding and divergent flow was observed, then the applicability of NAS may be limited depending on the location of the source relative to the recharge mound. Other boundary conditions had to be relatively simple and adequately described by steady state conditions.

The four sites chosen for TOS demonstration are located at: Seneca Army Depot in Romulus, New York; Hill Air Force Base in Ogden, Utah; Naval Submarine Base, Kings Bay Georgia; and an Alaska Department of Transportation and Public Facilities site in Fairbanks, Alaska.

### **6.3.2 Performance Objectives**

The objective of the demonstration is to assess the performance of NAS as a computational tool for estimating remediation timeframes following source zone remediation. To achieve this objective, NAS will be implemented to simulate contaminant concentrations at chlorinated solvents sites that represent a range of conditions. NAS is designed to first calibrate an analytical solution to steady-state plume contaminant concentration data and to then implement analytical and numerical solutions to simulate the transient response of plume concentrations due to source-zone treatment, depletion, or some combination of the above. In this demonstration, NAS was primarily implemented in the predictive mode, allowing for an assessment of the accuracy of TOR estimates.

Preliminary results of the application of NAS to the site data suggested several metrics that can be used to post audit TOR estimates:

1. Predicted/measured **inflection points** of contaminant concentration profiles.
2. Predicted **time of breakthrough**.
3. Predicted/measured **slopes** of contaminant concentration profiles.

**Table 6-1. Performance Objectives**

<b>Type of Performance Objective</b>	<b>Primary Performance Criteria</b>	<b>Expected Performance (Metric)</b>
Quantitative	Inflection point of concentration-time curve	The predicted inflection point of the concentration-time curve should coincide with the observed inflection point within one year.
Quantitative	Time of breakthrough	The predicted time of breakthrough of the concentration-time curve should coincide with the observed breakthrough within two years.
Qualitative	Slope of concentration-time curve following inflection point	The predicted slope of the inflection point of the concentration-time curve should be similar to the observed slope.

### 6.3.3 Performance Criteria

The performance of NAS was evaluated on the basis of accuracy, versatility, reliability, and applicability as described in Table 6-2.

**Table 6-2. Performance Criteria**

<b>Criteria</b>	<b>Description</b>	<b>Ranking</b>
Accuracy	NAS provides estimates of contaminant concentration changes over time. Predicted/measured contaminant concentration changes based on site monitoring data will be used to assess accuracy. As described previously, three metrics (1) predicted/measured inflection points of concentration changes, (2) predicted/measured time of breakthrough, and (3) slopes of predicted/measured time-concentration profiles, are used.	Primary
Versatility	Site selection will identify sites from each major region of the United States, so that hydrologic conditions will vary accordingly. The versatility of NAS to different hydrologic conditions is assessed by the accuracy achievable in each hydrologic setting.	Primary
Reliability	NAS uses complex analytical and numerical simulations to obtain TOR estimates. Implementation of NAS requires that these simulations run reliably. Reliability can be quantified by comparing the number of simulations performed to problems encountered.	Secondary
Applicability	NAS is a screening tool and is not designed to apply to all sites. Nevertheless, NAS should be flexible enough to be applied to more than half of the sites considered. During site selection, a record will be kept of sites considered, and sites to which NAS is deemed applicable. As stated previously, the selection criteria will include: <ul style="list-style-type: none"> <li>• Five years of annual monitoring data that includes both the geochemical and contaminant chemistry and water levels.</li> <li>• Ground water velocities exceeding 5 ft/year</li> <li>• Darcy flow (i.e., not conduit flow)</li> <li>• Unidirectional ground water flow fields and boundary conditions that can be reasonably simulated by the analytical code</li> </ul>	Secondary

### 6.3.4 Performance Confirmation Methods

The effectiveness of the demonstrations was primarily evaluated based on the two primary performance criteria (accuracy and versatility). The success of each demonstration was based on the ability of NAS to attain the performance metrics and the robustness of performance over the range of sites (Table 6-3).

**Table 6-3. Performance and Performance Confirmation Methods**

<b>Performance Criteria</b>	<b>Expected Performance Metric (pre demo) (Examples)</b>	<b>Performance Confirmation Method (Examples)</b>
<b>PRIMARY CRITERIA (Quantitative Performance Objectives)</b>		
<b>Inflection point of concentration-time curve</b>	The predicted inflection point of the concentration-time curve should coincide with the observed inflection point within one year.	Contaminant concentration/time curves at least one mid-plume well, and preferably several, over time.
<b>Time of breakthrough</b>	The predicted time of breakthrough of the concentration-time curve should coincide with the observed breakthrough within two years.	Contaminant concentration/time curves at least one mid-plume well, and preferably several, over time.
<b>PRIMARY CRITERIA (Qualitative Performance Objectives)</b>		
<b>Slope of concentration-time curve following inflection point</b>	The predicted slope of the inflection point of the concentration-time curve should be similar to the observed slope.	Contaminant concentration/time curves at least one mid-plume well, and preferably several, over time.

Each site application of NAS followed the procedure listed below with some minor variation:

1. Run NAS simulations for a range of source mass scenarios;
2. Compare results to available data from source zone and down-gradient monitoring wells;
3. Determine inflection points, time of breakthrough, slope of concentration-time curve following inflection point, and compile data for each site;
4. Compare predictions to observations (following stated quantitative and qualitative performance metrics as specified in Table 6-3);
5. Quantify error and perform goodness-of-fit analysis
6. Refine estimates of source zone mass and return to Step 1.

## **6.4 Performance Assessment**

### **6.4.1 Seneca Army Depot, NY – Ash Landfill**

#### **6.4.1.1 Site Background**

The Seneca Army Depot Activity (SEDA) is located in Romulus, New York. The site (Ash Landfill) is located along the western boundary of the SEDA with an area of approximately 130



acres, and, between 1941 and 1979, received the ash from the incineration of solid waste produced at the depot (Parsons 2004). Ground water and solid sampling for chlorinated volatile organic compounds (CVOCs), conducted between 1979 and 1999, revealed the presence of an approximately 18-acre (longitudinal and transversal extension of 1,300 ft and 625 ft, respectively) chlorinated plume, emanating from the north western side of the landfill (Parsons 2004) (Figure 6-1). Sampling revealed that the highest CVOC concentration was registered in well MW-44. This suggested that the contaminant source was located somewhere nearby this well. Accordingly, between 1994 and 1995, a remedial treatment was performed which consisted of excavation and thermal treatment of VOCs impacted soil; removing approximately 35,000 tons of soil (1.5 acres). After the soil was treated, it was backfilled into the excavation area. The benefits of this remedial action have been observed as the levels of CVOCs in the ground water have decreased by more than 95 percent in the treated area. However, other wells, such as PT-18 and MW-29, continued registering significant contaminant levels in the years following the removal action. The existence of an alleged CVOC source near well PT-18A may account for the limited concentration reduction in these wells.

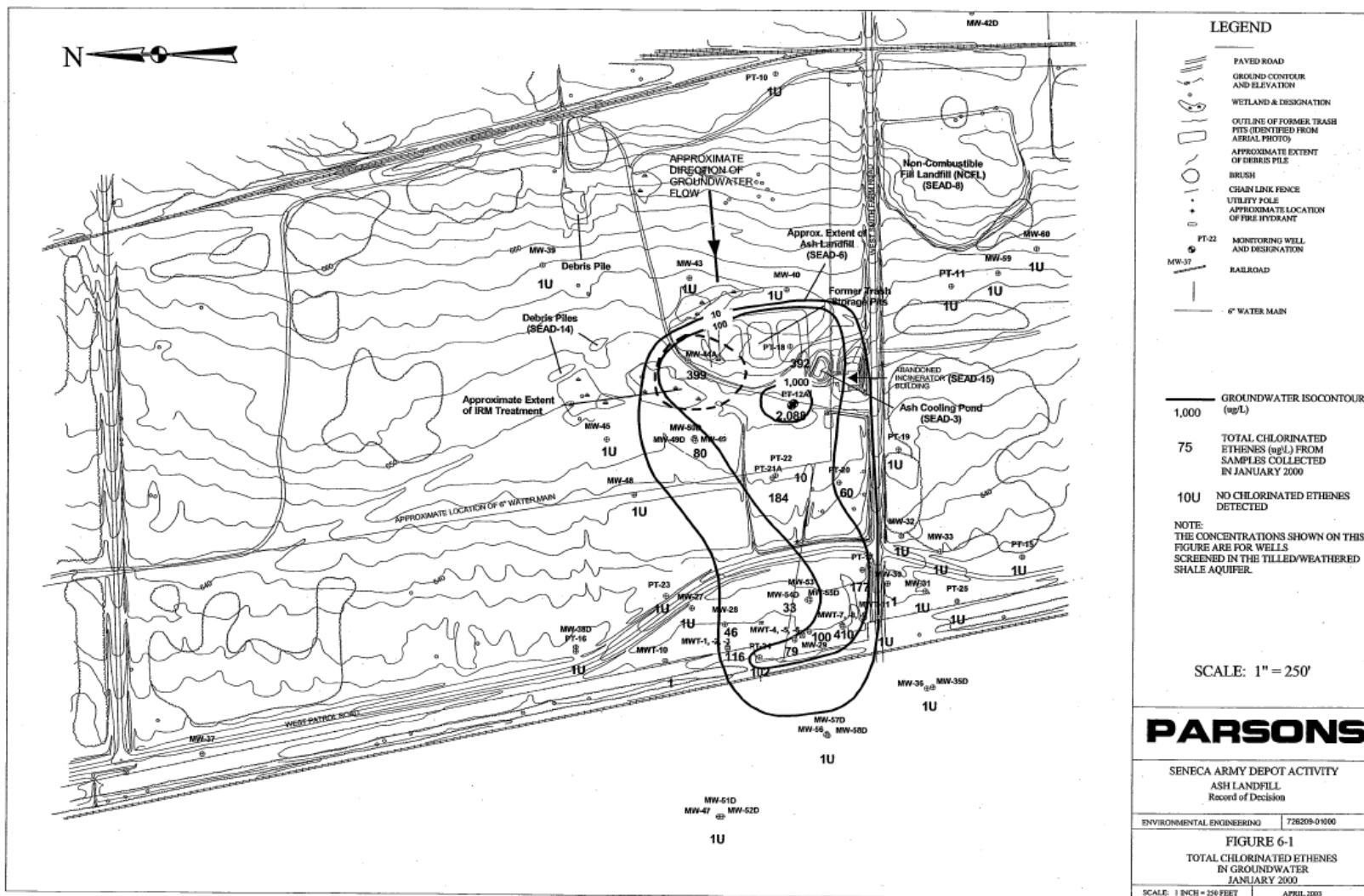
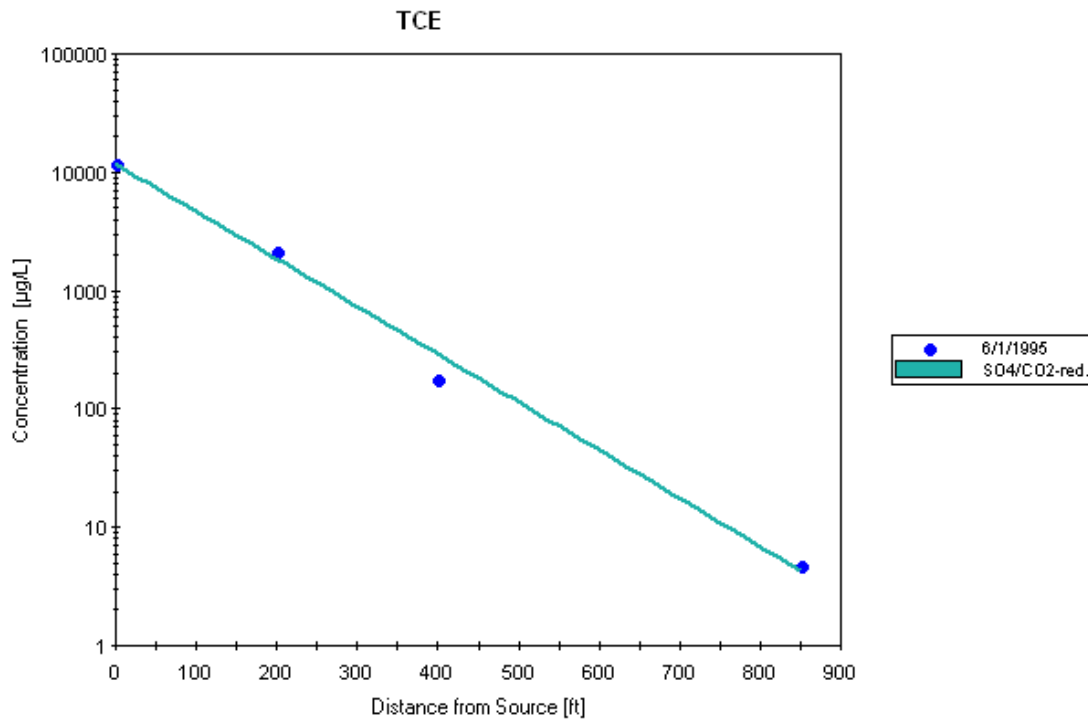


Figure 6-1. Site map of Ash Landfill at the Seneca Army Depot, NY (Parsons 2004).

#### **6.4.1.2 NAS Application**

TCE concentration in the well MW-44 source zone declined from 12,000 to 5,300  $\mu\text{g/L}$ . As a consequence of this partial source removal, the concentration levels at the downgradient wells showed a declining trend with time but not to levels expected if the source were completely removed. For predicting the impact of complete excavation on DOS and TOS, the source zone concentration input to NAS would be zero. In this case, the observed post-remediation source zone TCE concentration was used as input to NAS.

Figure 6-2 shows the stable pre-remediation TCE plume and the best-fit analytical solution using data collected immediately prior to the completion of the source excavation. Due to the lack of DCE concentration data before the partial source treatment period, the NAS application was based entirely on the TCE data. For the purpose of implementing the DOS/TOS feature, the field-observed TCE source concentration following source excavation was used as input to NAS. NAS was then used to simulate concentration versus time at wells PT12A and PT22, located at distances of 180 and 400 ft downgradient of the source, respectively.

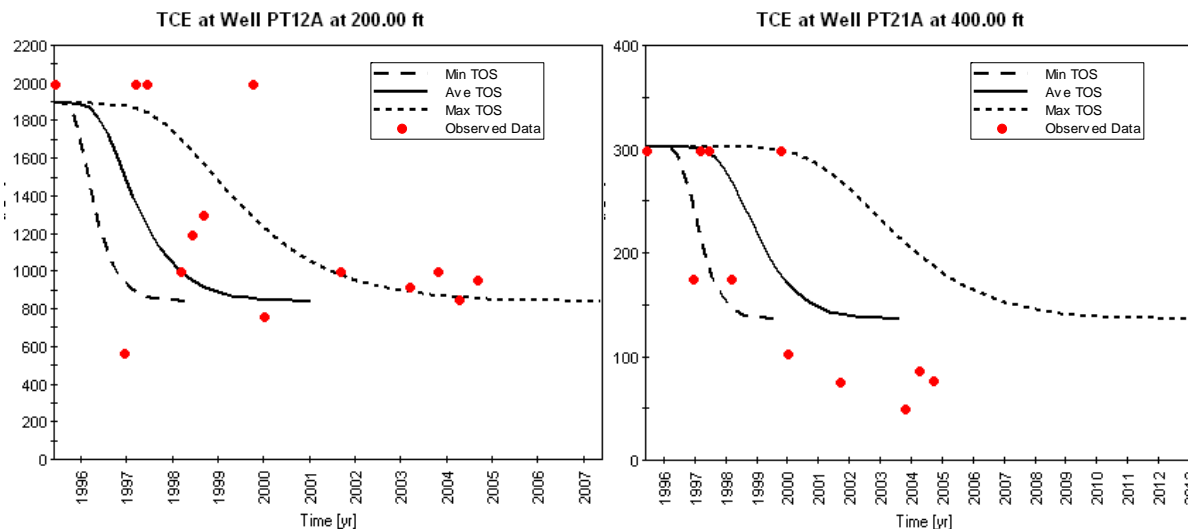


**Figure 6-2. Observed and NAS-simulated TCE concentration versus distance along plume centerline prior to source concentration reduction.**

Breakthrough curves at wells PT12A and PT22 are shown in Figure 6-3. Data gaps in the mid-1990s and along with the time fluctuation in concentrations, hinders the accurate estimation of the observed breakthrough time and concentration slopes. The inflection points are difficult to judge from the data, but in general, a reasonable fit was obtained at both wells. However, NAS was successful in simulating time of equilibrium at both wells and the equilibrium concentration at the well closest to the source.

Analysis of the hydraulic gradient indicated seasonal variability in the flow direction in the vicinity of the source. Variability in the ground-water flow combined with the reduction in the source width following excavation provides a reasonable explanation for the fluctuation in VOC concentrations over time. Use of the field-observed TCE source concentration resulted in an excellent fit to the final observed concentration at PT21A, but a poorer fit to the data is noted at

PT12A. The inability of NAS to match the final concentration at PT21A is due to the reduced source volume and the repositioning of the plume centerline following source excavation.



**Figure 6-3. Observed and NAS-simulated TCE concentration versus time at downgradient wells based on the observed source concentration reduction.**

## 6.4.2 Hill AFB, UT – OU2

### 6.4.2.1 Site Background

Hill Air Force Base (AFB) is in Ogden, Utah. Operable Unit 2 (OU2) is situated along the northeastern boundary of the base and from 1967 to 1975 was used as a dumping site for an estimated 45- to 50-thousand gallons of chlorinated organic solvents and degreasing agents. DNAPL sources were composed primarily of TCE with smaller amounts of tetrachloroethene (PCE) and 1,1,1- trichloroethane (1,1,1-TCA). Over the next 30 years the DNAPL had migrated north/northeast in the direction of ground water flow, settling into approximately five separate areas underlying the dumping site. Remediation began in 1993 with the implementation of a source recovery system, which includes a ground water recovery well field and process treatment facility. In 1996, a slurry containment wall reaching to the underlying clay aquitard was constructed, after which, an additional DNAPL pool was discovered outside the wall; this part of the source zone being labeled as Panel 5. In 1997, the Griffith Pool DNAPL extraction system, a system of 17 extraction wells in and around Panel 5, was installed. From 1992 to 2002 several

individual experimental DNAPL recovery operations and innovative remediation techniques were implemented in the source area and have resulted in a total DNAPL recovery of approximately 43,823 gallons, or approximately 90% of the estimated initial source volume (Air Force Center 2003). Figure 6-4 depicts the site map and the TCE plume (extending nearly 1,500 ft from the source zone) in the ground water system at OU2 in 2003.

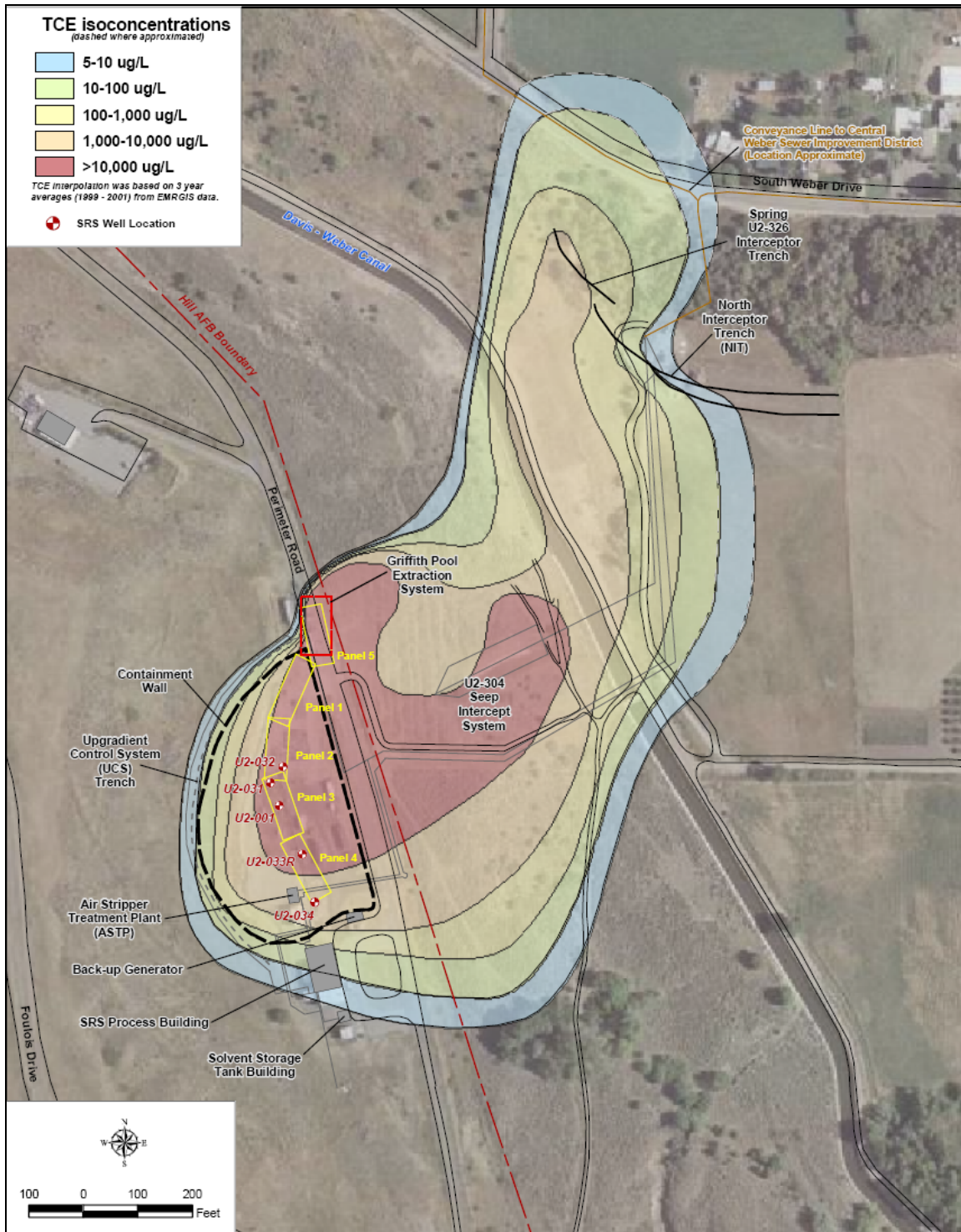
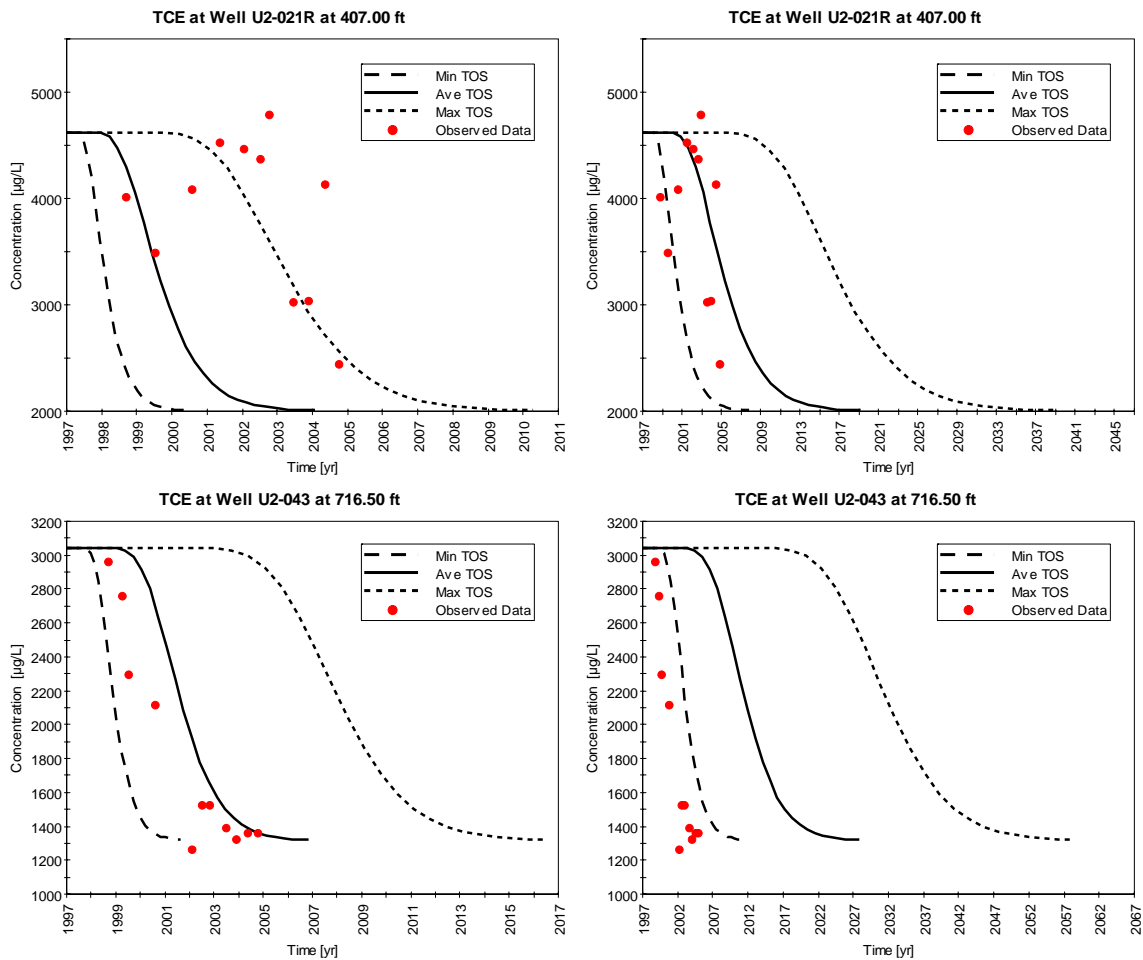


Figure 6-4. Site map of OU2 at Hill AFB Ogden, UT (Air Force Center 2003).

#### **6.4.2.2 NAS Application**

Analytical solutions used in NAS are based on the assumption that the hydrostratigraphic unit is homogeneous so that contaminant velocities do not vary along the entire length of the plume. At OU2, NAS was applied to data from monitoring wells located in the Alpine formation (closest to the wall) and 16 ft downgradient of the interface between the Alpine and Weber formations. The TCE simulations shown in Figure 6-5 are based on hydraulic conductivity representative of the Alpine formation but with two different values of the horizontal hydraulic gradient. A recharge mound near the containment wall resulted in a steep hydraulic gradient and high velocity (1.8 ft/d). An improved fit to the data at both wells was observed using a velocity (0.6 ft/d) representative of conditions downgradient of the wall. The range in TOS results reflects variability in the fraction of organic carbon. Although NAS was not specifically designed to simulate the effects of a containment wall on a plume, these results suggest that NAS is versatile and useful in this application.





**Figure 6-5. TCE concentration vs. time at wells downgradient of the slurry wall based on hydraulic gradient near the source (left) and further downgradient (right).**

### 6.4.3 NSB Kings Bay, GA – Site 11

#### 6.4.3.1 Site Background

Naval Submarine Base (NSB) Kings Bay encompasses more than 16,000 acres near the Georgia-Florida border in Camden County, GA. Site 11 is the location of a former 25-acre landfill at NSB Kings Bay, known as the Old Camden County Landfill that was operated by the county during the mid-1970s to 1980. A variety of wastes from the local Kings Bay community and the Navy were disposed of in the landfill, including solvents and municipal waste. A RCRA Facility Investigation (RFI) conducted in the early 1990's discovered a chloroethenes plume (Figure 6-6)

migrating from a PCE source zone (Chapelle et al. 2005). Source zone investigations revealed a 120-ft long by 40-ft wide DNAPL PCE source, with ground water concentrations ranging from 3.5 to 8.5 mg/L. A plume of CVOCs extended toward a residential area located outside the facility to the west of the landfill (Chapelle and Bradley 1998). Following the investigation, pumping wells were installed to exert hydraulic control on the plume as an interim measure. Beginning in 1998, a source zone ERA was implemented, consisting of in situ chemical oxidation using Fenton’s reagent followed by injection of emulsified vegetable oil. The latter component was designed to promote a return of redox conditions favorable to reductive dechlorination so that MNA could be employed as the final remediation step. The successful removal of the PCE source and subsequent plume reduction has been documented (Chapelle et al. 2003; Chapelle et al. 2005).

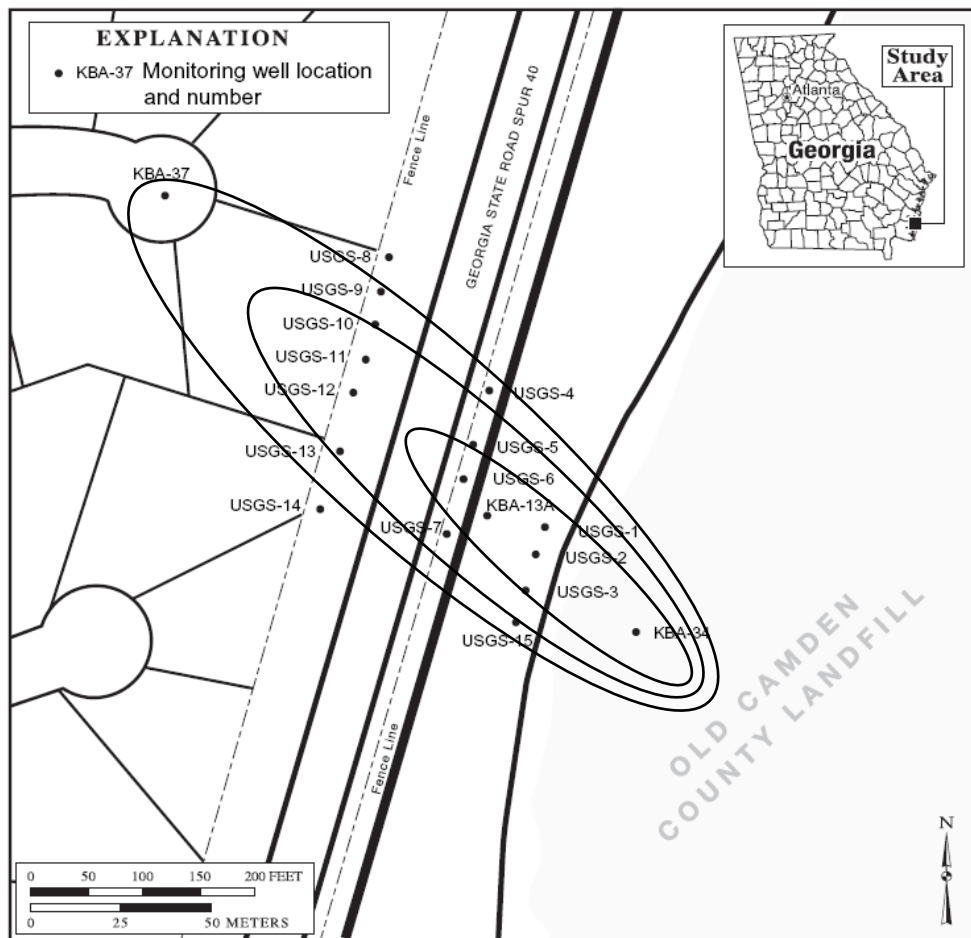
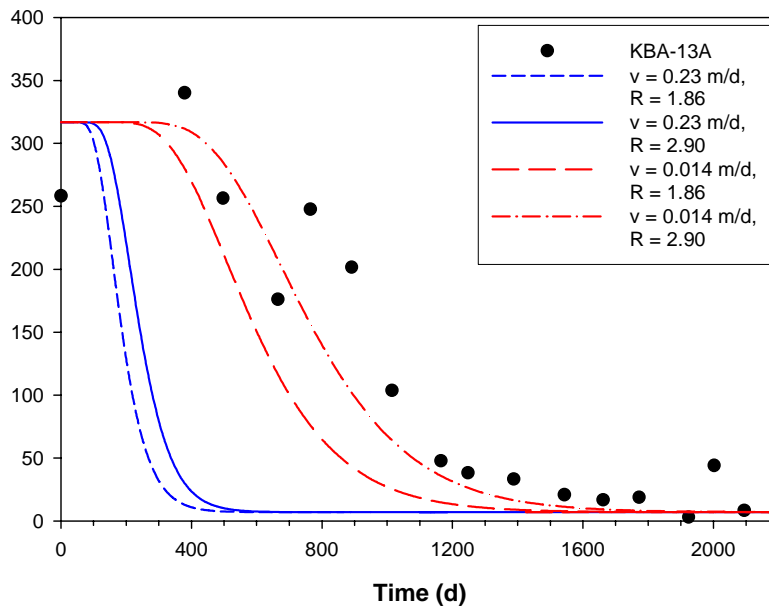


Figure 6-6. Chloroethene plume and monitoring wells at Site 11, NSB Kings Bay.

### 6.4.3.2 NAS Application

Prior to source treatment, Chapelle and Bradley (1998) estimated the range in the ground water velocity (0.014 to 0.23 m/d) using Darcy's Law and the range in field-measured hydraulic conductivity, horizontal hydraulic gradient (0.006), and an estimate of effective porosity (0.25). Retardation factors were based on the fraction of organic carbon (0.0019) and published values of the organic carbon partition coefficients. Because PCE rapidly depleted along the ground water flow path and was absent from the downgradient monitoring wells (KBA-13A and USGS-5) in the pretreatment plume, the range in the estimated composite retardation factor for total chlorinated ethenes is 1.86 to 2.90. The resulting range in the contaminant velocity (0.0050 to 0.12 m/d) shows that the maximum and minimum values vary by a factor of 25.

Figure 6-7 shows a comparison of observed data at KBA-13A ( $L = 49$  m) with two sets of solutions for the reduction in the total chlorinated ethene concentration versus time; one solution set represents the maximum estimated ground water velocity (0.23 m/d) using the range of retardation factors (1.89-2.90) and the other represents the initial minimum estimated contaminant velocity range. Results using the initial estimated input parameters show an underestimate of the actual concentration time trend with the best match occurring with the minimum contaminant velocity.



**Figure 6-7. Observed (circles) and predicted total chlorinated ethene concentrations showing the full range of ground water velocity and retardation factor values based on initial estimates.**

A tracer-based value of the ground water velocity is obtained from the breakthrough curve in the sulfate concentration at KBA-13A presented in Chapelle et al. (2005). A pulse of sulfate was observed in several observation wells resulting from the use of ferrous sulfate with the Fenton's reagent in the source zone and subsequent transport with the natural gradient. The resulting velocity (0.055 m/d) is simply the travel distance between KBA-34 and KBA-13A divided by the travel time (895 d) to the peak sulfate concentration. The results using the tracer-based velocity estimate in Figure 6-8 show improved agreement between the observed and calculated concentration trend when compared to the initial estimates. However, an improved velocity estimate is only available when the 6-yr monitoring program is approximately 40% complete because the sulfate breakthrough at KBA-13A was not sufficiently ahead of the decrease in the concentration of total chlorinated ethenes to allow an earlier updated prediction. For the tracer-based velocity the minimum value of *RMS* (30) is achieved for a retardation factor of 2.28.

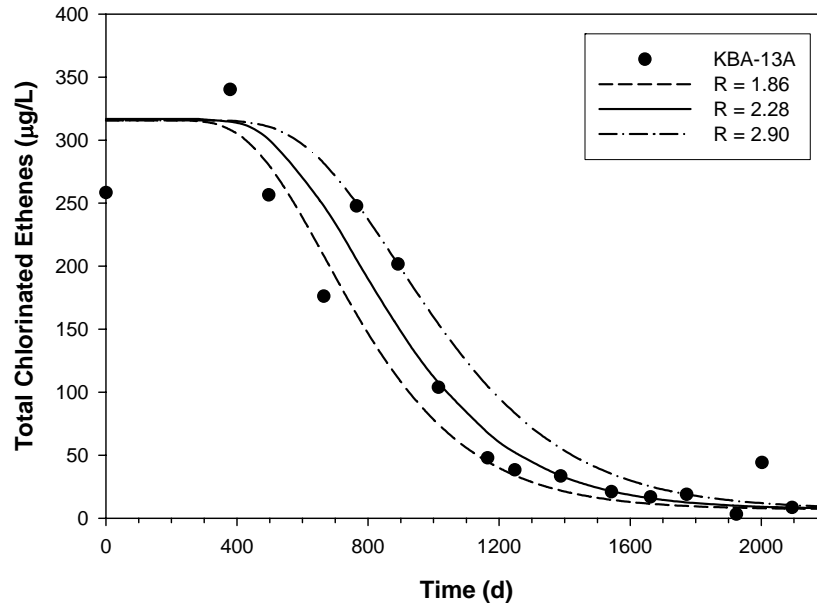


Figure 6-8. Observed and NAS-predicted total chlorinated ethene concentrations using ground water velocity ( $v = 0.055$  m/d) determined from the tracer breakthrough and the range of retardation factors, including the case ( $R = 2.28$ ) where the error is minimized.

#### 6.4.4 Alaska DOT&PF – USGS (Peger Road) Site

##### 6.4.4.1 Site Background

The Peger Road facility is located in Fairbanks, AK and is operated by the Alaska Department of Transportation and Public Facilities (ADOT&PF). A variety of solvents and petroleum hydrocarbons were used at this former equipment maintenance and testing facility during the 1970s and 1980s. Release of these compounds has resulted in the formation of discrete TCE, PCE, and benzene plumes that have been characterized by the Alaska Department of Environmental Conservation (ADEC) (ADEC 2005). A plume of TCE contamination extends from the maintenance lab to approximately 19<sup>th</sup> Ave (Figure 6-9). Approximately 700 cubic yards of TCE-contaminated soil were excavated for the expansion of the Materials Laboratory on site, with the excavated soil being land-spread to promote the volatilization of TCE

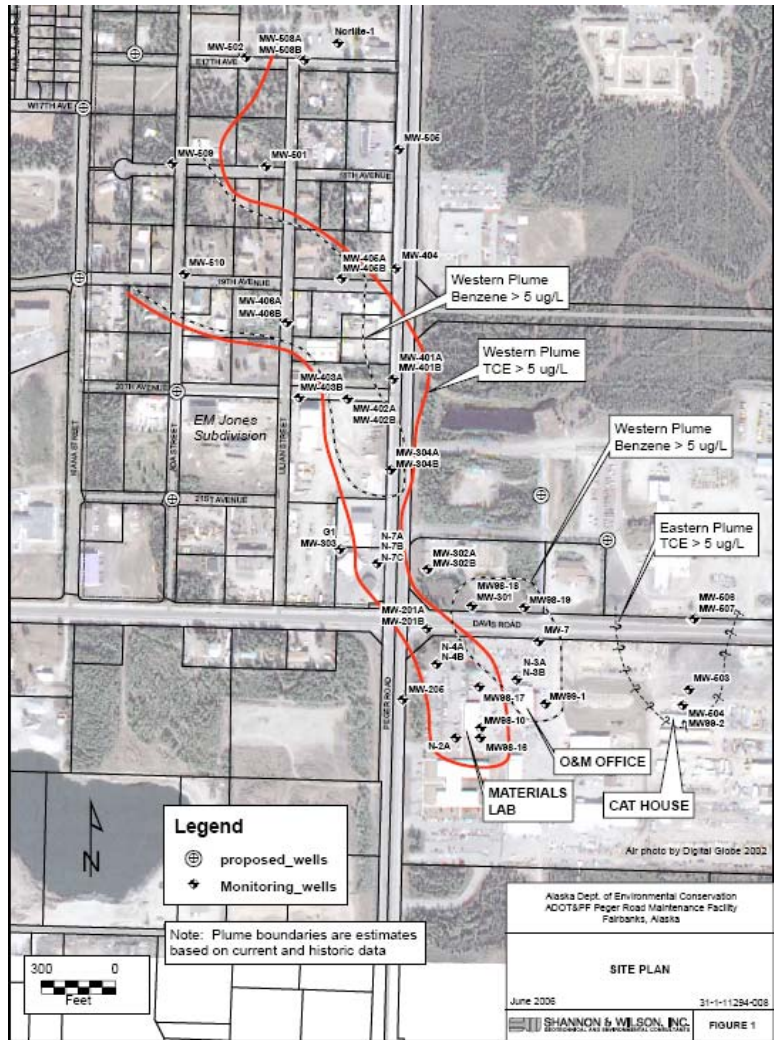


Figure 6-9. USGS (Peger Road) study site in Fairbanks, AK (ADEC 2005).

### 6.4.4.2 NAS Application

The results of NAS simulations of TOS immediately downgradient of the source area at Well MW98-17 (distance = 140 ft) are shown in Figure 6-10. As in all TOS simulations, the assumption is made that a source-area removal action has been undertaken (in this case, in 1998), and that a plume of remediated water is moving through the observation well. The simulated concentration profile curves represent the expected behavior of the plume for the case of minimum, average, and maximum rates of ground-water flow. Also shown on Figure 6-10 are the observed data points measured at the site.

Inspection of Figure 6-10 indicates that observed TCE concentrations at Well MW98-10 clearly fall outside the envelope of uncertainty for maximum and minimum rates of ground-water flow. This behavior is expected because no source-area removal was undertaken in 1998 as assumed by the simulation. Interestingly, however, the overall shape of the observed TCE concentration decline is not dissimilar to the predicted behavior assuming the lowest rates of ground-water flow. One interpretation of these results is that a source of TCE remains in or near the source area, but that this source is being depleted over time. Furthermore, this depletion is rapid enough that the observed behavior of the plume mimics a source-removal action.

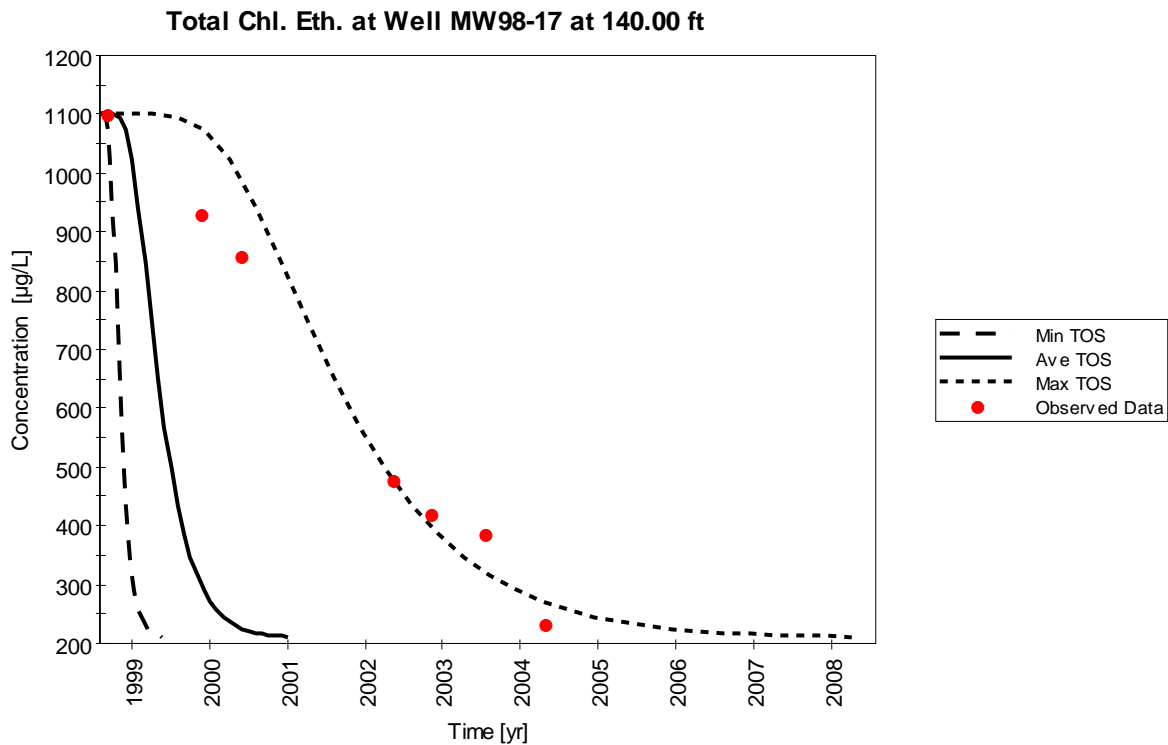


Figure 6-10. NAS simulation of time of stabilization at well MW98-17.

## 6.5 Overall Performance Assessment and Conclusions

### 6.5.1 Accuracy

Overall, the DOS/TOS feature was satisfactory in meeting quantitative and qualitative performance objectives based on the match between NAS and the data inflection points and concentration versus time slopes, respectively. The other quantitative performance objective,

time of breakthrough, was also satisfactory except at the Seneca site, where data variability prevented a credible determination of breakthrough. Factors affecting the degree of accuracy were reflected in the uncertainty associated with the contaminant velocity estimates and source characteristics (width and concentration) following remediation.

It is important to restate that site applications using the DOS/TOS feature was not a curve-fitting exercise. NAS self-calibrates a steady-state solution to the pre-remediation plume concentration data and then calculates concentration versus time at downgradient monitoring wells using the field-measured source concentration following remediation. The best matches between the observed and simulated concentrations, including inflection points, were achieved at the monitoring wells closest to the source (travel distances ranging from 18 to 407 ft with an average of 185 ft from source). In general, less accurate results were observed at monitoring wells located further downgradient from the source. As was noted in Seneca Army Depot application, decrease in the source width following remediation can reposition the plume centerline and potentially reduce the concentration at some monitoring wells. NAS only accounts for a reduction in the contaminant concentration leaving the source zone and does not account for changes in the source width following remediation. The issue is amplified at sites where time fluctuations in the direction and magnitude of the ground water velocity impact plume concentrations. Time fluctuations in concentration can be expected in situations where the contaminant mass flux “misses” the well if the direction of ground-water flow changes seasonally. The most accurate results were observed at NSB Kings Bay where the ground water velocity was calculated based on tracer test data. These findings suggest that accurate determinations of the ground water velocity and sorption parameters are required for improved accuracy of TOS following source zone remediation at all sites.

### **6.5.2 Versatility**

Site hydrogeology did not appear to be a factor in the performance of NAS. The sites reflected diverse and complex hydrogeologic settings. A reasonable match between observed data and NAS simulation results of TOS was obtained. Similarly, the mode of source remediation was not a factor in the performance of NAS. However, as was noted in the Accuracy section, reduction of the source width can affect post-remediation concentration data and represents an



inconsistency with the DOS/TOS feature. Even for the case of a containment wall, the NAS application resulted in an adequate match with observed data at monitoring wells located a sufficient distance away from the wall where the groundwater flow returned to a natural condition.

### **6.5.3 Reliability**

No significant reliability problems were encountered in the implementation of NAS. NAS version 2.2.0 was utilized for the site applications.

### **6.5.4 Applicability**

NAS was designed to be used as a stand-alone screening tool but can be applied to sites either as a precursor to a comprehensive (numerical) solute transport modeling investigation or as a follow-up to previous modeling studies. One finding of this demonstration was that NAS proved to be applicable to all four sites, independent of hydrogeology, contaminants, characteristics of the source zone, or ERA. Therefore, the simplifying assumptions associated with the NAS solution methodology do not appear to render NAS ineffective but, in fact, demonstrate the applicability and utility of NAS to a wide range of contaminated sites.

The results of this demonstration strongly suggest that because NAS is based on sound science, it can serve as an effective tool for decision-making and data analysis at a wide range of contaminated sites and is not limited to a small subset of “simple sites” because of its simplicity. However, there are many sites where complex hydrogeology, highly non-uniform groundwater flow, and the desire to simulate complicated remediation strategies will dictate the use of a comprehensive numerical model.

## **6.6 References**

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## 7 Conclusions

### ***7.1 Advantages and Limitations of the Technology***

NAS offers several advantages relative to comprehensive ground water modeling of sites. Even when NAS estimates TOR using the SEAM3D NAPL Dissolution Package, the user is not required to specify numerical parameters (e.g., grid spacing) or any spatial input parameters. Because NAS includes a simple self-calibrating analytical model, the amount of time and effort required is much less a site model for ground water flow and solute transport. However, at the sites with complex hydrogeology and patterns of ground water flow, comprehensive ground water modeling offers greater capabilities relative to NAS. While hydrogeology and flow patterns obviously play a large role, an accurate and complete characterization of the source area is essential to effective remediation of the source zone (NRC 2004). Likewise, any mathematical model may not be accurate if the source term is estimated based on limited information. Modeling tools, including NAS, are useful in developing and refining site conceptual models of the aqueous plume and source zones and in exposing site characterization deficiencies.

In comparison to conventional engineered remediation technologies, MNA offers a number of advantages (<http://www.afcee.brooks.af.mil>):

1. During intrinsic bioremediation, contaminants can be ultimately transformed to innocuous byproducts (e.g., carbon dioxide, ethene, chloride, and water in the case of chlorinated solvents; and carbon dioxide and water in the case of fuel hydrocarbons), not just transferred to another phase or location within the environment;
2. MNA is minimally intrusive and allows continuing use of infrastructure during remediation;
3. Except for assessment and monitoring efforts, natural attenuation does not involve generation or transfer of waste;
4. MNA is often less costly than other currently available remediation technologies;
5. MNA can be used in conjunction with, or as a follow-up to, other intrusive remedial measures;

6. MNA is not subject to limitations imposed by the use of mechanized remediation equipment (e.g., no equipment downtime).

MNA has the following potential limitations:

1. Time frames for complete remediation may be long;
2. Responsibility must be assumed for long-term monitoring and its associated cost, and the implementation of institutional controls;
3. Natural attenuation is subject to natural and anthropogenic changes in local hydrogeologic conditions, including changes in ground water flow direction or velocity, electron acceptor and donor concentrations, and potential future releases;
4. The hydrologic and geochemical conditions amenable to MNA are likely to change over time and could result in renewed mobility of previously stabilized contaminants (e.g., manganese and arsenic) and may adversely impact remedial effectiveness;
5. Aquifer heterogeneity may complicate site characterization, as it will with any remedial approach; and
6. Intermediate products of biodegradation (e.g., vinyl chloride, VC) can be more toxic than the original compound (e.g., trichloroethene, TCE)

## ***7.2 Expected Benefits of Research***

The NAS methodology has been implemented to assess remediation timeframes associated with combined ERAs and MNA at multiple facilities. These site applications have determined usability of the software and applicability of the incorporated methodology. At some facilities (e.g., NSB Kings Bay and NAS Pensacola), these estimated timeframes were crucial for winning regulatory acceptance of the remediation strategy. Cost-benefit analyses have been made at these sites to provide estimates of cost savings associated with using MNA as a final remediation strategy. The chief benefit of NAS will be to increase regulatory acceptance of MNA, thereby decreasing overall costs of environmental remediation. In addition, the latest version of NAS has facilitated the combined use of MNA with ERAs so that the environmental benefits of each technology can be maximized while minimizing the overall costs of remediation.

### **7.2.1 Regulatory and User Issues**

Following approval for dissemination, the DoD ESTCP Report (Widdowson et al. 2007) will be released and sent to key individuals within the regulatory community (e.g., USEPA, Interstate Technology and Regulatory Council (ITRC)). In addition, the results of the site applications will be presented to state regulators at a planned series of short courses and seminars. Also, recommendations from ESTCP, ITRC, and others will be utilized to help determine the most appropriate ITRC group and vehicle for interaction with the general public. User buy-in is evident by the support provided by Navy Engineering Field Divisions. This is exemplified by the recently funded NAS upgrade to allow for incorporation of a source removal term. Earlier versions of NAS have been the subject of Navy supported conference presentations (e.g., the annual Remedial Project Manager (RPM) Conference in Port Hueneme) and a Remediation Innovative Technology Seminar (RITS) course module. Furthermore, NAS has already been available for public use, through free download from its support website (<http://www.nas.cee.vt.edu>). User concerns, reservations, and buy-in factors all point to the user's willingness to utilize the NAS approach versus a more comprehensive modeling effort. Concerns with implementation continue to be addressed using feedback from users. Experience to-date suggests that these concerns will not be difficult to overcome, as most users are not trained to generate comprehensive models for site characterization or remediation. Due to its ease-of-use, low time requirements per iteration, underlying biogeochemical and spatial foundations, and anticipated level of accuracy relative to more comprehensive models, it is believed that users will continue to be receptive to this approach. A modest amount of training will be required, or perhaps familiarity with support documentation. However, with very little hydrogeologic and chemical training, the user can negotiate the data input frames and generate decision-quality outcome by following simple intuitive directions.

### **7.2.2 Cost Assessment**

To date, cost estimates associated with MNA have not been based on reliable estimates of remediation timeframes. NAS, a methodology and tool for estimating the time of remediation associated with MNA, will allow users to make informed decisions regarding its application. A cost assessment was included in the DoD ESTCP demonstration (Widdowson et al. 2006). The

assessment included a comparison between the estimated cost to implement NAS and the estimated cost associated with implementing a comprehensive flow and transport model to evaluate MNA, and also included an estimate of the life cycle costs of a long-term performance monitoring program developed in conjunction with NAS TOR estimates. While the accuracy of these life-cycle cost estimates is largely dependent on the TOR and monitoring requirements, the estimated cost of implementing a comprehensive numerical model was found to be over 5 times greater than the estimated cost of using NAS. With the validation of NAS at a variety of sites, improved estimation of capital and operations and maintenance (O&M) costs is achievable. Budget requirements for long term monitoring programs can be forecasted based on estimates of timeframes. Combining the NAS tool with cost assessment tools allows better program planning to meet the future needs of cleanup programs, and can afford remedial project managers (RPMs) the ability to develop optimization strategies, employing cost-benefit analyses when comparing MNA to engineered remedial actions or combinations of remedial actions and MNA.

## **7.3 Continued and Future Work**

### **7.3.1 Exact Analytical Solution for TOS**

The current NAS TOS solution scheme is based on the Domenico (1987) approximate analytical solution as described in Chapter 5: Time Estimates for Reaching Compliance Using Source Remediation Combined with Monitored Natural Attenuation. Recently, the use of this solution method has been questioned (Srinivasan et al. 2007, West et al. 2007). The Domenico derivation uses an approximate approach to solve the boundary value problem, whereas the exact solution is derived without using those approximations that may introduce an unknown amount of error. Srinivasan et al. (2007) explored the limits of the Domenico solution and found that for nonzero longitudinal dispersivity values, the solution does introduce an amount of error. Results suggest that the accuracy of the approximate solution is highly variable and depends on site parameters. West et al. (2007) goes on to suggest that, in remedial-action screening tools, the approximate Domenico variations should be replaced by the more accurate exact analytical solutions.

To complement, and compare with, the approximate analytical solution used in NAS, this section presents an exact analytical solution to estimate the time required to achieve a groundwater

concentration-based remedial action objective (RAO) using a combined remedy of contaminant source reduction and monitored natural attenuation. Solutions are also presented for determining the decrease in the source zone groundwater concentration required to reach a site-specific RAO at a downgradient point of compliance (POC) and the time trend in the contaminant concentration following source concentration reduction.

### 7.3.1.1 Mathematical Model

To illustrate the method a two-dimensional exact analytical solution for a reactive solute is utilized (Wexler 1992). Physical mass transport in the aquifer is governed by advection and hydrodynamic dispersion. Mass loss due to natural attenuation is expressed in terms of a lumped-parameter first-order model. Sorption is described using a linear equilibrium isotherm. The governing equation of mass balance for the aqueous-phase COC is

$$D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} - v_x \frac{\partial C}{\partial x} - \lambda C = R \frac{\partial C}{\partial t} \quad (7-1)$$

where  $C$  is the solute concentration [M/L<sup>3</sup>];  $x$  is distance in the longitudinal direction [L];  $y$  is distance in the transverse direction [L];  $t$  is time [T];  $D_x$  and  $D_y$  are the longitudinal and transverse hydrodynamic dispersion coefficients [L<sup>2</sup>/T], respectively;  $v_x$  is the groundwater velocity [L/T];  $\lambda$  is the first-order decay rate [T<sup>-1</sup>]; and  $R$  is the retardation factor [-].

A number of simplifying assumptions are evident in the mathematical model and analytical solution selected to illustrate the method. While these assumptions are not necessary to implement the method, it is prudent to describe the limitations of the solution. Groundwater flow is uniform, steady, and unidirectional. Molecular diffusion is assumed negligible relative to hydrodynamic dispersion so that  $D_x = \alpha_x v_x$  and  $D_y = \alpha_y v_x$  where  $\alpha_x$  and  $\alpha_y$  are longitudinal and transverse dispersivities [L], respectively. The two-dimensional geometry of the problem implies that vertical dispersion is negligible or that the solute concentration is uniformly distributed with depth. In cases where microbial processes primarily control attenuation of a plume, the first-order model suggests that biodegradation is not limited by a second species (i.e., an electron donor in the case of reductive dechlorination of chlorinated solvents) and that the half-saturation constant  $\gg C$ . Degradation is assumed to occur in the aqueous phase only, as literature strongly suggests that sorbed compounds are not readily bioavailable and degrade at a

significantly lower rate relative to compounds present in the aqueous phase (Criddle et al. 1991). The biodegradation rate constant ( $\lambda$ ) does not vary along the flow path between the contaminant source and the POC, and other input parameters are constant over space and time.

The solution is modified from Wexler (1992) for an aquifer of infinite width with finite-width solute source. A finite source of width  $Y$  and uniform concentration ( $C_o$ ) is fixed along the  $y$  axis at the influent boundary and is assumed to be constant with time before remediation. The source and remaining boundary conditions are

$$\begin{aligned}
 C(0, y, t) &= C_o & -Y/2 \leq y \leq Y/2 \\
 &= 0 & \text{otherwise} \\
 \frac{\partial C}{\partial x} \Big|_{x \rightarrow \infty} &= 0 \\
 \frac{\partial C}{\partial y} \Big|_{y \rightarrow \pm\infty} &= 0
 \end{aligned} \tag{7-2}$$

### 7.3.1.1.1 Transient Solution

The solution to Equation (7-1) subject to the specified boundary conditions and a uniform zero concentration initial condition is:

$$\begin{aligned}
 C(x, y, t) &= \frac{C_o x}{4\sqrt{\pi\alpha_x v_c}} \exp\left(\frac{x}{2\alpha_x}\right) \int_0^t \tau^{-3/2} \exp\left[-\left(\frac{\lambda}{R} + \frac{v_c}{4\alpha_x}\right)\tau - \frac{x^2}{4\alpha_x v_c \tau}\right] \\
 &\quad \left\{ \operatorname{erf}\left[\frac{y+Y/2}{2\sqrt{\alpha_y v_c \tau}}\right] - \operatorname{erf}\left[\frac{y-Y/2}{2\sqrt{\alpha_y v_c \tau}}\right] \right\} d\tau
 \end{aligned} \tag{7-3}$$

Equation (7-4) describes the contaminant concentration profile along the plume centerline

$$\begin{aligned}
 C(x, 0, t) &= \frac{C_o x}{2\sqrt{\pi\alpha_x v_c}} \exp\left(\frac{x}{2\alpha_x}\right) \int_0^t \tau^{-3/2} \exp\left[-\left(\frac{\lambda}{R} + \frac{v_c}{4\alpha_x}\right)\tau - \frac{x^2}{4\alpha_x v_c \tau}\right] \\
 &\quad \left\{ \operatorname{erf}\left[\frac{Y}{4\sqrt{\alpha_y v_c \tau}}\right] \right\} d\tau
 \end{aligned} \tag{7-4}$$



### 7.3.1.1.2 Steady-State Solution

When the contaminant plume reaches stability or as  $t \rightarrow \infty$ ,  $\partial C/\partial t = 0$  and the steady-state solution is applicable. The steady-state solution to Equation (7-4) is difficult to solve, due to the integral that cannot be simplified further, and requires evaluation through numerical integration. The solution may be more easily obtained by solving for a large value of time,  $t^{SS}$ , such that  $\partial C/\partial t \approx 0$ . Equation (7-5) describes the contaminant concentration profile along the plume centerline at a time approximating steady-state.

$$C(x,0,t^{SS}) = \frac{C_o x}{2\sqrt{\pi\alpha_x v_c}} \exp\left(\frac{x}{2\alpha_x}\right) \int_0^{t^{SS}} \tau^{-3/2} \exp\left[-\left(\frac{\lambda}{R} + \frac{v_c}{4\alpha_x}\right)\tau - \frac{x^2}{4\alpha_x v_c \tau}\right] \left\{ \operatorname{erf}\left[\frac{Y}{4\sqrt{\alpha_y v_c \tau}}\right] \right\} d\tau \quad (7-5)$$

### 7.3.1.2 Solution for Source-Area Engineered Remedial Action

The method of superposition (Van Genuchten 1981) may be employed to simulate the effects of concentration reduction at the source due to an ERA. The superposition approach is not dependent on the plume first reaching stability, but for simplicity in illustrating the method, the steady-state solution is assumed to be applicable to describe concentrations in the pretreatment plume. The total decrease in the source concentration ( $\Delta C_o$ ) may be implemented over time using a series of sequential steps or may be implemented as an instantaneous decrease which occurs at time  $t = t^{SS}$ . The solution for  $t > t^{SS}$ , along the plume centerline, is written using the latter approach as

$$\begin{aligned}
C(x,0,t) = & \frac{C_o x}{2\sqrt{\pi\alpha_x v_c}} \exp\left(\frac{x}{2\alpha_x}\right) \int_0^{t^{ss}} \tau^{-3/2} \exp\left[-\left(\frac{\lambda}{R} + \frac{v_c}{4\alpha_x}\right)\tau - \frac{x^2}{4\alpha_x v_c \tau}\right] \\
& \left\{ \operatorname{erf}\left[\frac{Y}{4\sqrt{\alpha_y v_c \tau}}\right] \right\} d\tau \\
& - \frac{\Delta C_o x}{2\sqrt{\pi\alpha_x v_c}} \exp\left(\frac{x}{2\alpha_x}\right) \int_0^t \tau^{-3/2} \exp\left[-\left(\frac{\lambda}{R} + \frac{v_c}{4\alpha_x}\right)\tau - \frac{x^2}{4\alpha_x v_c \tau}\right] \\
& \left\{ \operatorname{erf}\left[\frac{Y}{4\sqrt{\alpha_y v_c \tau}}\right] \right\} d\tau
\end{aligned} \tag{7-6}$$

where  $t$  is the time measured from the point in time when contaminant mass first enters the aquifer.

Equation (7-6) is the difference between the steady-state solution (Equation (7-5)) and the general solution (Equation (7-4)) evaluated at  $t \geq t^{ss}$ . Because it is practical to measure time relative to completion of the ERA,  $t$  is time measured from the instantaneous decrease in the source concentration. An inherent assumption in this solution is that the NAC, source dimensions, and transverse dispersivity do not significantly change following the source area ERA.

### 7.3.1.2.1 Reduction in Source-Area Concentration

The objective of the DOS component of the time of remediation framework presented in Chapelle et al. (2003) is to determine the target source area concentration ( $C_o^{Rem}$ ) to meet the regulatory-required concentration at a prescribed distance ( $L$ ) downgradient of the source along the plume centerline. The steady-state solution (Equation (7-5)) at  $x = L$  is set equal to the compliance concentration (e.g., MCL)

$$C(L,0,t^{SS}) = C_o^{Rem} f(L) = MCL \quad (7-7)$$

$$\text{where } f(L) = \frac{L}{2\sqrt{\pi\alpha_x v_c}} \exp\left(\frac{L}{2\alpha_x}\right)$$

$$\left\{ \int_0^{t^{SS}} \tau^{-3/2} \exp\left[-\left(\frac{\lambda}{R} + \frac{v_c}{4\alpha_x}\right)\tau - \frac{L^2}{4\alpha_x v_c \tau}\right] \left\{ \operatorname{erf}\left[\frac{Y}{4\sqrt{\alpha_y v_c \tau}}\right] \right\} d\tau \right\}$$

The target  $\Delta C_o$  is found by replacing  $C_o^{Rem}$  with  $(C_o - \Delta C_o)$  in Equation (7-7), so that

$$\Delta C_o = C_o - (MCL)f(L)^{-1} \quad (7-8)$$

By solving Equation (7-5) for the case where  $x = L$  and substituting  $C_o/C(L,0)$  for the term  $f(L)$  In Equation (7-8), a simplified expression for the target decrease in the source concentration ( $\Delta C_o$ ) is

$$\Delta C_o = C_o \left(1 - \frac{MCL}{C_L^{SS}}\right) \quad (7-9)$$

where  $C_L^{SS}$  is the steady-state concentration at the POC prior to the ERA. This result suggests that the target  $\Delta C_o$  is independent of the dimensionality of the problem and that is directly proportional to the regulatory-required concentration at the POC.

### 7.3.1.2.2 Time of Stabilization

The time of stabilization ( $t_s$ ) occurs when the compliance concentration is reached at the POC, after the ERA is completed and the source concentration is reduced. The accuracy of the  $t_s$  estimate is dependent on the desired maximum relative error between the approximation concentration and the compliance concentration. Due to the integral in the exact analytical solution, it is difficult to derive a general expression for  $t_s$ . Therefore, using Equation (7-6),  $t_s$  may be solved through trial-and-error by incrementally increasing  $t$  until the requirement of the desired maximum relative error is satisfied, as represented by Equation (7-10).

$$\begin{aligned}
C(L,0,t_s) = & \frac{C_o L}{2\sqrt{\pi\alpha_x v_c}} \exp\left(\frac{L}{2\alpha_x}\right) \int_0^{t^{ss}} \tau^{-3/2} \exp\left[-\left(\frac{\lambda}{R} + \frac{v_c}{4\alpha_x}\right)\tau - \frac{L^2}{4\alpha_x v_c \tau}\right] \\
& \left\{ \operatorname{erf}\left[\frac{Y}{4\sqrt{\alpha_y v_c \tau}}\right] \right\} d\tau \\
- & \frac{\Delta C_o L}{2\sqrt{\pi\alpha_x v_c}} \exp\left(\frac{L}{2\alpha_x}\right) \int_0^{t_s} \tau^{-3/2} \exp\left[-\left(\frac{\lambda}{R} + \frac{v_c}{4\alpha_x}\right)\tau - \frac{L^2}{4\alpha_x v_c \tau}\right] \\
& \left\{ \operatorname{erf}\left[\frac{Y}{4\sqrt{\alpha_y v_c \tau}}\right] \right\} d\tau \approx MCL
\end{aligned} \tag{7-10}$$

### 7.3.1.3 NAS Implementation

This exact analytical solution scheme was implemented in the current beta version of NAS, to compare with the existing NAS approximate analytical solution. Further development and testing of this functionality in NAS will provide improved assessment of the significance of potential errors with the approximate solution, and comparison with the exact solution.

### 7.3.2 NAS/SEAM3D Modifications

In an expanded analysis of one of the NAS case studies (Niagara Falls USGS site, Yager 2002), an attempt to more appropriately model the site has offered the first instance that NAS has been used to this extent in this capacity. To utilize a more accurate conceptual model, the liberty has been taken to modify NAS quite extensively with functions found useful or necessary for this site in particular. Some of these functions, upon further development and testing, may be incorporated into the next public version.

#### 7.3.2.1 NAS Modifications

Current modifications to NAS include:

- User may specify any contaminant and redox datasets from which NAS estimates are derived from.
- User may specify the well at which the NAC begins to be calculated from. The original NAS default was the first well (i.e., source well). This is useful when there is limited or

poor concentration data from wells in the upgradient part of the plume, or when the plume is in an unsteady state.

- TODs, and Concentration vs. Time curves, may now be calculated for any well. Originally, NAS made these calculations for just the first well.
- For multiple contaminant datasets, NAS can calculate a decay rate, averaged over all datasets, for each contaminant, or the user may specify a hard-wired decay rate.
- The user may also specify hard-wired values for retardation factor, longitudinal dispersivity, and ratio of longitudinal to transverse dispersivity (thereby transverse dispersivity, as well).
- The user can choose which well in the current dataset has the concentration that will be the initial concentration at the source zone for the TOD (SEAM3D) simulation.
- Originally, for the initial concentration distribution of the TOD (SEAM3D) simulation, NAS used the first well (i.e., source well) concentration, with a degrading downgradient distribution based on the decay rate of the first redox zone. The user can now specify to have the initial contaminant distribution based on the observed downgradient centerline concentration profile. Thereby, the initial conditions can now accurately represent the observed data with initial concentration values being extrapolated between wells. This is useful in examples where the concentration profile may not be at steady state, or if the observation well is at a point further downgradient from the source.
- NAS has been expanded to analyze multiple user-defined stress periods, in one simulation. An example would be an application simulating both pre-pumping and pumping datasets. This would enable NAS to create a more accurate conceptual model for estimating both MNA-only and Pump-and-Treat Concentration vs. Time. The MNA-only TOD would be based on NACs / decay-rates from the pre-pumping datasets, and the Pump-and-Treat TOD would be based on the NACs / decay-rates from the pumping datasets. This would enable post-audit analysis with multiple pre- and during pumping datasets, with conceptually accurate MNA-only and Pump-and-Treat Concentration vs. Treat predictions vs. observed data in one simulation, on one graph.
- The user may now specify a two-dimensional, multiple-well pumping field. Wells may be located at any longitudinal and lateral distance from the source area, in both upgradient and downgradient directions. Wells may be added to, or removed from, each stress period

being simulated, and well locations and pumping rates may also vary between each stress period.

- To allow improved comparison between observed data and the range of NAS predicted data, in the TOD output graph the user may select a range option that graphs only the two boundaries lines that represent the highest and lowest concentration vs. time values that takes into account the range of all parameter estimates in the current simulation (i.e., ranges in velocity, initial source mass, mass removal options, and pump-and-treat vs. MNA).
- NAS (SEAM3D) now also gives complete control over the type and frequency of observation well (\*.OBS), mass (\*.MAS), and concentration (\*.UCN) output reporting. All SEAM3D output types may be available to the NAS user if desired, and may be specified by any time or step frequency.
- NAS now incorporates a function to display head and concentration data, from the TOD (SEAM3D) simulations, in two-dimensional space and time in both graphical and tabular form. Graphs and tables may be copied, print, or saved to file for reporting purposes.

### **7.3.2.2 Other SEAM3D-Specific Modifications**

Current modifications to SEAM3D include (See Appendix B for the new SEAM3Dv5.0 Input Instructions):

- The SEAM3D Fortran code has been modified to enable larger NAPL source zones.
- The new NPL Package in SEAM3D was revised to facilitate multiple stress periods.
- NAS / SEAM3D Fortran was modified to not simulate unnecessary species as it had been previously (e.g., for Chlorinated Ethenes, NAS was previously required to also simulate O<sub>2</sub>, NO<sub>3</sub>, Methanogenesis, and a Substrate as species). This has the potential to significantly reduce run-times, primarily for simulations with larger grids and / or smaller time-step sizes.
- NAS / SEAM3D was enabled to incorporate functionality similar to, but more robust than, the MT3DMS SAVELAST Program. This is ideal for simulations where it may be more advantageous to simulate stress periods separately, for example due to run-time considerations between non-pumping stress periods and pumping stress periods that may require considerably more computation time. Separate modeling periods (e.g., that

represent pre-pumping periods) may then be calibrated individually, without the requirement or redundantly re-running these periods during the separate calibration of subsequent modeling periods (e.g., that represent pumping periods). For these multi-period simulations, NAS / SEAM3D saves the final head, concentration, and NAPL mass values at the conclusion of each modeling period, which will in turn be used as starting values for any subsequent modeling period simulations.

- NAS / SEAM3D has been modified such that the mass output files itemize the mass removed from sinks to separately record mass removed from pumps and mass removed from the decay / reaction terms as well. This, along with the output from a new modified MT3DMS / SEAM3D Transport Observation (TOB) Package, facilitates the calibration of NAS parameters to observed mass removal rates.

### **7.3.2.3 Expanded NAS Case Study of Niagara Falls Site**

The goal using this dataset was to compare the NAS predicted mass fluxes (NAPL dissolution / Biodegradation / Mass removal from pumping) with those from the USGS report (Yager 2002). See Figure 7-1 for a detailed map of the site, and location of the pumping wells. The NAS dataset stress periods considered both pre-pumping and pumping phases of the site. Table 7-1 displays the separate pre-pumping and pumping phases throughout the history of the site, and the individual stress periods they were simulated as in NAS.

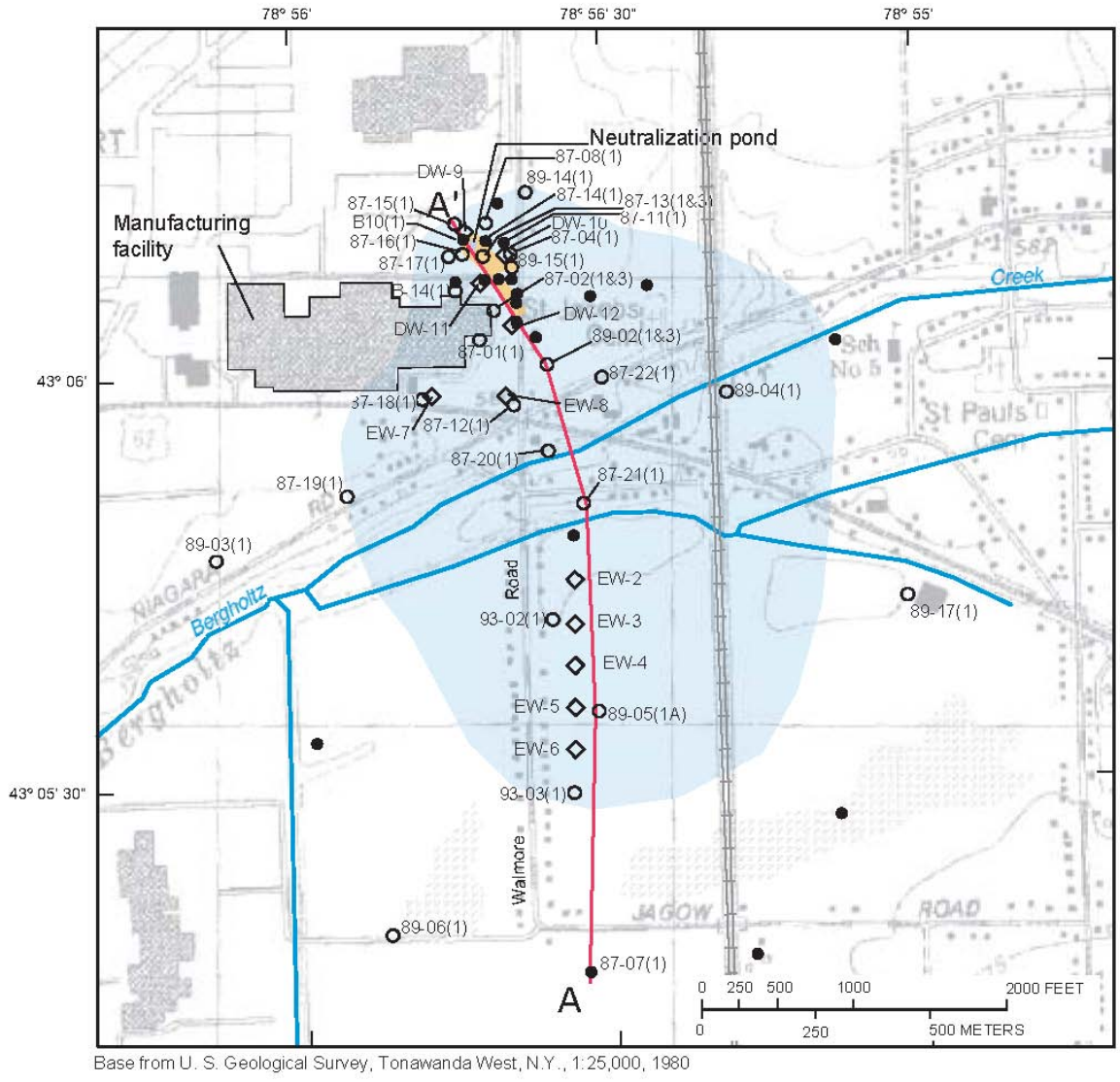
The purpose of the initial stress periods was to find conditions that approach those of the site during pre-pumping conditions. NAS attempts to approximate a “pre-pumping” NAC though no pre-pumping data is available. The first stress period is an initial condition of zero NAPL mass, with NAPL mass being loaded at a particular rate for a period of approximately 20 years (~from 1950 to 1970), followed by a second stress period with no mass loading, and only natural attenuation processing occurring for a period of approximately 23 years (~from 1970 to 1993), until the first pump-and-treat system wells are initiated. The only dataset parameters that are not based on reported data, and are trial-and-error, are the NAPL mass loading rate used in the first NAPL stress period, and the hardwired NAC / decay rate (there are no pre-pumping data available to estimate an MNA-only NAC).

The next step was to match NAS to the observed well data during the known pumping periods. The NAS dataset simulates a two-dimensional grid of 12 pumping wells over 5 different pumping stress periods as documented in the report. The objective was to calibrate NAS's mass fluxes: Mass In (NAPL dissolution) and Mass Out (biodegradation, pumping) to those from the USGS report.

Through trial-and-error, the pre-pumping period of the Niagara site was able to be calibrated. The USGS report estimated ~20 yrs NAPL mass loading to the neutralization pond, excavation/capping of the pond, and then ~20 yrs of NA-only before the first wells started pumping. During the NA-only period, NAS was able to calibrate well to the USGS reported Mass In (NAPL dissolution) and Mass Out (biodegradation) mass fluxes (See Table 7-2). Only the NAPL mass loading rate (1st period), and decay rate needed to be calibrated through trial-and-error. To attain these values, the NAPL mass (50% TCE / 10% DCE) was loaded to the pond at 4.04 gm/d/cell, over a defined source area of 1095 cells, for 20 years. Therefore, overall NAPL mass loading rate was 4.42 kg/d, for a total of 32294 kg loaded to the source over the duration on the stress period.

In regard to the NAS output for the pumping periods, the NAPL dissolution, biodegradation, and pumping mass fluxes did not compare as well, with the NAS values being approximately one-third of the USGS reported values. For the NAS-calculated head and TCE concentration at the end of each stress period, see Figure 7-2 through Figure 7-8. For the NAS-calculated vs. observed TCE concentrations (which do compare fairly well) along the wells simulated as the approximate centerline in NAS, see Figure 7-9 through Figure 7-16. Model parameters will continue to be adjusted, and simulations will be run again in the hopes that more closely matched mass flux and concentration versus time values may be obtained.





**EXPLANATION**

- Plume of dense nonaqueous-phase liquids in 1990
- Area in which concentration of chlorinated ethenes exceed 1 micromolar in 1990
- A-A' Geologic section
- Monitoring well
- 87-19(1) Monitoring well sampled in this study
- EW-6  Pumped well
- Number in parentheses is zone designated by Golder Associates (1991b)

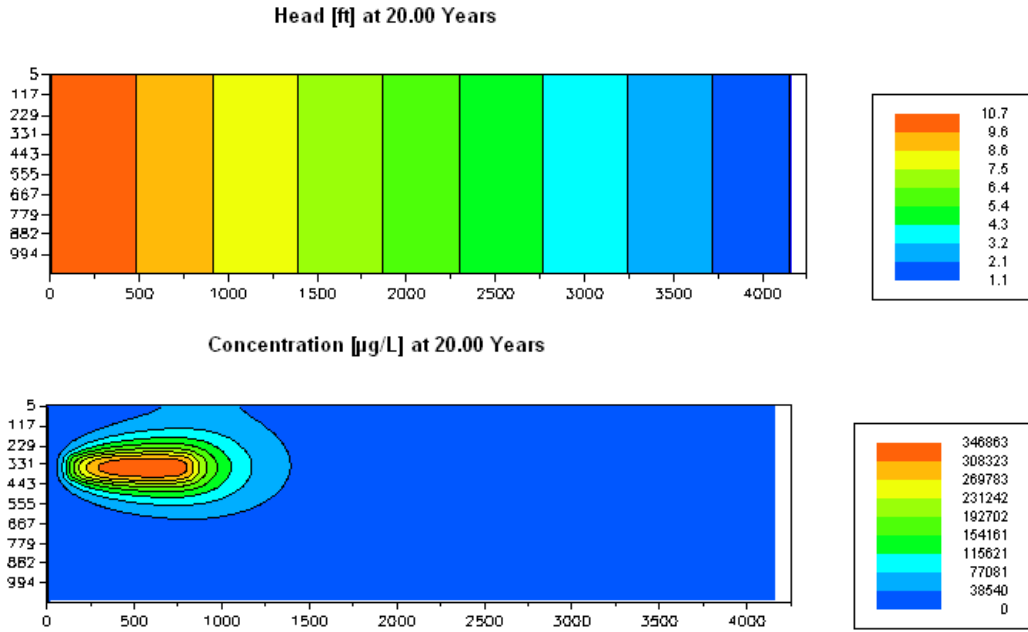
**Figure 7-1. Map of USGS study site near Niagara Falls, NY (Yager 2002).**

**Table 7-1. Site timeline as documented in the USGS Report, and simulated as stress periods in NAS.**

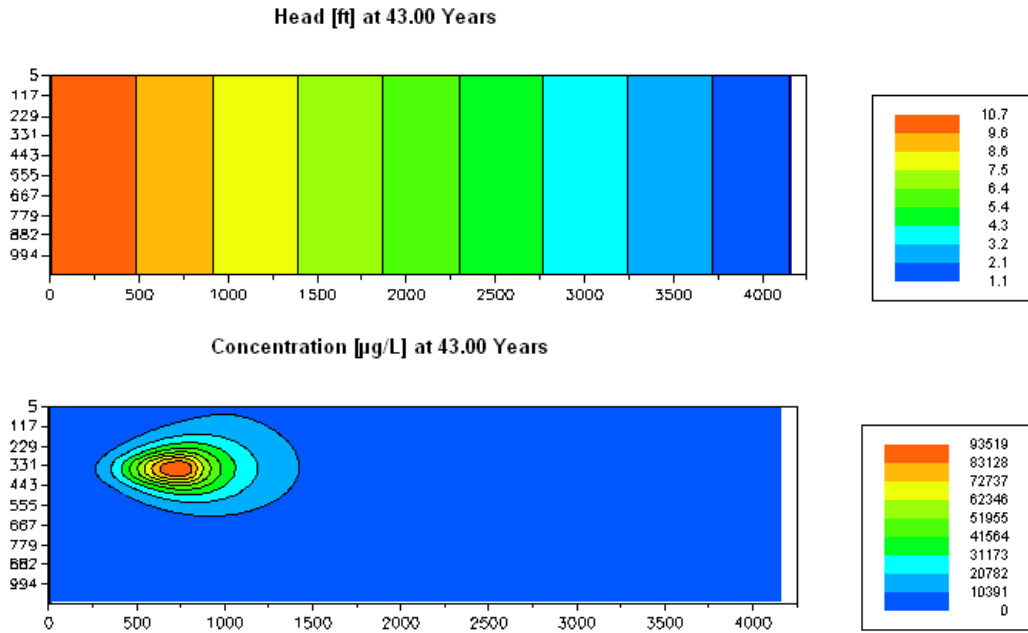
<b>Stress Period</b>	<b>Begin</b>	<b>Duration (Years)</b>	<b>Process</b>	<b>Description</b>	<b>Additional Information</b>
1	4/1950	20	NAPL Mass Loading	Contaminant loading to the neutralization pond	4.42 kg/d loading rate
2	4/1970	23	Natural Attenuation	NA-only period between mass loading and P&T startup	
3	3/1993	2	Pump&Treat	Off-Site Well System Start-up	EW 2-6
4	4/1995	1	Pump&Treat	On-Site Well System Start-up	EW 2-8; DW 9-12
5	4/1996	2	Pump&Treat	Well EW-6 taken off-line	EW 2-5,7-8; DW 9-12
6	5/1998	0.5	Pump&Treat	Well DW-9 taken off-line	EW 2-5,7-8; DW 10-12
7	9/1998	4	Pump&Treat	Well EW-13 added to On-Site System	EW 2-5,7-8; DW 10-13

**Table 7-2. Comparison of TCE mass flux, before and during pump-and-treat remediation, as computed by USGS and NAS.**

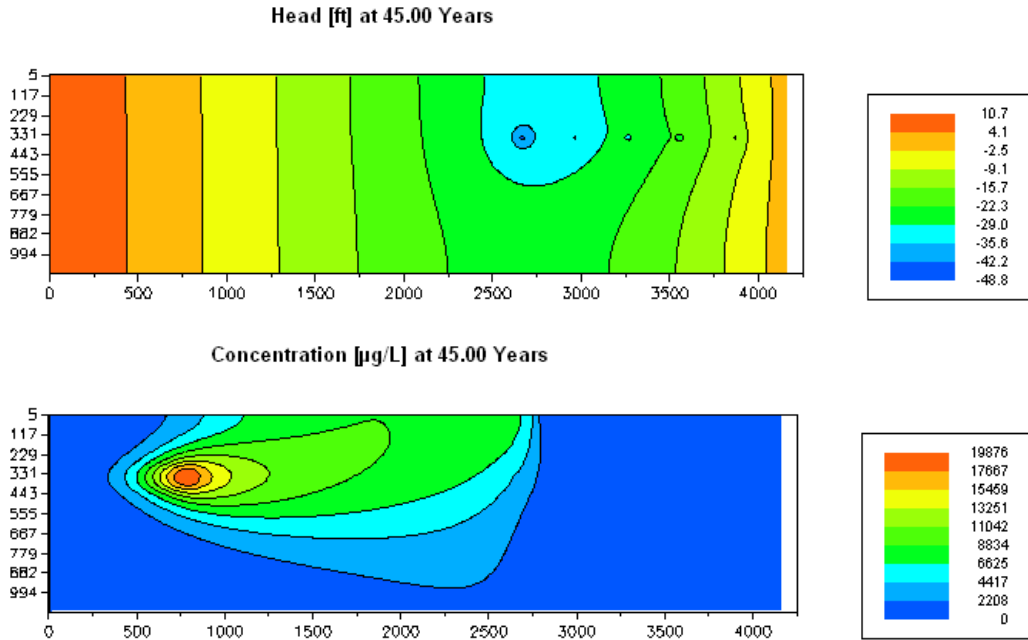
	<b>Mass Flux of TCE (kg/yr)</b>	
	<b>USGS</b>	<b>NAS</b>
<b>Prior to pumping, May 1980 - May 1990</b>		
<b>Mass In</b>		
DNAPL dissolution	185	186
<b>Mass out</b>		
Removed by biodegradation	181	184
<b>Mass in plume May 1990 (kg)</b>	<b>42</b>	<b>184</b>
<b>Pump-and-treat remediation, March 1993 - April 1998</b>		
<b>Mass In</b>		
DNAPL dissolution	440	157
<b>Mass out</b>		
Removed by biodegradation	259	75
Removed by pumping	181	68
<b>Mass in plume May 1998 (kg)</b>	<b>42</b>	<b>6</b>



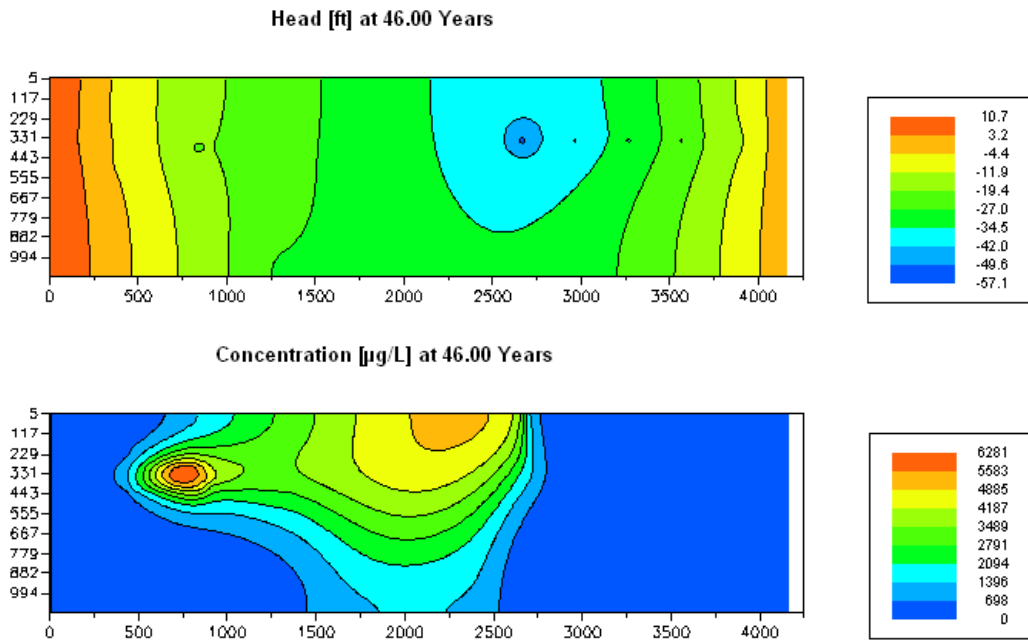
**Figure 7-2. NAS calculated Head and TCE Concentration at end of Stress Period 1**



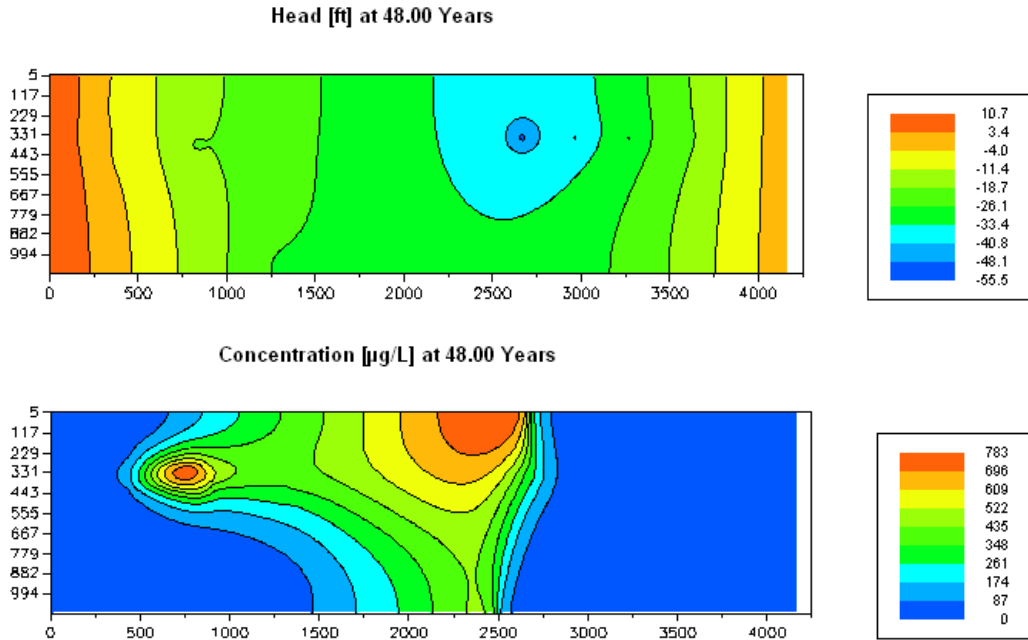
**Figure 7-3. NAS calculated Head and TCE Concentration at end of Stress Period 2**



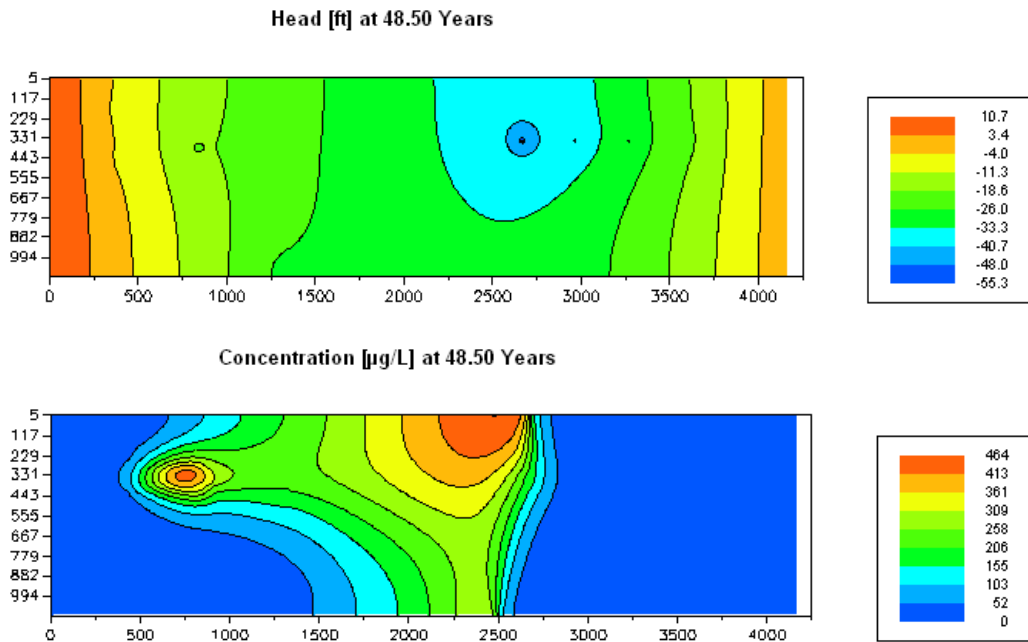
**Figure 7-4. NAS calculated Head and TCE Concentration at end of Stress Period 3**



**Figure 7-5. NAS calculated Head and TCE Concentration at end of Stress Period 4**



**Figure 7-6. NAS calculated Head and TCE Concentration at end of Stress Period 5**



**Figure 7-7. NAS calculated Head and TCE Concentration at end of Stress Period 6**

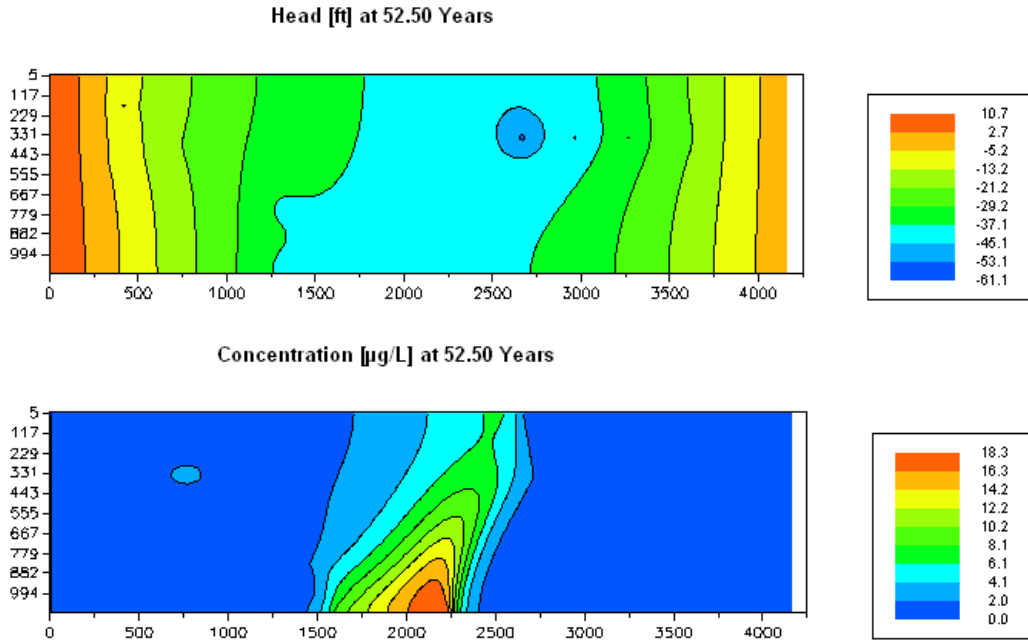


Figure 7-8. NAS calculated Head and TCE Concentration at end of Stress Period 7

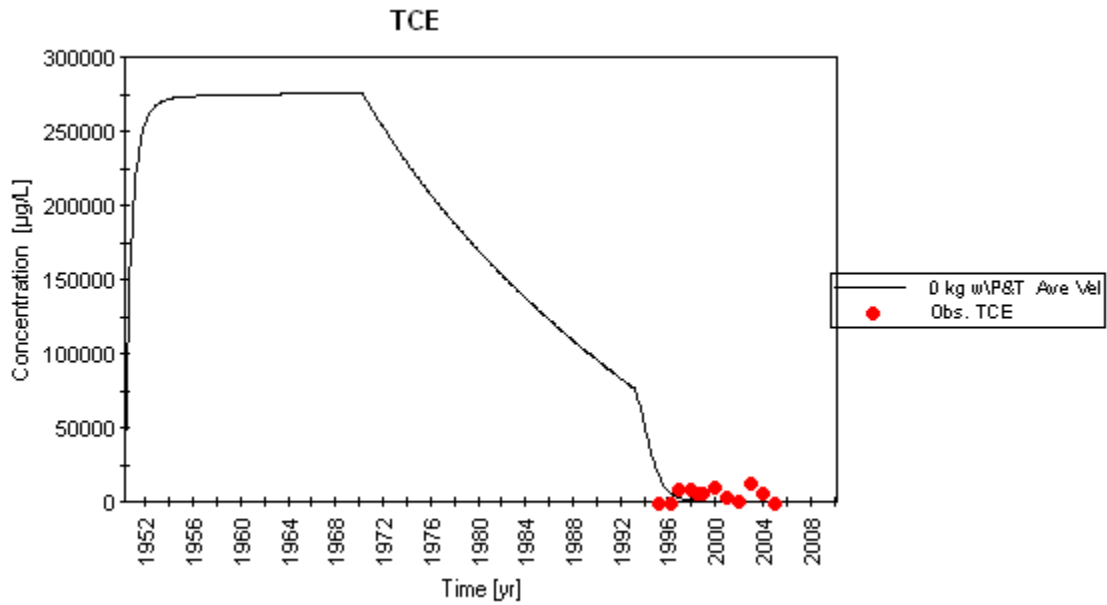


Figure 7-9. NAS-calculated vs. observed TCE at Well DW-12

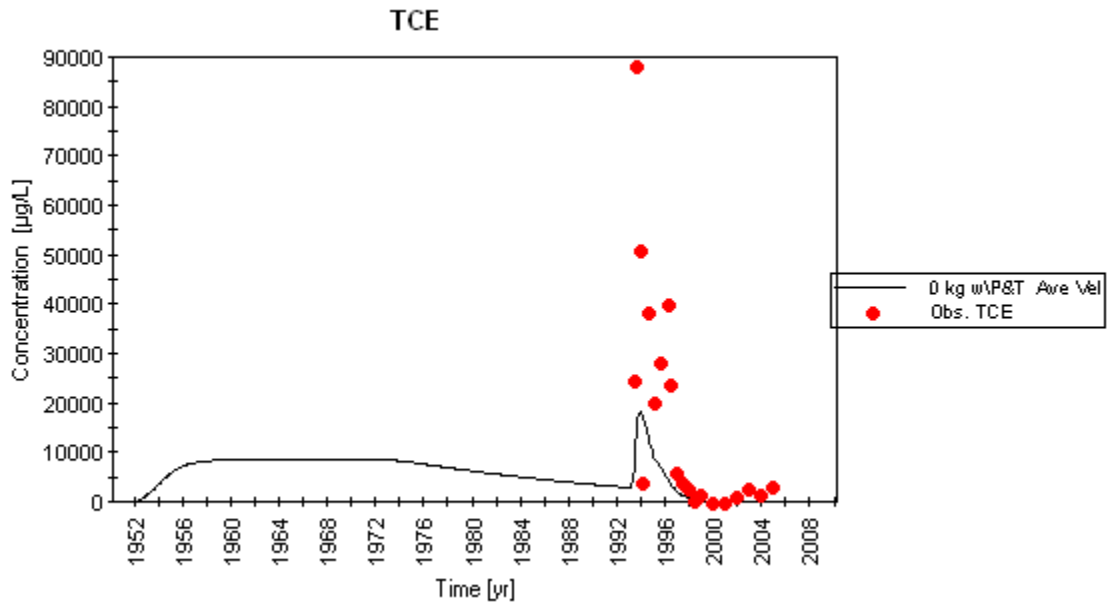


Figure 7-10. NAS-calculated vs. observed TCE at Well 87-20(1)

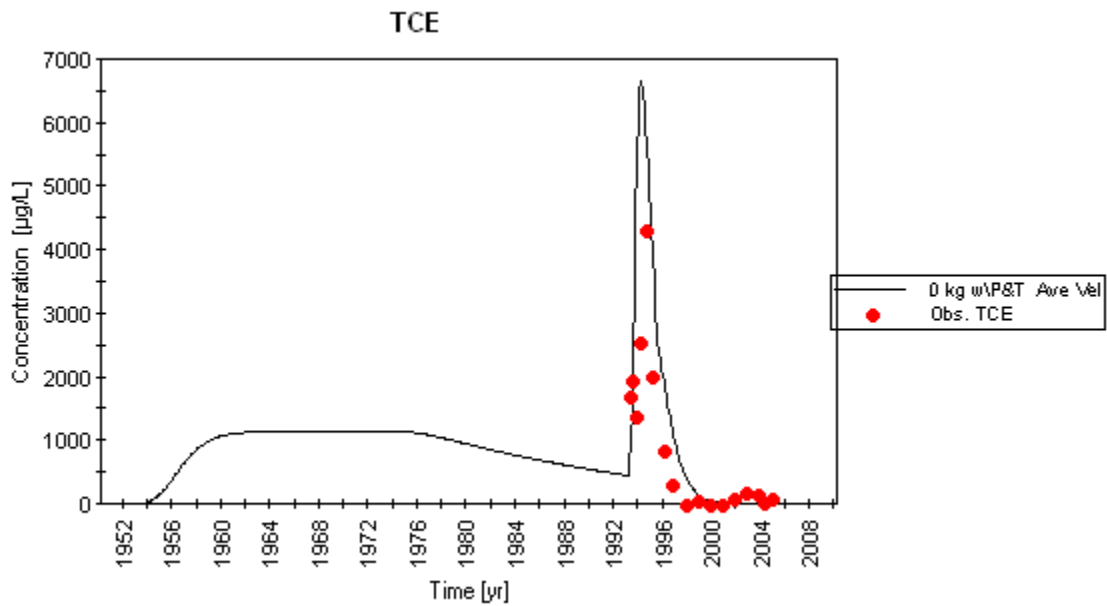


Figure 7-11. NAS-calculated vs. observed TCE at Well EW-2

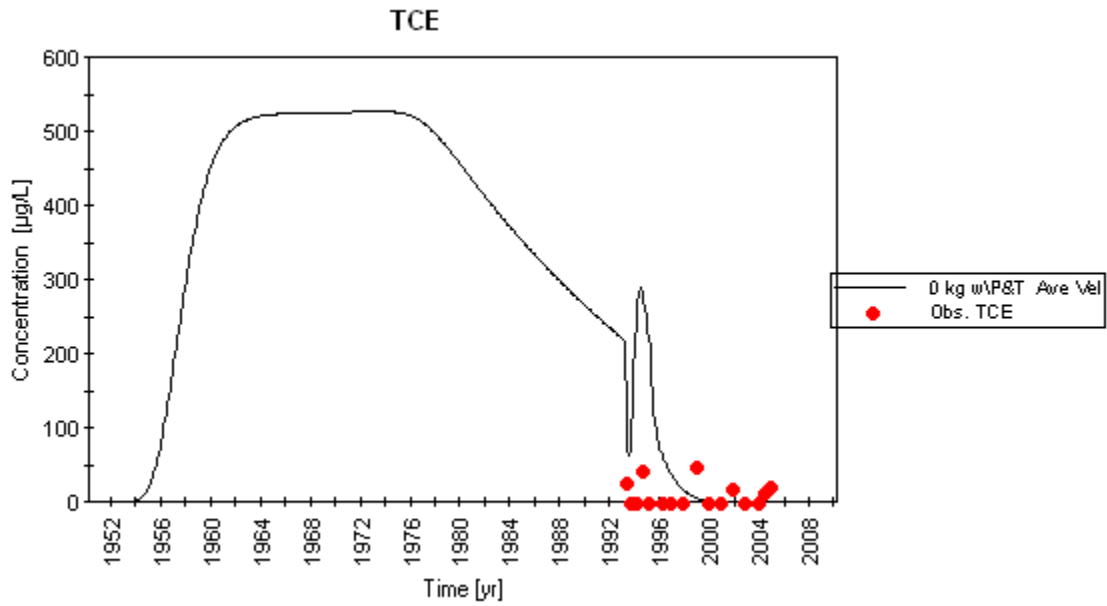


Figure 7-12. NAS-calculated vs. observed TCE at Well EW-3

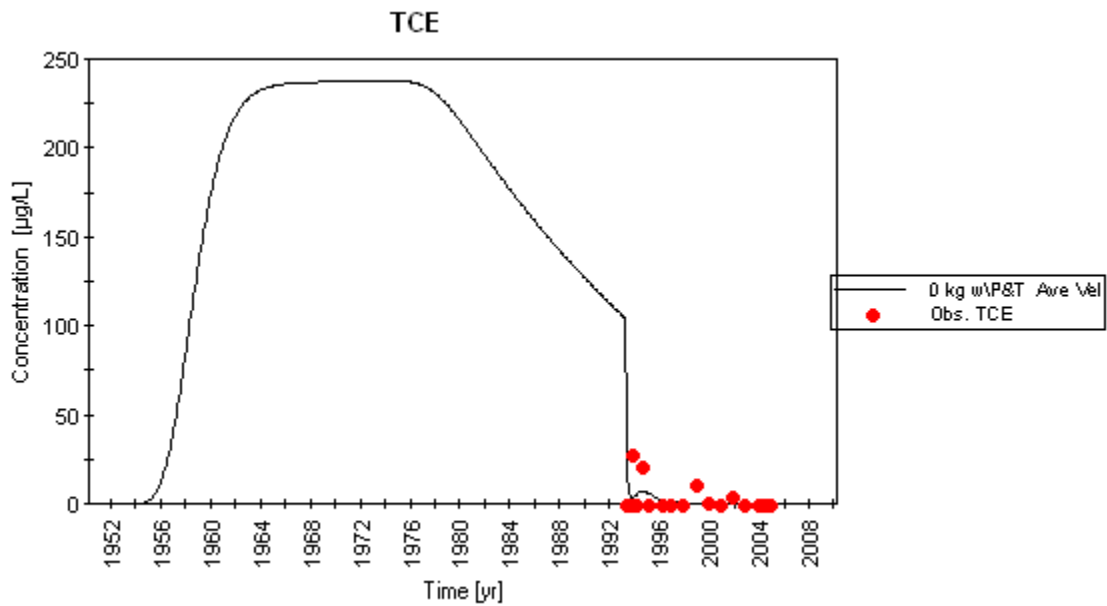


Figure 7-13. NAS-calculated vs. observed TCE at Well EW-4



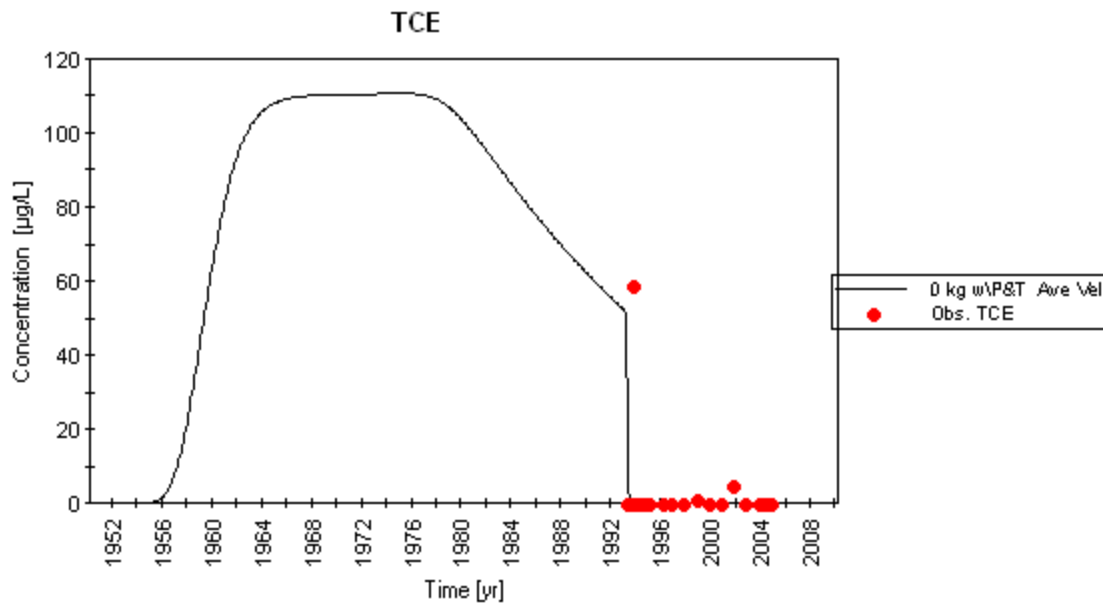


Figure 7-14. NAS-calculated vs. observed TCE at Well EW-5

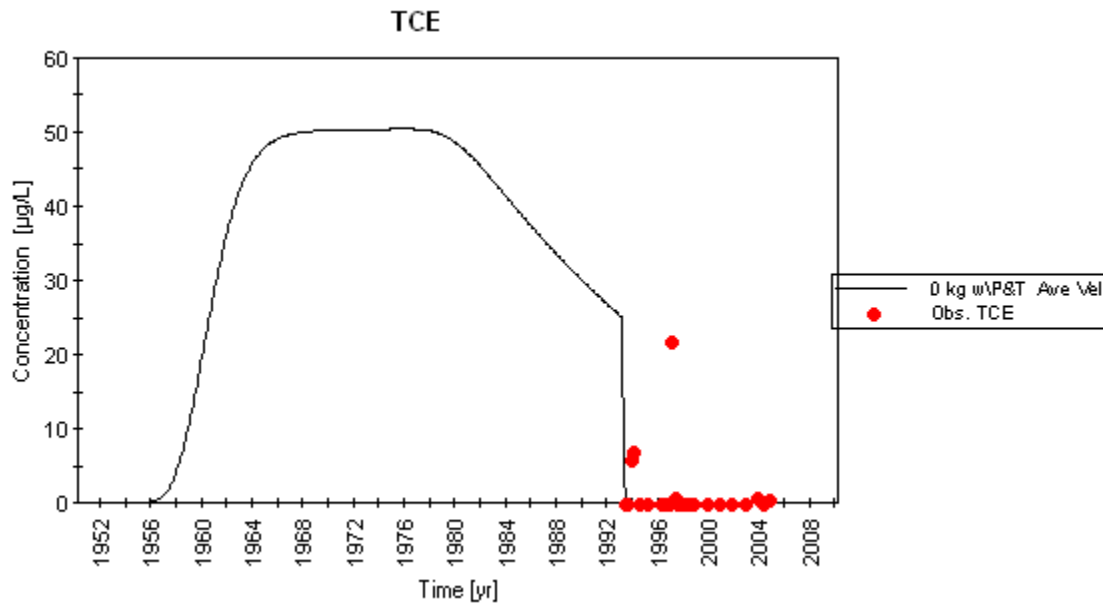


Figure 7-15. NAS-calculated vs. observed TCE at Well EW-6

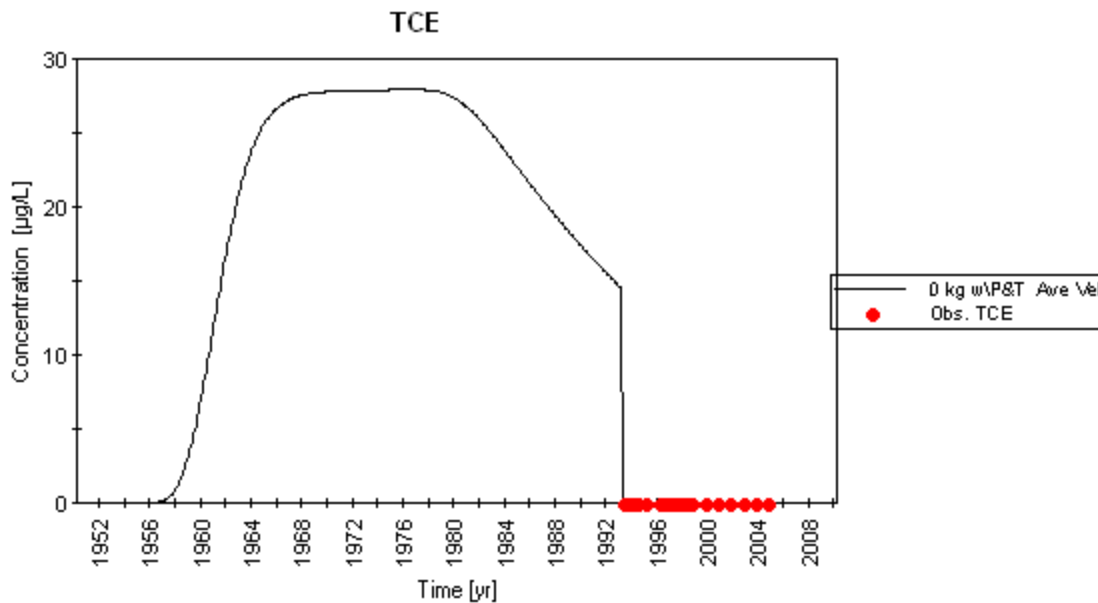


Figure 7-16. NAS-calculated vs. observed TCE at Well 93-03(1)

### 7.3.3 Assessing the Sustainability of MNA

MNA is often considered as part of a remediation strategy that may be required to operate over relatively long timeframes. It has become a priority of regulatory agencies to better understand and evaluate the long-term sustainability of MNA processes. With this goal, the U.S. Geological Survey, Virginia Polytechnic Institute and State University, and Oak Ridge National Laboratory, have collaborated on a Strategic Environmental Research and Development Program (SERDP) project to develop a methodology for assessing the efficiency and sustainability of MNA (Chapelle et al. 2007). The methodology centers on assessing the balance between contaminant generation and attenuation, and includes three general principles that can be used to evaluate the short- and long-term sustainability of MNA:

- Using a computer model to estimate the time required for contaminants to attenuate in the subsurface under ambient conditions.
- Estimating the energy (e.g., organic carbon) required for the biodegradation reactions to completely degrade the contaminants.

- Comparing the required amount of energy to the amount of energy source in the subsurface, given the estimated time of remediation.

An enhanced version of SEAM3D (Sequential Electron Acceptor Model, 3 Dimensional) is currently being developed to more appropriately facilitate this methodology. The model will consider a complete mass balance assessment of required electron donors (e.g., organic carbon) and acceptors (e.g., chloroethene), and assess the sustainability based on contaminant generation and attenuation, and availability of reaction-sustaining energy. Upon completion of the software enhancements and testing, the revised SEAM3D version and the MNA sustainability methodology may then be incorporated into NAS. This new NAS functionality will provide site managers and regulator with the ability to determine, based on sustainability assessment, whether MNA may be an appropriate part of the remediation strategy.

#### **7.3.4 Expanded Time of Remediation Options**

Based on input from current users, it would appear that additional options for manipulating TOR estimates would prove valuable. This can be accomplished by interconnecting the modules of NAS such that the interaction of input and output between each module may be improved. NAS may be modified so that the user may input a desired SCC or TOD and NAS will determine how much source contaminant mass needs to be removed for the TSC module, and then automatically estimate the TOS. As well, NAS may be modified so that the user may input the RCC or TOS at a specified POC and NAS will use the target source concentration to automatically calculate the necessary TOD. If the pump-and-treat module is being used, all components of TOR (i.e., TOS and TOD) may compare stand-alone MNA with that of incorporating the pumping well field, based on the different attenuation capacities of each scenario.

#### **7.3.5 Post-Audit Data Analysis**

Post-audit data analysis functions of NAS are expected to be expanded, and may include: evaluation of predicted versus observed inflection points, as well as predicted versus observed slope, along the transient source-reduction breakdown (C vs. T) curves in the TOS/DOS module; evaluation of predicted versus observed slope along the transient NAPL-dissolution breakdown (C vs. T) curves in the TOD module. Creation of an algorithm for optimizing NAS parameters, based on user-defined timeframe estimates, with automated interaction between each module;

and documentation of levels of confidence for determination of uncertainty in natural attenuation rates and remediation timeframe estimates.

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## Appendices

## **Appendix A: NAS User's Guide**

# **NATURAL ATTENUATION SOFTWARE (NAS)**

## **User's Manual**

### **Version 2**

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# **NATURAL ATTENUATION SOFTWARE (NAS)**

## **User's Manual**

### **Version 2**

by

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## **DISCLAIMER**

NAS is made available on an as-is basis without guarantee or warranty of any kind, expressed or implied. The US Navy, USGS, Virginia Tech, any of the authors accept no liability resulting from the use of NAS or its supporting documentation. Implementation of NAS and interpretation of the predictions of the model are the sole responsibility of the user.

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## ***Introduction***

### **Purpose and Scope**

Natural Attenuation Software (NAS) is a screening tool to estimate remediation timeframes for monitored natural attenuation (MNA) to lower groundwater contaminant concentrations to regulatory limits, and to assist in decision-making on the level of source zone treatment in conjunction with MNA using site-specific remediation objectives.

NAS is designed for application to ground-water systems consisting of porous, relatively homogeneous, saturated media such as sands and gravels, and assumes that groundwater flow is uniform and unidirectional. NAS consists of a combination of analytical and numerical solute transport models. Natural attenuation processes that NAS models include advection, dispersion, sorption, non-aqueous phase liquid (NAPL) dissolution, and biodegradation. NAS determines redox zonation, and estimates and applies varied biodegradation rates from one redox zone to the next. NAS models are implemented in three main interactive modules to provide estimates for:

1. **Required Source Reduction:** target source concentration required for a plume extent to contract to regulatory limits (i.e., **Distance of Stabilization (DOS)**),
2. **Time of Stabilization (TOS):** time required for a plume extent to contract to regulatory limits after source reduction.
3. **Time of Remediation (TOR):** time required for NAPL contaminants in the source area to attenuate to a predetermined target source concentration, and

With the successful development of the initial version of NAS and application of NAS to several contaminated sites, several critical needs had been identified. Software enhancements have been implemented to improve NAS and maximize its utility for site managers. Including general operational and functional revisions, NAS has expanded source contaminant specification options to include chlorinated ethanes, chlorinated



methanes, and chlorinated benzenes, and to allow for the analysis of any other user-defined contaminants that may be subject to microbially-mediated transformations (e.g., heavy metals, radioisotopes). Included is the capability to model co-mingled plumes, with constituents from multiple contaminant categories. To enable comparison of remediation timeframe estimates between MNA and specific engineered remedial actions (ERAs), NAS was modified to incorporate an estimation technique for timeframes associated with pump-and-treat remediation technology for comparison to, or in conjunction with, MNA. NAS is now able to model sites with existing or proposed pumping wells, based on user-specified site hydrogeologic and source data. NAS also includes expanded analysis tools for improved performance assessment. Sustainability of natural attenuation processes over time may also be assessed. Users may analyze historically successive, site-measured, contaminant concentration and redox indicator data, to allow for comparisons of NAS-predicted versus observed trends, and to monitor changes in natural attenuation capacities and redox conditions over time.

### **Minimum Site Data Requirements**

First, detailed site information about hydrogeology, redox conditions, and contaminant concentrations must be entered. Table A-1 provides a summary of the basic site data required by NAS. NAS is primarily designed as a screening tool early in the remedial strategy selection process following completion of site investigation and characterization. If the data NAS requires is not available, then time of remediation estimates can not and should not be made. However, another use of NAS is to reveal site data deficiencies that can be addressed during the remedial strategy selection process and to develop monitoring strategies.

**Table A-1. Summary of Basic NAS Site Data Requirements**

<b>Hydrogeology</b>	<b>Required</b>
Hydraulic conductivity	Best estimate, maximum, minimum values
Hydraulic gradient	Best estimate, maximum, minimum values
Weight percent organic carbon	Best estimate, maximum, minimum values
Total Porosity	Best estimate
Effective Porosity	Best estimate
Contaminant source width	Best estimate
Contaminant source length	Best estimate
Average saturated thickness impacted by contamination	Best estimate
<b>Redox Indicators</b>	
Concentration: Dissolved oxygen, Ferrous iron, Sulfate	Values from 1 or more wells along the solute plume centerline
(Optional) Concentration: Nitrate, Mn(II), Sulfide, Methane, Dissolved hydrogen	Values from 1 or more wells along the solute plume centerline
<b>Contaminant</b>	
Concentration: Contaminant	Values from 2 or more wells along the solute plume flow path

### **Overview of the NAS Interface**

Figure A-1 shows a flowchart describing how the NAS software can be used to address time of remediation questions. After data entry, NAS estimates site-specific groundwater flow rates, biodegradation rates, and sorption properties. Based on the range of estimates, NAS then produces either analytical or numerical solutions of the TOR equation. One option employs analytical solutions to determine the target reduction in the source area concentration to meet site-specific remediation goals. This approach and solution addresses plume concentration questions, such as what is the distance of stabilization for given source-area contaminant concentrations, and what is the time of

stabilization if source-area concentrations are changed. For the distance of stabilization question, NAS calculates the allowable maximum source-area concentration, based on a regulatory maximum concentration level at a given point downgradient of the source. Then, NAS estimates how long it will take for the plume to reach the lower steady-state configuration once source-area concentrations have been lowered by engineering methods. Once both the distance of stabilization and the time of stabilization are acceptable, based on site-specific regulatory criteria, MNA can become an integral component of site remediation.

The other option is a mass-based approach to determine the target reduction in the source area NAPL or residual mass to reduce the TOR based on site-specific remediation goals. To achieve this solution, NAS uses the SEAM3D code (Waddill and Widdowson, 1998) to solve the solute transport equation in conjunction with a groundwater flow code (MODFLOW). The solution provided by NAS is tailored to estimate the length of time required by a given NAPL mass to dissolve and lower contaminant concentrations at the source area below a given user-supplied threshold.

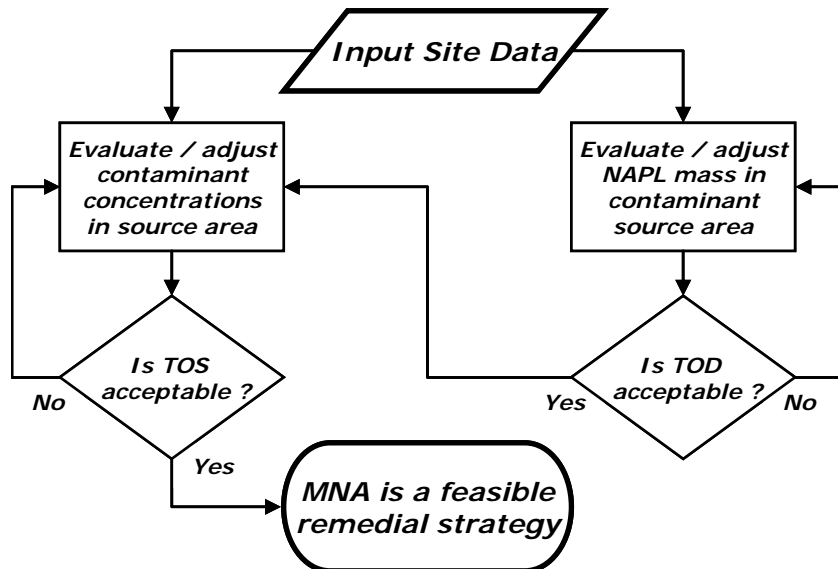


Figure A-1. Flow Chart for the Application of NAS

## Getting Started

### Installation

To install NAS, click on the 'setup.exe' file and follow the instructions given. NAS has been designed to run in Windows operating systems.

Once NAS has been installed, the program may be started by clicking on the 'Start Button' (located at the lower left of the computer screen), then pointing to the 'Programs' folder, the 'Natural Attenuation Software' Subfolder, and finally the NAS program file. This procedure is shown in Figure A-2 for a computer system running WindowsXP.

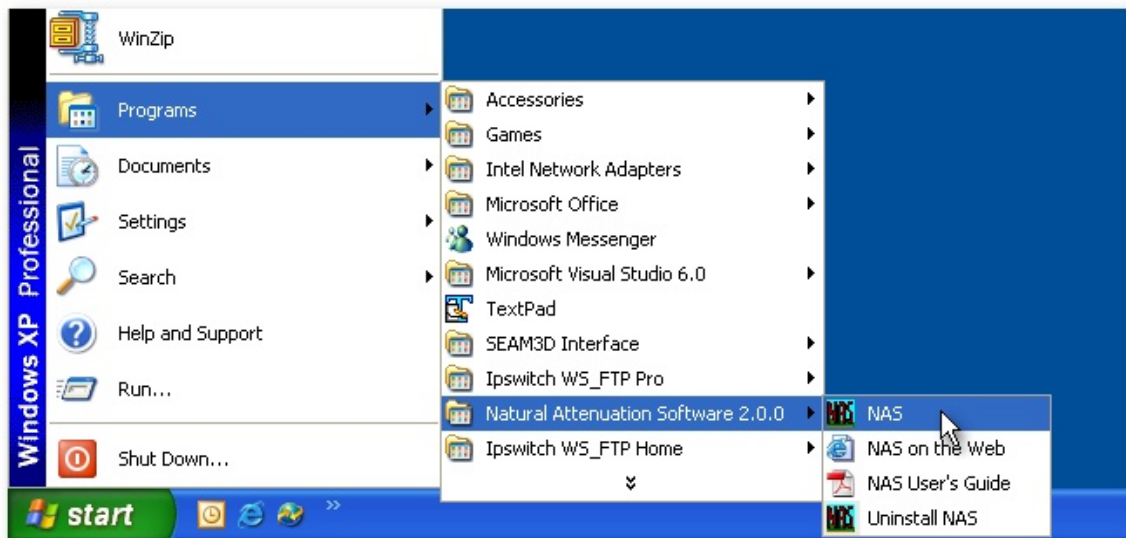


Figure A-2. NAS from Start Button

### Description of Program Directory

This section describes the Program Directory installed by the NAS setup program. Folders and files in the NAS Program Directory include:

**Documentation:** This directory stores the NAS User's Guide and any other Help documentation that may be distributed by a future version of NAS.

**Tutorials:** This directory stores the example NAS project files referenced by the NAS software. New tutorial files may be distributed to this folder by a future version of NAS.

**Program Executables:** ‘NAS.exe’ and ‘NASShell.exe’ are the main program executables and should not be removed from the directory.

**Contaminant Database:** ‘NASDB.unf’ and ‘NASDBDefault.unf’ are the NAS contaminant database files, in binary format, and should not be accessed/edited by the user. NAS can export/import this database to/from Excel format as will be discussed in a later section.

**Program Support Files:** ‘LF90.EER’, ‘Olch2d-u.cnt’, and ‘Olch2d-u.hlp’ are support files necessary for the proper functioning of NAS and should not be removed from the directory.

For proper functioning of NAS, all folders and files mentioned in this section should not be removed or changed. NOTE: It is also advised to not save NAS Project Files (\*.nas) in the NAS Program Directory; save them in separately created directories instead.

## **Navigating the Main Menus**

The first NAS screen shown after clicking on the NAS Program File is the main NAS working window with the Menu shown in Figure A-3. The NAS Main Menu allows the user to either perform various file operations or to enter one of the NAS program functions. Main Menu items include file operations (File), site data entry (Site), Source Concentration Reduction, and Distance/Time of Stabilization calculations (DOS/TOS), Time of Remediation calculations (TOR), tabular and graphical output of site data and results (Output), functions for managing program windows (Window), and NAS documentation and support (Help).

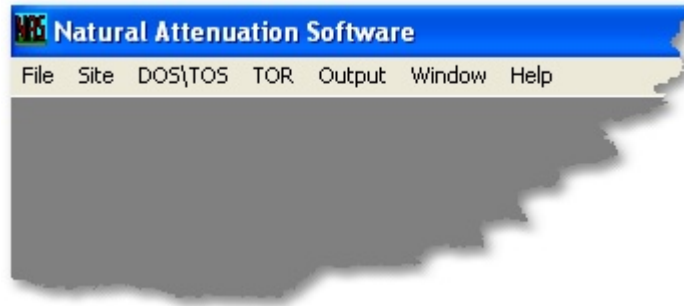


Figure A-3. NAS Main Menus

## File

The file operations available to NAS are shown in Figure A-4.

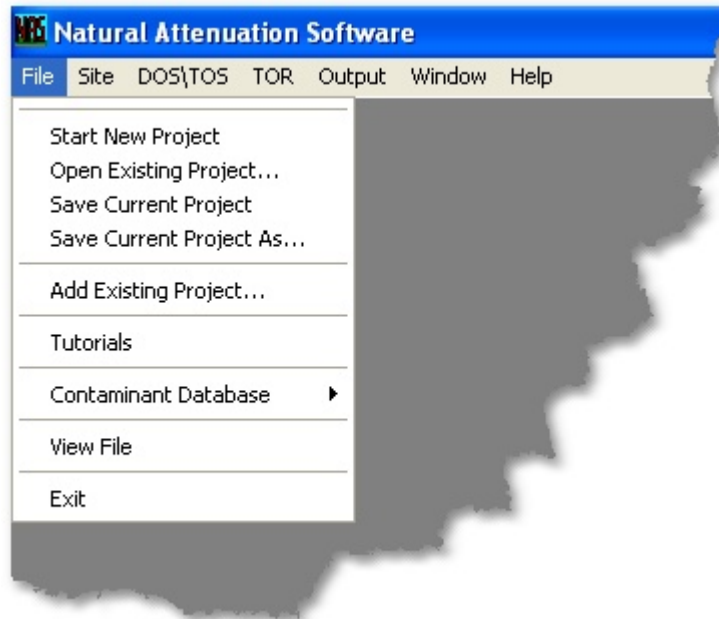


Figure A-4. File Menu

### *Start New Project*

To start a new project, open NAS and select the ‘Start New Project’ menu item. This action will take you to the ‘General Tab’ of the ‘Site Data’ Form. This form will be discussed in greater detail in a following section.

### *Open Existing Project*

To open an existing project, open NAS and select the ‘Open Existing Project’ menu item. A standard Windows file open dialog box will appear, in which you may select the drive

and directory where the NAS input file is listed. Note that the default naming convention for NAS project files is \*.nas. The input format for this file is shown in Appendix . Users familiar with the format may manually edit \*.nas files. Any \*.nas file may also be automatically opened in NAS by double-clicking the file in a Windows explorer window. This action will take you to the ‘General Tab’ of the ‘Site Data’ Form. This form will be discussed in greater detail in a following section.

### ***Save Current Project (As)***

To save a project currently loaded in NAS, select the ‘Save Current Project As’ or ‘Save Current Project’ menu item. Selecting the ‘Save Current Project As’ menu item will open a standard Windows file save dialog box. The current project is saved to the directory specified by the user by typing a name in the File Name field and clicking the Save Button. Clicking the Cancel button on the save dialog will take the user back to the NAS Main Menu screen without saving changes. Selecting the ‘Save Current Project’ menu item will save the project to the current specified \*.nas file. If filename has not yet been specified, the ‘Save Current Project As’ function will be implemented.

### ***Add Existing Project***

To add the contaminant and redox indicator profile data sets from an existing \*.nas file to the currently loaded \*.nas file, select the ‘Add Existing Project’ menu item. NAS will automatically parse the additional data sets into the current projects contaminant and redox data set lists.

### ***Contaminant Database***

For data management and reporting purposes, NAS provides a database of contaminant sources that may be managed by the user, and may be accessed by selecting the ‘Contaminant Database’ menu item shown in Figure A-5.

### **Export To Excel**

Selecting the ‘Export to Excel’ sub-item opens a Microsoft Excel file listing all contaminant sources that are currently stored by NAS. The format for this file is shown in

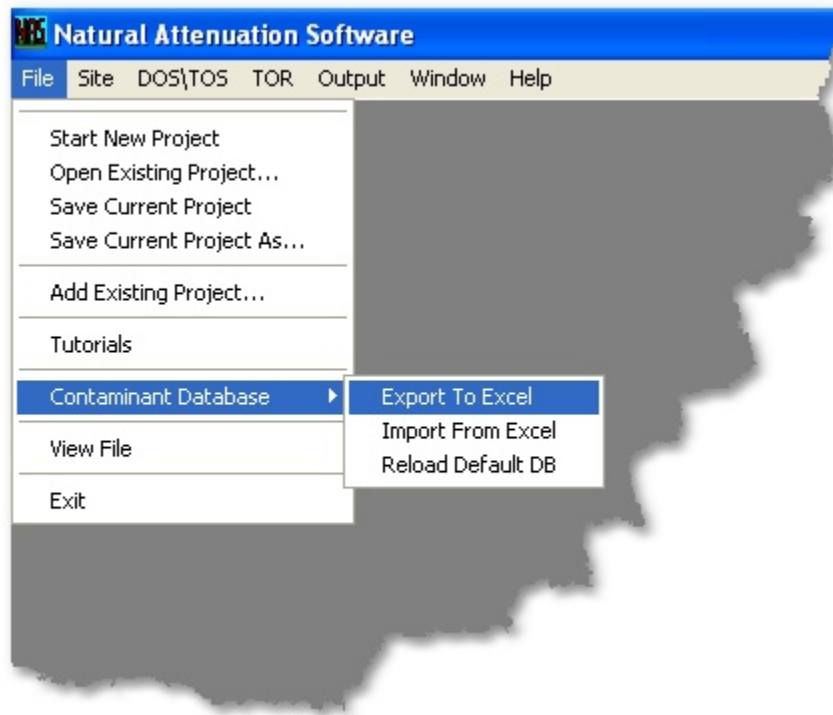
Appendix . The database file is saved as ‘NASContDB.xls’ in the NAS Program Files directory.

### **Import From Excel**

Users familiar with the format may manually edit the database file (e.g., adding additional contaminants groups) and then import it back into NAS. The user is advised to first make a backup copy before editing the database file.

### **Reload Default Database**

If users develop errors in their database, or simply wish to revert back to the original database supplied with the current version of NAS, the user may select the ‘Reload Default DB’ sub-item.



**Figure A-5. File – Contaminant Database Menu**

### ***Tutorials***

NAS provides the user with example \*.nas files in a ‘Tutorials’ directory in the NAS Project Files directory. To view a tutorial file, open NAS and select the ‘Tutorials’ menu item. A standard Windows file open dialog box will appear, in which you may select one



of the example files in the ‘Tutorial’ directory. This action will take you to the ‘General Tab’ of the ‘Site Data’ Form. This form will be discussed in greater detail in a following section.

### File View

NAS provides the user with a Microsoft Notepad-style file viewer shown in Figure A-6. To view a text file, the user may select ‘View File’ menu item. A standard Windows file open dialog box will appear, in which you may select any text file (e.g., \*.nas). You then have full Notepad functionality and may view, edit, change, and save the file.

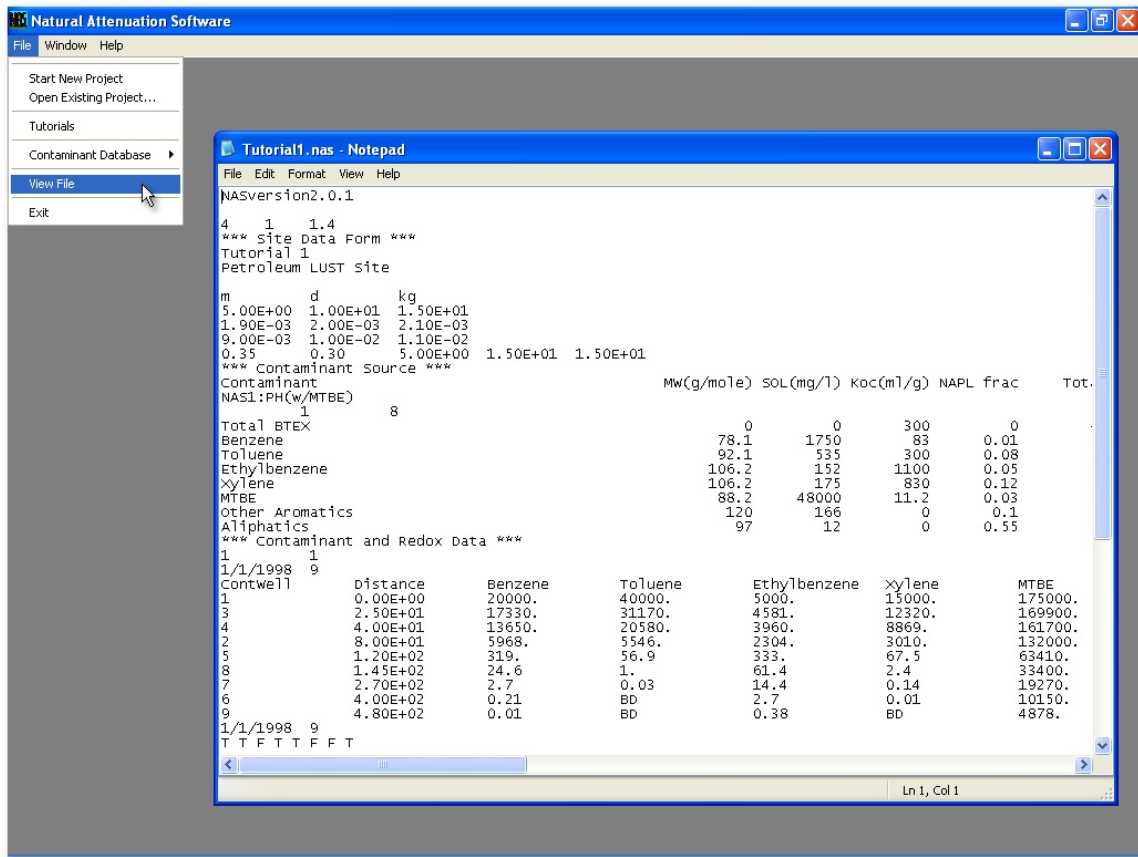


Figure A-6. Notepad-Style File Viewer

### Exit

Selecting the ‘Exit’ menu item will close NAS. If the user attempts to exit NAS without first saving the current project, NAS will prompt the user (via an informational message box) to make sure the user wishes to exit the project without saving changes.

## Windows

The 'Windows' menu, shown in Figure A-7, enables the user to arrange multiple forms within the main NAS Window. The lower part of the menu allows navigation to any NAS form open in the main Window.

### *Cascade*

Select the 'Cascade' menu item to cascade all nonminimized forms.

### *Tile*

Select the 'Tile' menu item to tile all nonminimized forms horizontally.

### *Arrange Icons*

Select the 'Arrange Icons' menu item to arrange all minimized form icons.

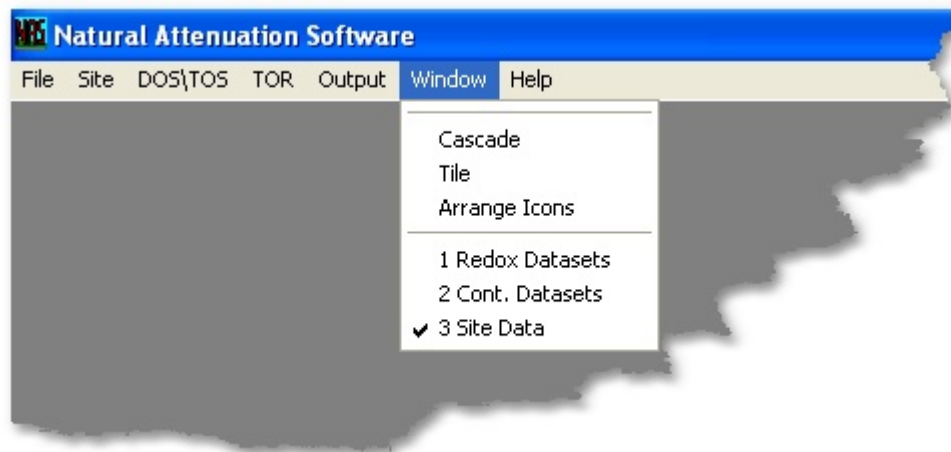


Figure A-7. Window Menu

## Help

NAS Help topics and useful information can be accessed through the 'Help' menu. See Figure A-8 and Figure A-9.

### *Documentation*

The user may view the NAS User's Guide, and any other useful documentation that may become available, by selecting the 'Documentation' menu. See Figure A-8.

## NAS on the Web

The user may access the website developed to support NAS, by selecting the ‘NAS on the Web’ menu item. See Figure A-8.

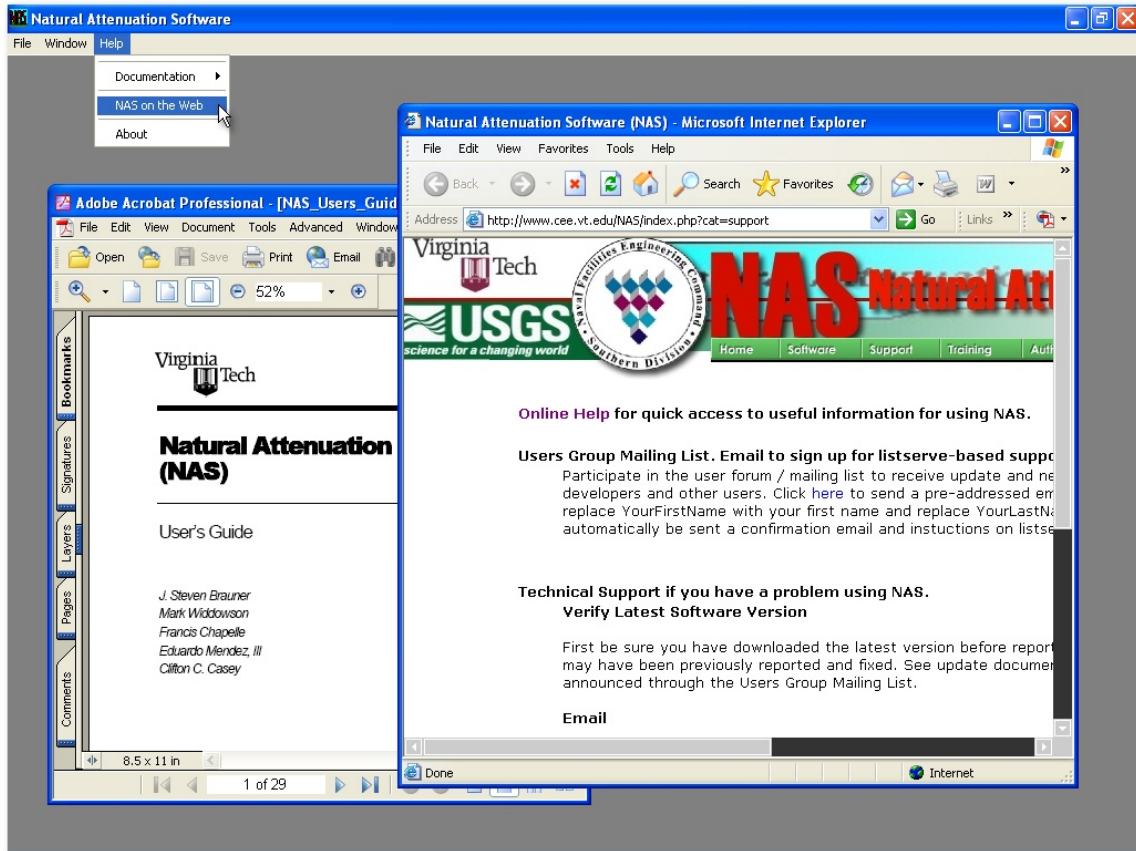


Figure A-8. NAS Help

## About

The ‘About’ menu item allows the user to review information about the authors, their contact information, and the current version of NAS. A ‘System Information’ button may also be clicked to provide system information that may be useful if it is ever necessary to contact NAS Technical Support. See Figure A-9.

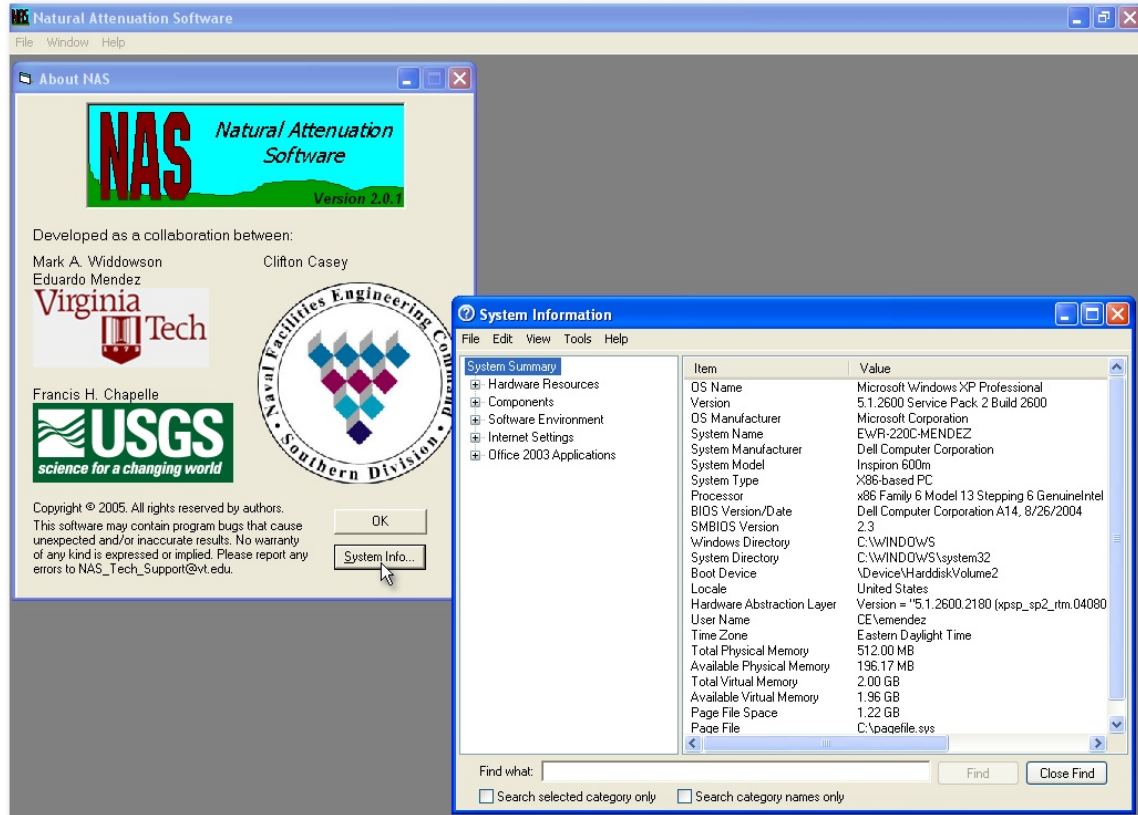


Figure A-9. About NAS and System Information Screens

## Site Data Assessment

### Navigating the Site Data Window

Site data, including hydrogeologic parameters, contaminant source delineation and characterization, monitoring well locations, and concentrations of both contaminants and redox indicators, is entered using the Site Data form. The user is presented with a series of questions that are answered by the user via option buttons, check boxes, text boxes, or data entry. The user is required to enter all requested site data before performing any data analysis or source reduction/time of stabilization (DOS/TOS) or time of remediation (TOR) calculations (Note that the DOS/TOS and TOR program functions are disabled by NAS until all required site data has been entered.). Furthermore, the user is required to enter all requested data on a particular tab prior to NAS displaying the Next button that allows the user to proceed to the next tab. The user can always go back to change data that has been entered previously (by clicking on the appropriate tab to display the desired

data entry field), but can not proceed to a new tab until all required information has been provided on the preceding tab.

To enter the site data entry window, start a new project or open an existing project, and then click on 'Site' menu on the NAS Main Menu screen. NAS automatically disables any tabs in which the user has not previously entered data.

## **Data Entry**

### **General Data**

The Site Data – General Tab prompts the user to (1) enter descriptive text for the identification of a particular site and (2) select units of measurement. See Figure A-10.

Site Identification. Data entry for the descriptive text consists of a Facility Name, Site Name, and Additional Description for the new project. NAS does not require the user to enter information for any of these entries, as they are solely there for the benefit of the user in identifying a particular site or simulation.

**Facility Name:** User-specified text. Format: Character (up to 50 places). (Optional)

**Site Name:** User-specified text. Format: Character (up to 50 places). (Optional)

**Additional Description:** User-specified text. Format: Character (up to 50 places). (Optional)

Units Specification. NAS requires specification of units of measurement for length, mass, and time by choosing the appropriate option buttons. The selection of units of measurement will affect both the units displayed on screen for the various input and output variables used in NAS and any calculations based on empirical relationships that are unit-specific. The user should be careful to assure that values for all input variables are in the units specified by NAS. Failure to specify input values in the correct units may lead to erroneous calculations.

**Length:** User choice of meters or feet. Format: Option Button. (Required)

**Mass:** User choice of kilograms or pounds. Format: Option Button. (Required)

**Time:** User choice of days or years. Format: Option Button. (Required)

**Concentration:** NAS uses default units for concentration, as specified throughout the NAS interface.

The screenshot shows a software window titled "Site Data" with a blue header bar. Below the header is a tabbed interface with five tabs: "General", "Hydrogeology", "Contaminants", "Contaminant Data", and "Redox Indicator Data". The "General" tab is active. The main content area is light beige and contains three numbered sections:

- 1. Enter the site name and any additional text you would like to use to describe your site.**
  - Facility Name:
  - Site Name:
  - Additional Description:
- 2. Choose the units for your site:**
  - Length:  meters  feet
  - Mass:  kilograms  pounds
  - Time:  days  years
- 3. Concentration:**

Units for contaminant and redox indicator concentrations are fixed in NAS. Concentration units will be indicated by NAS on each relevant screen.

An "Update" button is located in the bottom right corner of the form area.

**Figure A-10. Site Data – General Tab**

## Hydrogeology

The Site Data – Hydrogeology Tab prompts the user to (1) enter values for hydrogeologic and aquifer properties and (2) delineate the contaminant source zone. See Figure A-11.

NAS requires the user to enter the values for hydraulic conductivity, hydraulic gradient, weight percentage of organic carbon, porosity, and aquifer thickness. For the first three parameters, the user may enter a high, best, and low estimate. If a range of values is not available, enter the best estimate for all fields of each parameter. Note that NAS does not check the magnitude of these entries to insure that the user has entered these values in the correct order, so the user should take care to enter this data correctly. Hydraulic conductivity and hydraulic gradient values are used with the user specified porosity to calculate the high, best, and low estimate for groundwater velocity. These values are used to calculate high, average, and low first-order contaminant decay rates. The weight percent organic carbon values are used to calculate a range of distribution coefficients and retardation factors for each contaminant.

**Hydraulic Conductivity:** User entry of high, best, and low estimates. Format: Number greater than zero. (Required)

**Hydraulic Gradient:** User entry of high, best, and low estimates. Format: Number greater than zero. (Required)

**Weight % Organic Carbon:** User entry of high, best, and low estimates. Format: Number greater than zero. (Required)

**Total Porosity:** User enters best estimate. Format: Number greater than zero and less than one. (Required)

**Effective Porosity:** User enters best estimate. Format: Number greater than zero and less than one. (Required)

NAS requires the user to delineate the contaminant source zone by enter an estimate for the contaminant source length, width, and thickness. The width estimate is used in the 2-D analytical solutions for determining the concentration at a downgradient point based on

a reduction in the source concentration, and the time of stabilization estimates. All three estimates are used in the 3-D numerical solution for time of remediation.

**Source Length:** User enters best estimate. Format: Number greater than zero. (Required)

**Source Width:** User enters best estimate. Format: Number greater than zero. (Required)

**Contaminated Aquifer Thickness:** User enters best estimate. Format: Number greater than zero. (Required)

1. Enter the following hydrogeologic and aquifer properties.

	Maximum	Average	Minimum	Average
Hydraulic Conductivity [m/d]	15.0	10.0	5.0	Total Porosity [m <sup>3</sup> /m <sup>3</sup> ] 0.35
Hydraulic Gradient [m/m]	0.0021	0.002	0.0019	Effective Porosity [m <sup>3</sup> /m <sup>3</sup> ] 0.3
Weight Percent Organic Carbon [%]	0.011	0.01	0.009	

Source Length (SX) [m]	15.0
Source Width (SY) [m]	15.0
Contaminated Aquifer Thickness (SZ) [m]	5.0

Update

Figure A-11. Site Data – Hydrogeology Tab

## Source Contaminants

The Site Data – Contaminants Tab prompts the user to (1) specify the contaminant source constituents, and (2) specify values for contaminant properties required by NAS for the analytical and numerical solutions. See Figure A-12.



The window on the left side of the form lists the contaminant groups available in the database. A following section of this document will describe how the user may manage the database, including editing existing groups as well as creating new user-defined groups. Groups prefixed by 'NAS1' are not editable and are required for NAS2 to properly read pre-NAS2 project files. The user may define the source by selecting groups from the window on the right, and/or by creating new ones. When the user is finished defining a new source, it may then be saved in the NAS database for use in future simulations.

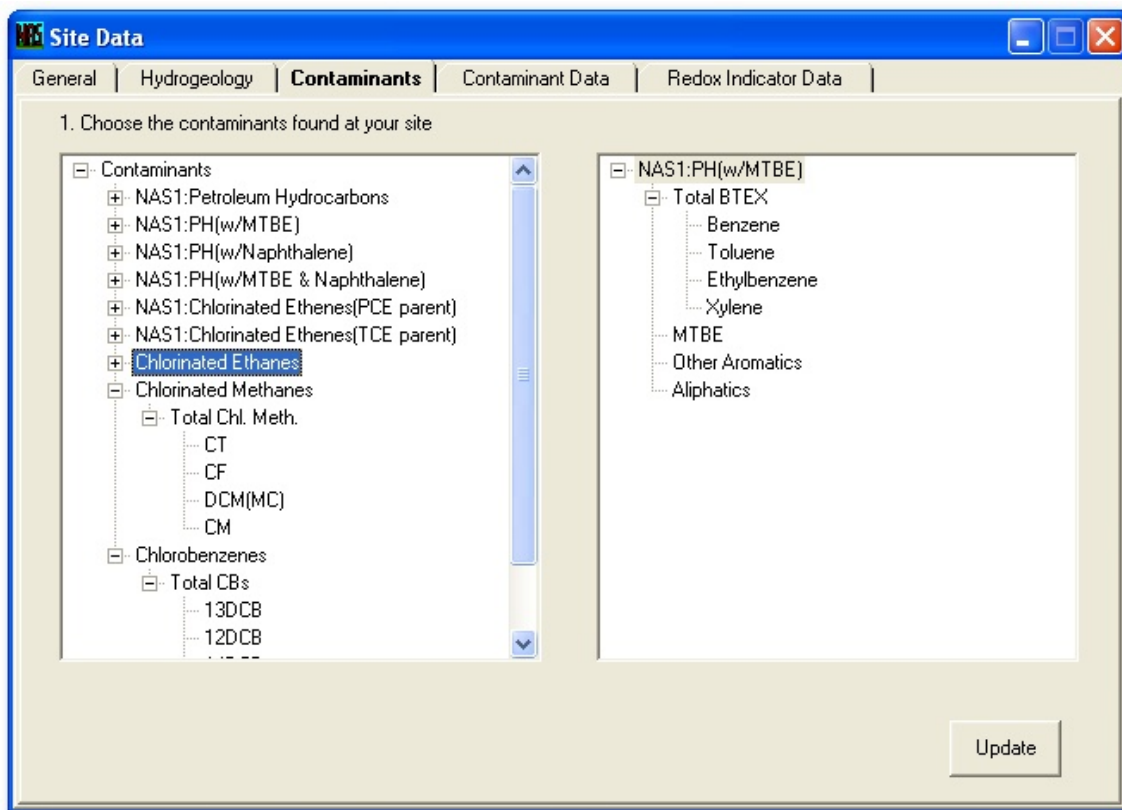


Figure A-12. Site Data – Contaminants Tab

## Contaminant Profile Data

The Site Data – Contaminant Data Tab prompts the user to (1) specify the date a contaminant profile data set was sampled, (2) specify the number of wells sampled for the data set, (3) specify the contaminant concentration profile, concentration versus

distance from source, in tabular form, and (4) manage data sets by adding or deleting wells or data sets. See Figure A-13.

NAS requires the user to enter the date the contaminant concentrations were sampled, the number of sample locations, the distance from the source to the contaminant well, and the contaminant concentration at each well. The date field, using a pop-up calendar, on the Contaminant Data tab is used to identify the data for convenience. The number of contaminant wells field is used to create the contaminant concentration data chart. The user is required to enter a number in this field when creating a new data site. The contaminant concentration data chart is then created using the Create Chart button. Note that the number of contaminant wells field disappears after the user clicks the Create Data button. If the user wishes to add or delete contaminant wells after creating the data chart, click the Add/Delete Wells button. The user may also add or delete a data set by clicking the Add/Delete DataSet button.

The contaminant data chart requires a distance from the source to the contaminant well and a contaminant concentration for each well. The distance from the source to the contaminant well should be measured from the front edge of the contaminant source and along the plume centerline. If data is unavailable for a particular contaminant at one or more wells, enter “NS” into the data chart (NS = Not Sampled). The NAS regression algorithm used to calculate Natural Attenuation Capacity (NAC) estimates for each contaminant will ‘skip’ NS entries. If a measurement is below detection, the user should enter “BD” into the data chart (BD = Below Detection). The NAS regression algorithm used to calculate NAC estimates for each contaminant will ‘skip’ BD entries if they are closer to the source than the maximum contaminant concentration, but will treat a BD entry downgradient of the maximum contaminant concentration as the furthest extent of the contaminant plume (independent of whether any above detection concentrations are entered downgradient of the BD entry). NAS does not require the user to enter a name for each contaminant well, but will store user names up to 15 places long.

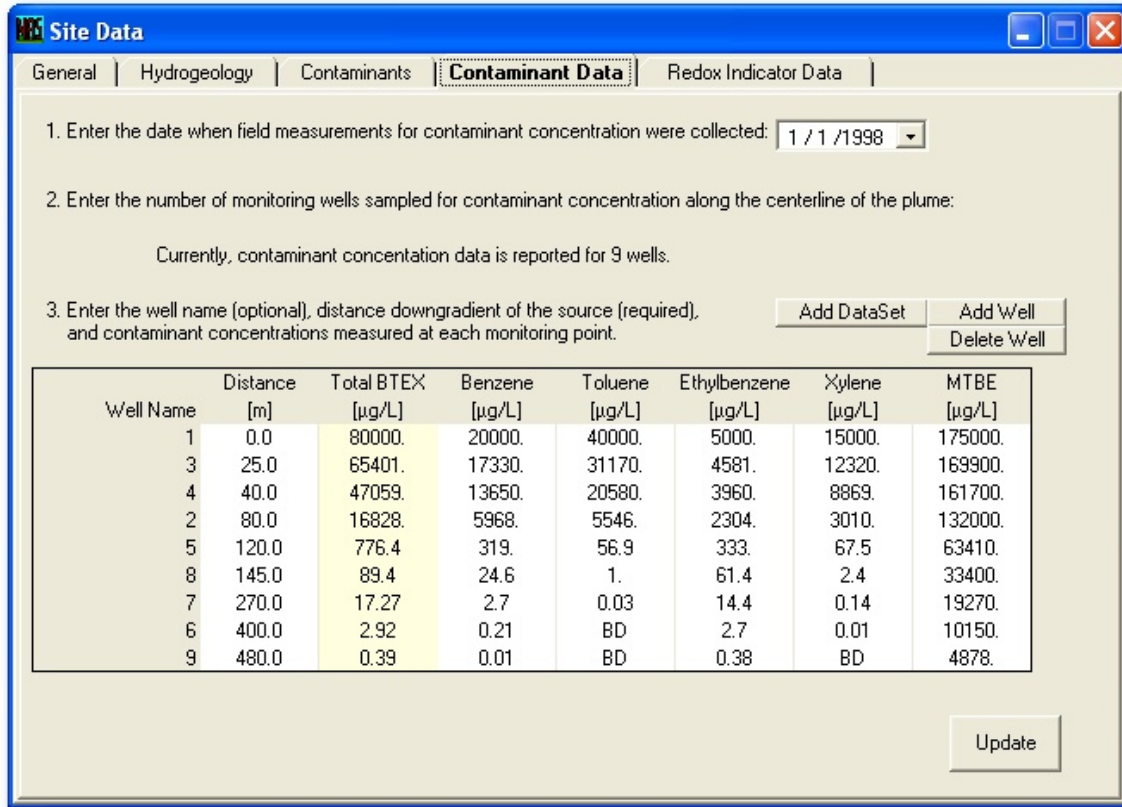


Figure A-13. Site Data - Contaminant Data Tab

## Redox Indicator Data

The Site Data – Redox Indicator Data Tab prompts the user to (1) specify the date a redox indicator profile data set was sampled, (2) specify which redox indicators were sampled for in the data set, (3) specify the number of wells sampled for the data set, (4) specify the redox indicator concentration profile, concentration versus distance from source, in tabular form, and (5) manage data sets by adding or deleting wells or data sets. See Figure A-14.

As with the Contaminant Data tab, the user is required to enter a date that the redox indicator concentrations were sampled. The user is required to enter oxygen, iron(II), and sulfate concentrations for each redox monitoring point, and may choose to enter data for nitrate, manganese(II), hydrogen sulfide, methane, or hydrogen by clicking the appropriate box on the Redox Indicator Data tab. The user must also specify the number of redox indicator monitoring points. The redox indicator monitoring points are initially

specified as being the same well set as the contaminant wells. The user may, thereafter, add or delete wells by clicking the Add/Delete Wells button, and/or manually editing well names and distances. The user may also add or delete a data set by clicking the Add/Delete DataSet button.

NAS uses the user-specified redox profile with the Flowchart in Figure A-38 in 0, to delineate the redox zones at the site. If NAS is unable to identify a redox condition, at a particular well, that is in agreement with all provided redox indicator concentrations, a 'User Specification of Redox Condition' dialog box will automatically appear and query the user for information. See Figure A-15. For the case shown in the figure, the geochemical data indicates that aquifer condition at Well 4 is sulfate/carbon dioxide-reducing, whereas the hydrogen data suggests that the aquifer is ferrogenic. Since the geochemical data is not in agreement with the hydrogen data, NAS prompts the user to decide the redox condition. The user may also manually change any pre-determined redox condition by returning to the Redox Indicator Data tab and using the drop-down menu in the 'Redox Condition' column of the table to change the condition at the desired well.

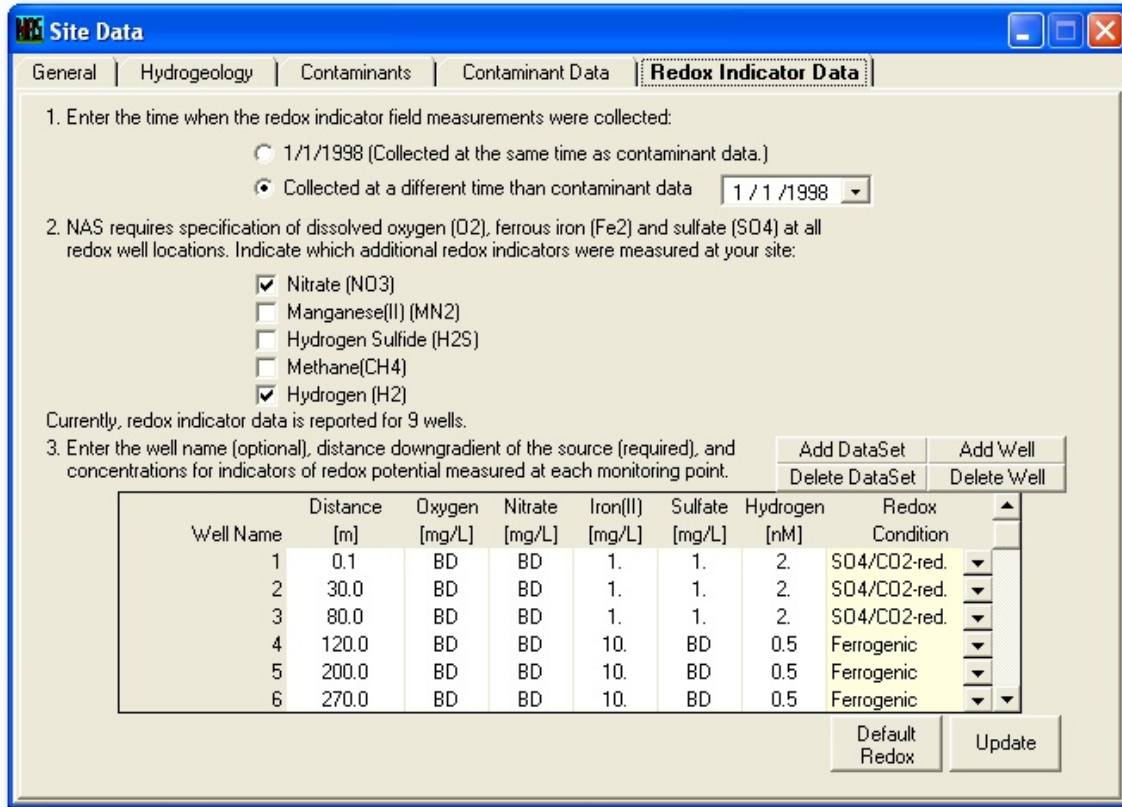


Figure A-14. Site Data – Redox Indicator Data Tab

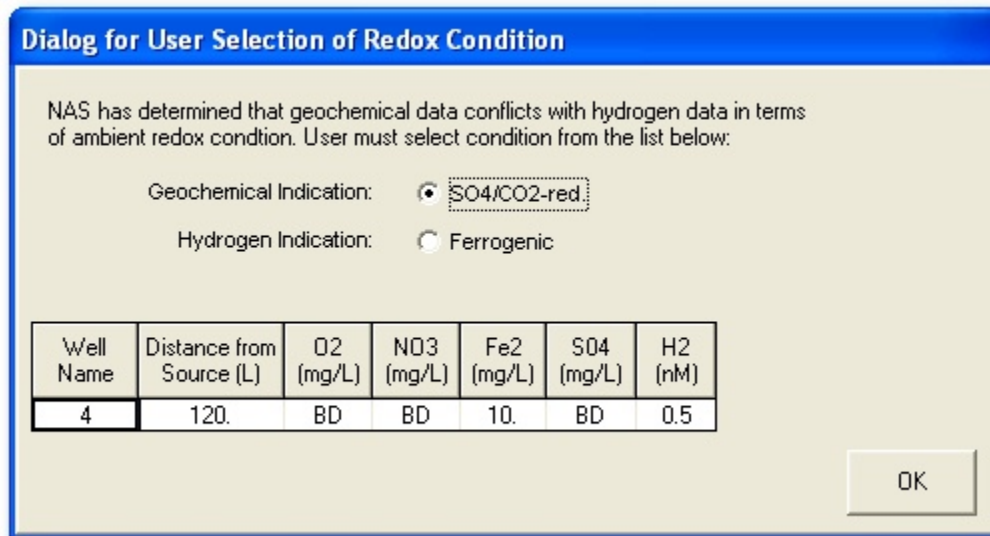


Figure A-15. Dialog Box for User Selection of Redox Condition

## Analyzing Output

### Tabular Output of Site Data

Figure A-16 contains an example of the tabular summary form that is created by NAS using the data entered in the Site Data form. NAS makes this form available if the user has progressed beyond the 'Site Data – General Tab'. The form may then be accessed through the 'Output -> Data and Results Tabular Summary' menu item. At the top of the form, a drop-down list is provided that quick-links to sections of the form. Sections include data input by the user and additional NAS-estimated values. Nas-estimated values for the table are based on the data sets currently selected in the Contaminant and Redox Dataset Lists. NAS-estimated values based on Site Data input are described as follows:

**Groundwater contaminant velocity:** Data from the Hydrogeology Tab is used to make high, best, and low estimates of groundwater contaminant velocity.

**Sorption Data:** Data from the Hydrogeology and Contaminants Tabs are used to estimate retardation factors for each contaminant.

**Redox Zonation:** Data from the Redox Indicator Data Tab is used to determine the redox zonation.

**Natural Attenuation Capacity:** Data from the Contaminant Data Tab is used to estimate Natural Attenuation Capacities (NACs) for each contaminant in each redox zone.

**Dispersivity:** Estimated NACs are used to determine the maximum plume length. This maximum plume length is then used, with a hardwired dispersivity ratio, to estimate longitudinal and transverse dispersivity values.

**Decay Rate:** Estimated NACs are used with estimated values for groundwater contaminant velocity and dispersivity to estimate decay rates for each contaminant in each redox zone.

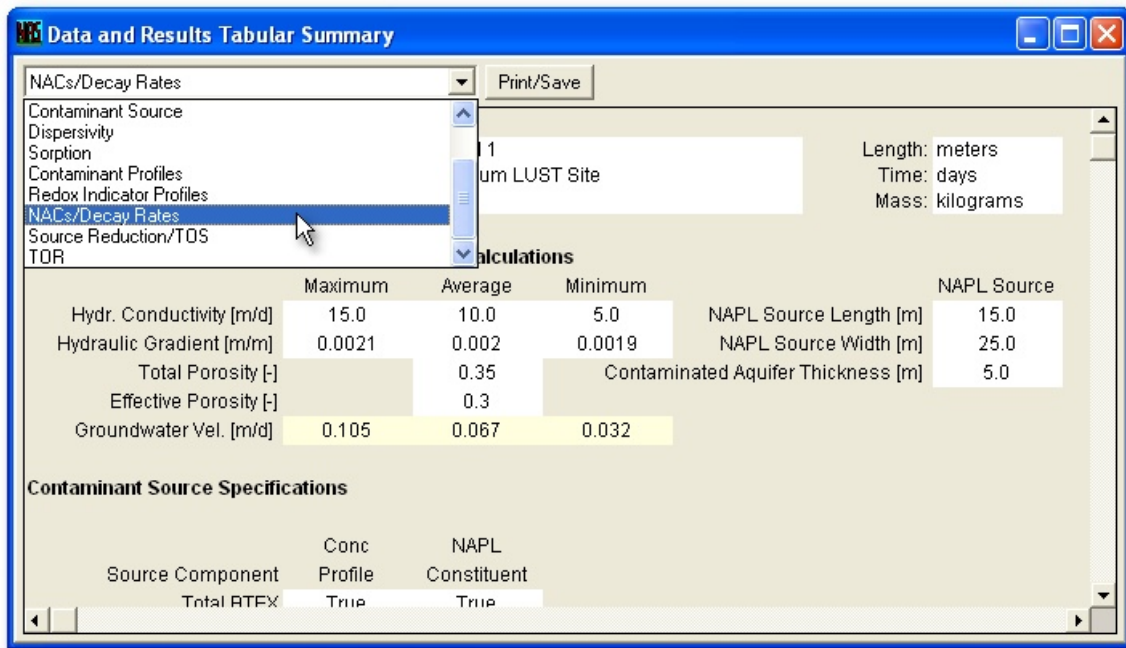


Figure A-16. Tabular Output

## Graphical Output of Site Data

Figure A-17 contains an example of the graphical summary form that is created by NAS using the data entered in the Site Data form. NAS makes this form available when all of the required Site Data information has been entered. The form may then be accessed through the 'Output -> Site Data Graphs' menu item.

The graph displays the redox condition (as a function of space) through background shading and the user-specified concentrations as dots. The user can choose which contaminant to display using the pull down menu on the left. The user also can choose whether to hide a trendline, display the best-fit trendline, or display the multi-zone model trendline using the pull down menu on the right of the Graphical Summary tab. The user may view a trendline based on the data sets currently selected in the Contaminant and Redox Dataset Lists, or view trendlines for all contaminant datasets, against the currently selected redox dataset.

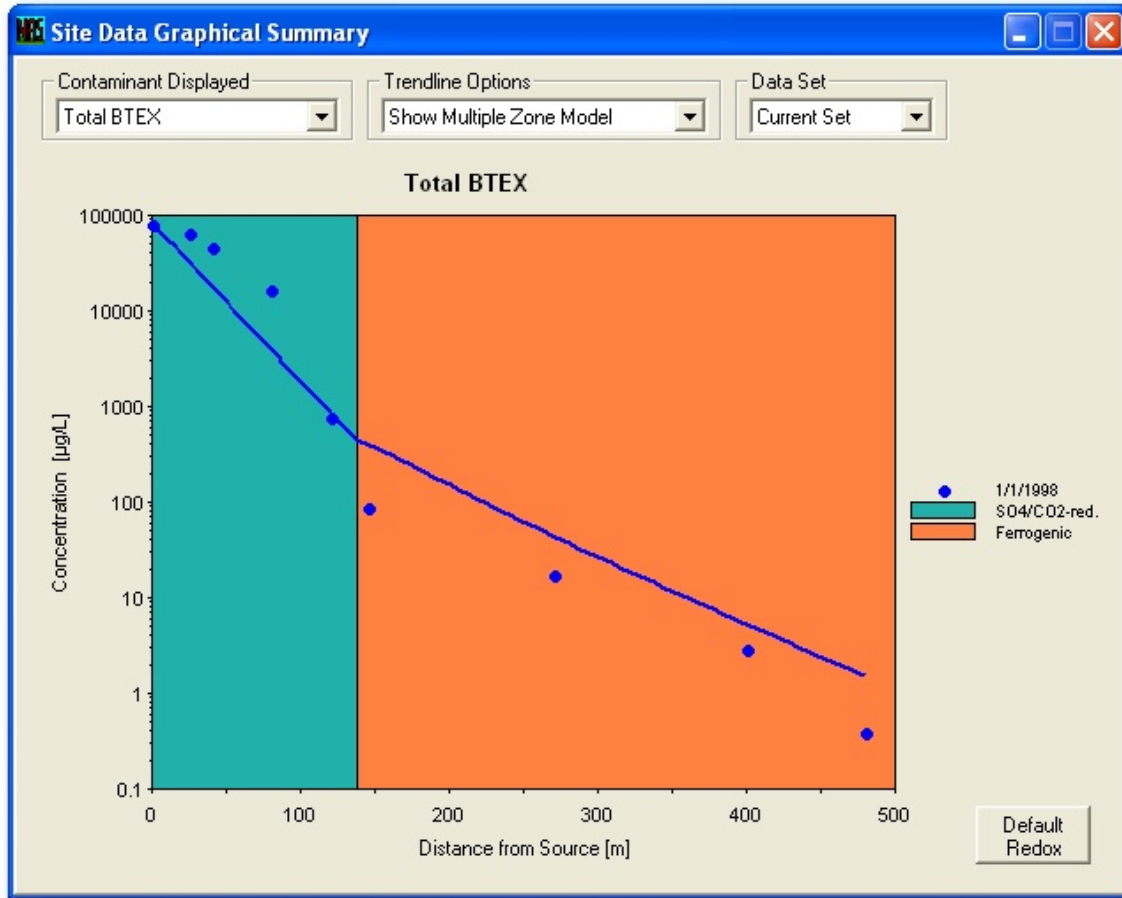


Figure A-17. Graphical Output – NAC/Redox Zonation

## Source Reduction and Time of Stabilization (DOS/TOS)

### Navigating the TOS Window

NAS enables the user to estimate the reduction in the source concentration and time of stabilization (TOS) to reach a user-specified compliance concentration at a point downgradient of the source by clicking the Source Reduction / Time of Stabilization (DOS/TOS) menu on the NAS Main Menu. The Source Reduction and Time of Stabilization form, Figure A-18, is a single window that does not require navigation, except to view the graphical solutions to a given problem.



## Data Entry

**Point of Compliance:** The Point of Compliance (POC) is defined as the closest downgradient point of contact between a receptor and the contaminant of concern (e.g., property line, river, drinking water well).

**POC at Well:** A drop-down box is provided for the user to select an existing concentration well to represent the Point of Compliance.

**Regulatory Compliance Concentration:** The Regulatory Compliance Concentrations (RCC) is defined as the concentration of each contaminant at the POC that is acceptable for your site.

## Analyzing Output

### Tabular Output

**Target Source Concentration:** If NAS calculates that the RCC is exceeded at the POC, NAS estimates the target source concentration required to produce the specified RCC after source removal and plume restabilization. If the RCC is not exceeded for a give location, NAS will display 'No Reduction Required' in the Target Source Concentration column and will not calculate TOS values, as no Source Reduction is required for this case.

**Time of Stabilization:** If a source reduction is required, NAS provides the user with a range of Time of Stabilization (TOS) estimates. TOS estimates are based on the groundwater contaminant velocities and decay rates previously estimated by NAS. These estimates give the user an idea of how long after a source reduction an effect would be seen on concentration reduction at the POC.

**Breakthrough Time:** NAS defines breakthrough time as the point at which 50% of the required concentration reduction at the POC has been reached. High, best, and low values for breakthrough time are estimated.

**Time to Equilibrium:** NAS defines time to equilibrium as the point at which the concentration has been reduced to approximately the RCC at the POC. High, best, and low values for time to equilibrium are estimated.

Contaminant	RCC [µg/L]	Well	Source Reduction		Time of Stabilization [years]					
			Conc [µg/L]	Target	Breakthrough Time			Time to Equilibrium		
					Current	Target	Maximum	Average	Minimum	Maximum
Total BTEX	5.0	1	80000	17411	28.1	13.1	8.2	48.3	22.7	14.3
Benzene	1.0	1	20000	17811	23.1	10.9	6.9	40.5	19.2	12.1
Toluene	1.0	1	40000	No Reduction Required						
Ethylbenzene	1.0	1	5000	734	43.2	19.7	12.1	67.5	31.3	19.4
Xylene	1.0	1	15000	No Reduction Required						
MTBE	100.0	1	175000	2767	30.8	14.6	9.3	60.8	28.9	18.3

Figure A-18. TOS - Input/Tabular Output Screen

## Graphical Output

NAS provides graphical representations to the source reduction/time of stabilization solutions. The steady-state solution graphs, concentration versus distance, are based on the multiple zone model, if the simulation has more than one redox zone. The transient solution graphs, concentration versus distance, are based on the single best-fit NAC values to the POC. NAS also provides a ‘TOS Concentration vs. Time Graph’ which is a concentration versus time to stabilization graph at the POC. The graphs may be accessed by clicking on the ‘Graph’ button located on the bottom-right of the ‘Source Reduction and Time of Stabilization’ form, or if the user has already entered the required TOS data, through the ‘Output -> DOS/TOS Graphs’ menu item in the NAS Main window.

## Steady-state solution graph

NAS provides a graphical view of the reduction in source concentration solution. Figure A-19 shows the ‘Steady-State Solution’ Tab of the ‘TOS Graphical Output’ Form. This

tab shows the Steady State solution (both existing and final) for the contaminants which may be selected from the drop-down list. Check boxes allow the user to turn marker lines on or off for the POC and RCC values.

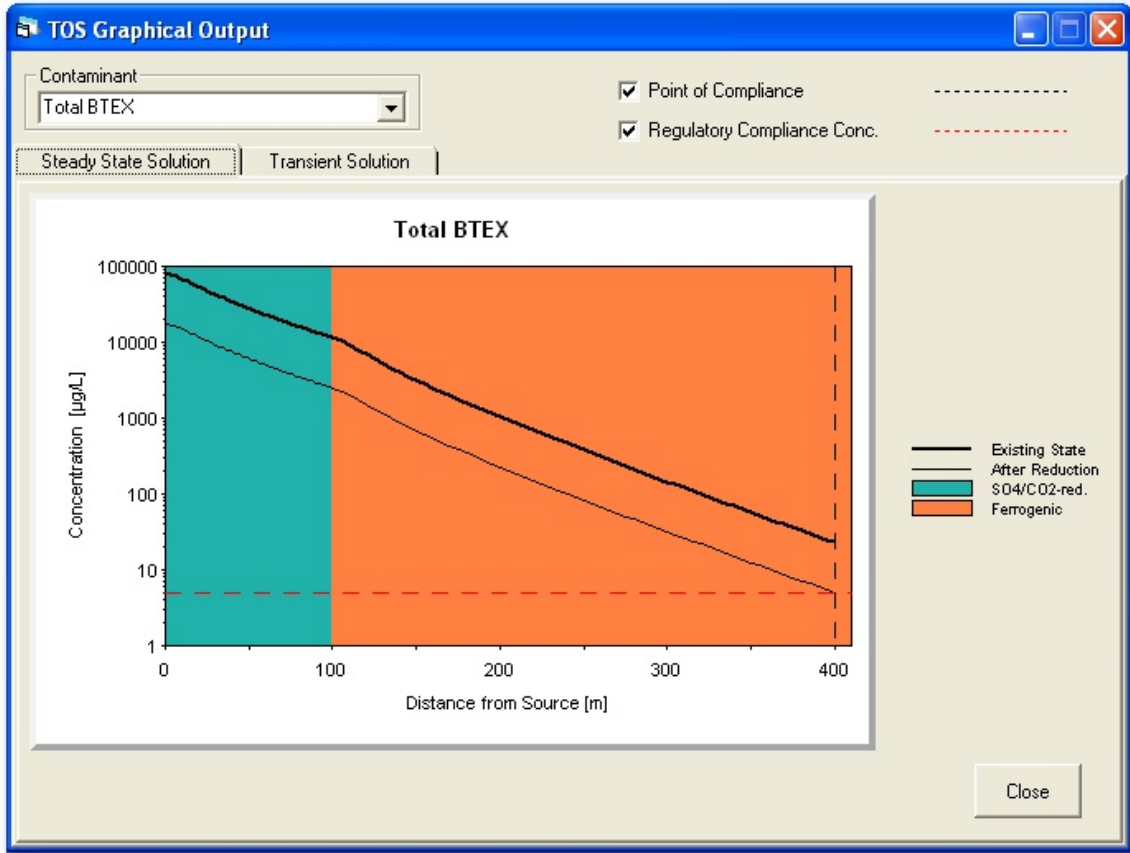


Figure A-19. TOS – Graphical Output – Steady-State Solution

### Transient solution graph

Figure A-20 depicts the transient solutions to the same problem, which may be viewed by clicking on the 'Transient Solution' Tab of the 'TOS Graphical Output' Form. The solutions may be viewed for each contaminant selected from the drop-down list. Check boxes allow the user to turn marker lines on or off for the POC and RCC values. The >> and << buttons are used to move the transient solution timestep forward or backward one step in time, with the corresponding total period of time beyond source reduction being visible in the text box.

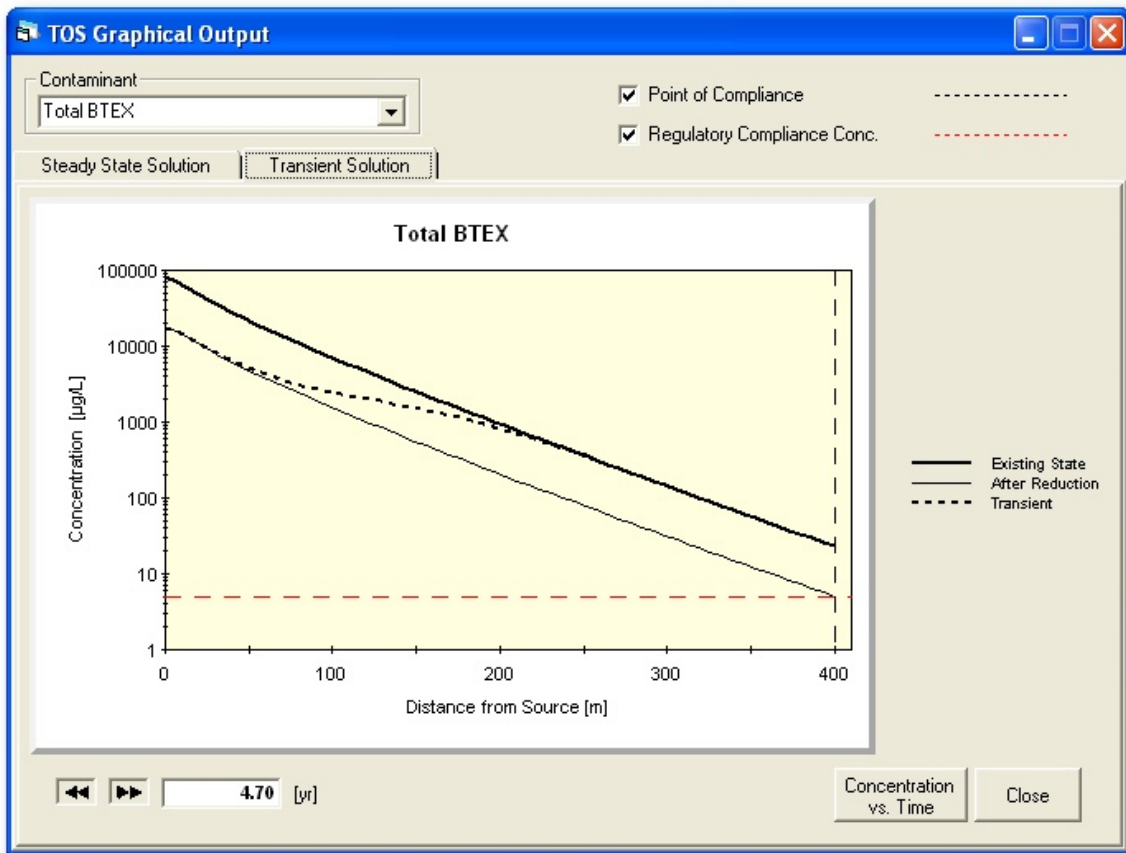


Figure A-20. TOS – Graphical Output – Transient Solution

### Concentration vs time graph

The ‘TOS Concentration vs. Time Graph’ shown in Figure A-21 can be accessed by clicking the ‘Concentration vs. Time’ button on the ‘Transient Solution’ Tab of the ‘TOS Graphical Output’ Form. This graph is a concentration versus time to stabilization graph at the POC. A drop-down calendar is provided for the user to change the date of source reduction if different from the current concentration data set date. A checkbox enables users to toggle between viewing the low, best, and high TOS solutions based on the range in velocity. Another checkbox allows NAS-predicted versus monitored well points to be plotted; this is particularly useful if more than one contaminant dataset is included in the simulation.

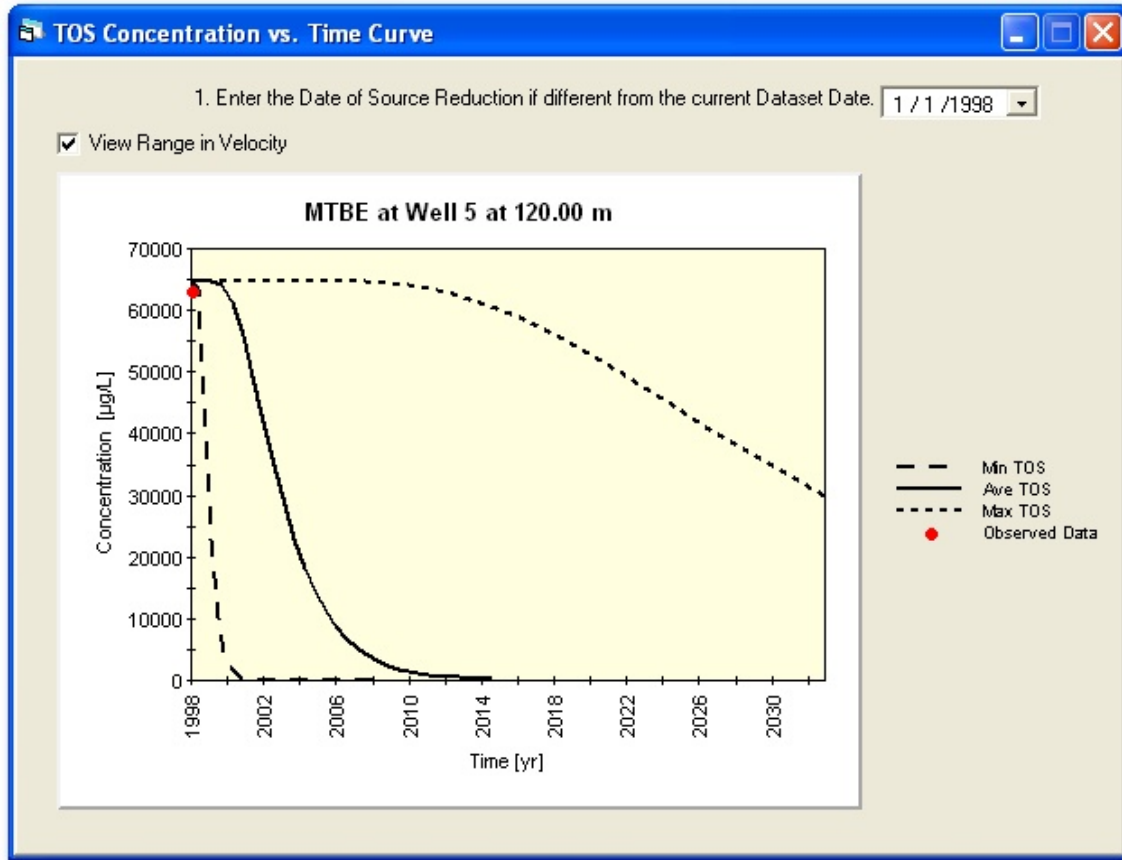


Figure A-21. TOS – Graphical Output – Concentration vs. Time

## ***Time of Remediation (TOR)***

### **Navigating the TOR Window**

Analysis for the Time of Remediation (TOR) requires the user to enter data and information needed to construct the input files for the SEAM3D numerical model. Note that time zero in the TOR analysis is the present or a future date at which NAPL source removal (partial or complete) has been implemented. The user enters NAPL properties, and an estimate (or estimates) for the NAPL mass through a series of tabs on the ‘Time of Remediation’ Form. The user is presented with a series of questions that are answered by check boxes, text boxes, or data entry. The user is required to enter all requested site data before performing TOR calculations. Furthermore, the user is required to enter all requested data on a particular tab prior to NAS displaying the Next button that allows the user to proceed to the next tab. The user can always go back to change data that has been

entered previously (by clicking on the appropriate tab to display the desired data entry field), but can not proceed to a new tab until all required information has been provided on the preceding tab.

To enter the Time of Remediation form, click on the TOR menu item in the NAS Main window. NAS automatically takes the user to the tab that contains the last data entry.

## **Data Entry**

### **NAPL properties**

Figure A-22 displays the NAPL Properties tab of the ‘Time of Remediation’ form. This tab includes contaminants from those specified by the user in the Contaminants tab of the Site Data form. The contaminants listed here are only those to which the user has assigned concentration profiles and/or specified to be in the NAPL source. The user may edit constituent properties (such as initial mass fraction) in this window, or the Site Data – Contaminants window, being sure to click the ‘Update’ button before saving or executing the simulation. Finally, NAS requires the user to specify the mass fraction of the NAPL for each compound. If one of the listed compounds is no longer found as a NAPL, enter zero for that compound. NAS requires the mass fraction of at least one constituent to be greater than zero. The sum of all NAPL mass fractions must be no greater than 1.0.

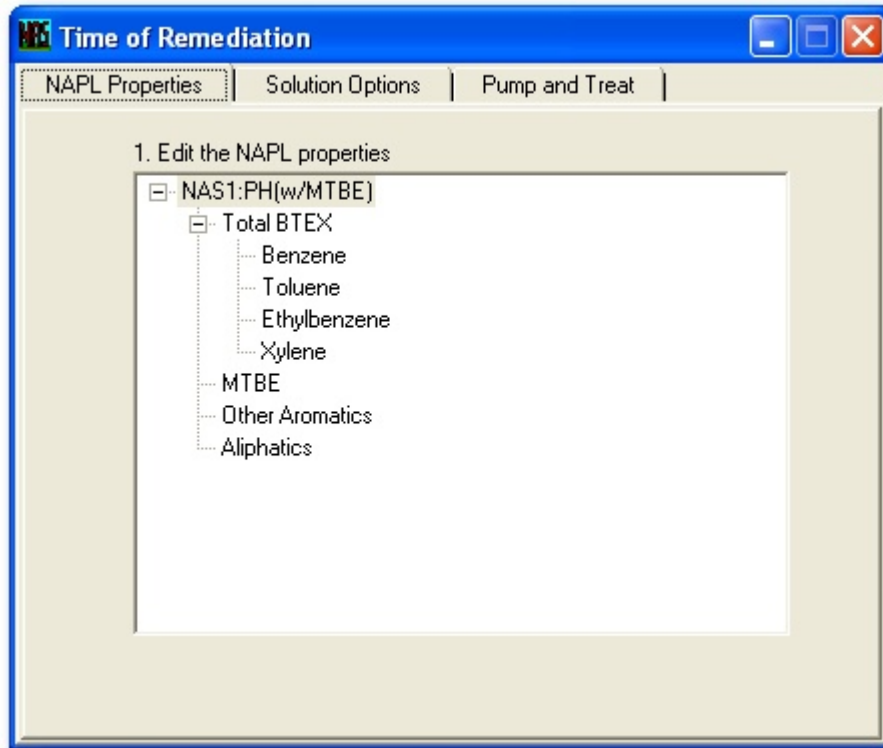


Figure A-22. TOR – NAPL Properties Tab

## NAPL Solution Options

Figure A-23 displays the ‘Solution Options Tab’ of the ‘Time of Remediation’ form. This tab allows TOR estimates based on user-specified options for NAPL mass, source removal, range in velocity, and time of analysis.

### NAPL mass options

NAS requires the user to specify at least one estimate for the NAPL mass and one remediation plan prior to performing the calculations necessary to estimate the TOR. The user may specify the current NAPL mass using one of the following options:

**Best Estimate Only:** The user is required to specify only one NAPL concentration.

**Range of Values – Specify Minimum and Maximum:** The user is required to specify three NAPL concentrations – a best estimate, a maximum, and a minimum

**Range of Values – Use Percent of Best Estimate:** The user is required to specify one NAPL concentration, and an estimate of how much variability is expected in this estimate.

### **Source removal options**

The user may also specify up to three remediation plans, and is given the following options:

**Estimate TOR if No NAPL Source is Removed:** NAS will calculate the starting NAPL mass using the values specified in NAPL mass chart.

**Estimate TOR for One NAPL Mass Removal Plan:** NAS will calculate the starting NAPL mass by reducing the NAPL mass (or masses) in the NAPL mass chart by the percentage specified by the user. Note that entering zero for this plan is identical to the no source removal option above.

**Estimate TOR for Two NAPL Mass Removal Plans:** Same as the Estimate TOR for One NAPL Mass Removal Plan option, except the user may enter two NAPL removal percentages.

**Estimate TOR for Three NAPL Mass Removal Plans:** Same as the Estimate TOR for One NAPL Mass Removal Plan option, except the user may enter three NAPL removal percentages.

### **Velocity Range**

A checkbox enables users to toggle between calculating TORs based on just the best estimate velocity, or to calculate with the range of TORs based on low, best, and high velocity estimates.



## Simulation Time

The time of analysis is the simulation time the MODFLOW and SEAM3D numerical models are set to. The maximum time of analysis given to analyze the selected options is 100 years for each simulation. The simulation time for TOR analysis can be shortened by specifying a time of analysis that is less than the default (and maximum) value of 100 years. This option is exercised by changing the Time of Analysis field located at the bottom of the Solution Options tab. It is advisable to do initial simulations with a lower analysis time, to prevent unnecessary runtimes.

**Time of Remediation**

NAPL Properties | Solution Options | Pump and Treat

1. Enter the estimated NAPL mass in the source area.

Range of values - Use percent of average

	Average	+/- % of Ave.
NAPL Mass [kg]	10.00	25
NAPL Residual	3.17e-05	3.97e-05/2.38e-05

2. Evaluate the impact of source removal.

Estimate TOR for 2 NAPL Mass Removal Plans

	Plan 1	Plan 2
% NAPL Removed	0	50

3. Maximum time of analysis (up to 100 years).

4. Check box to calculate for Range in Velocity:

Execute TOR

Figure A-23. TOR – Solution Options Tab

## Pump and Treat

Figure A-24 displays the ‘Pump and Treat’ Tab of the ‘Time of Remediation’ form. This tab allows the user to estimate TORs associated with pump-and-treat technology for comparison with, or in conjunction with, MNA. NAS can model sites with an existing (or proposed) pumping well, or optimally design a pumping well field, with well location,

pumping rate and duration, based on the previously specified site hydrogeology and source delineation data. If the 'Simulate Pump and Treat' checkbox is checked, NAS will simulate pump-and-treat for comparison with MNA. If pump-and-treat is simulated, required data includes:

**Average Saturated thickness:** A value for the average saturated aquifer thickness is required for the NAS estimate of pumping rate.

**Pumping well distance:** The distance from the source to the pumping well may either be specified by the user, or NAS will set it to the POC.

**Pumping rate:** The pumping well rate may either be specified by the user, or NAS will estimate it based on analytical solutions for hydraulic control and previously enter site data.

**Pumping duration:** The pumping duration may either be specified by NAS (in which case the pumping duration would be the total extent of the simulation time), or specified by the user (in which case it may be any value between zero to the total simulation time). If the pumping duration is less than the total simulation time, then the TOR simulation will consist of a pump-and-treat period followed by an MNA-polishing period for the remainder of the total simulation time.

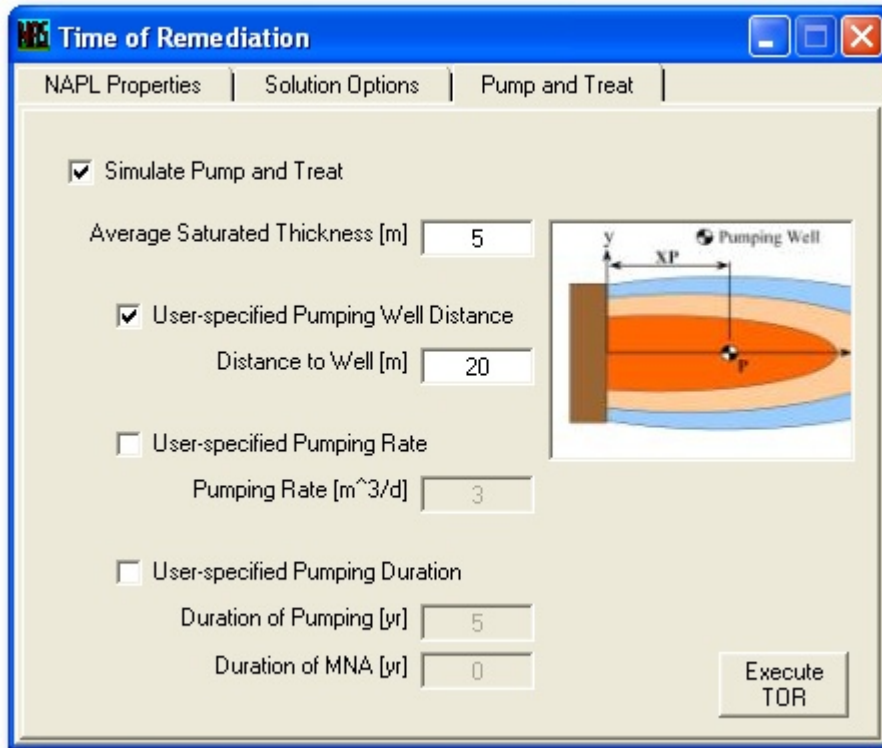
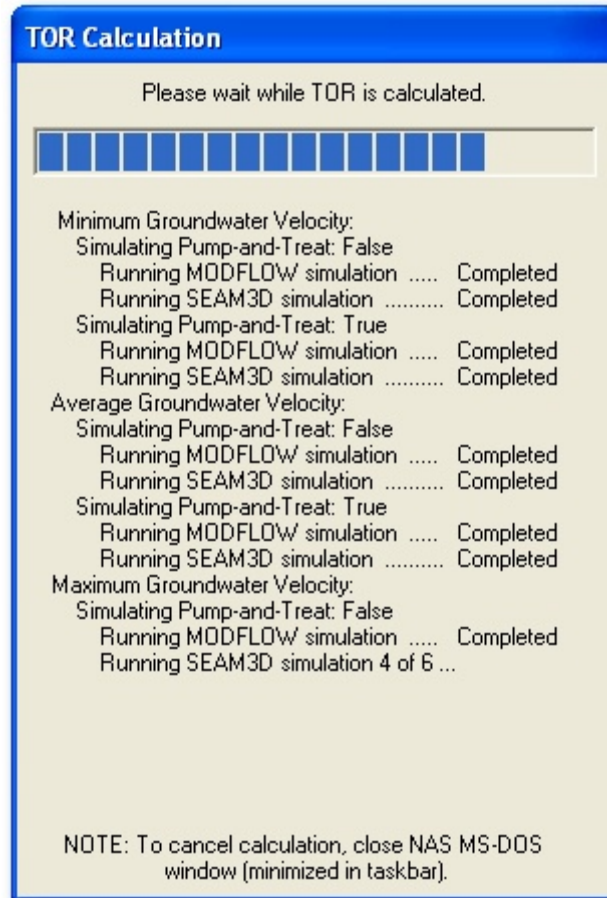


Figure A-24. TOR – Pump and Treat Tab

### Executing the TOR Simulation

When the user has completed specifying the solution options, the ‘Execute TOR’ button may be clicked on either the ‘Solutions Options’ or ‘Pump and Treat’ tab. This command initiates the MODFLOW and SEAM3D numerical solutions. The number of simulations that NAS will run is dependent on how the user specifies the NAPL mass, Remediation Plan, velocity range, and pump-and-treat options. The fastest TOR analysis, when SEAM3D is run only one time, is to specify a best estimate for the NAPL mass and only one remediation plan (either zero removal or a single percentage removal plan). The simulation time will reach a maximum when the user specifies a range of NAPL mass estimates, three remediation plans, velocity range, and pump-and-treat with MNA-polish period, which may require up to eighty-one separate SEAM3D simulations. Although this option will take more time, it gives the user more data to analyze for TOR estimates.

Figure A-25 shows the ‘Executing TOR’ window that displays the progress of the TOR calculation. NOTE: If the calculation seems to have locked up due to an excessive amount of time, or you need to prematurely end the simulation, you may end the numerical model calculation by closing its associated Microsoft-DOS window, that is minimized in the Windows Taskbar.



**Figure A-25. ‘Execute TOR’ Progress Dialog Box**

Upon successful completion of the required simulations, a text file with the concentration versus time results is created with the same filename as the \*.nas project file, and a file extension of \*.obs. This file is created/saved in the same directory as the \*.nas project file. These results then become available in the ‘TOR Tabular and Graphical Output’ Form which becomes visible after the simulation is complete.

## **Analyzing Output**

The table and graph output for TOR will be automatically accessed immediately after a successful simulation run, or if the user has previously run a simulation, may be accessed through the 'Output -> TOR Table and Graph' menu item in the NAS Main window. This form provides drop-down boxes for the user to view results based on different contaminant, mass estimate, removal plan, velocity, and pump-and-treat options.

## **Time of Remediation Table**

For NAS to calculate TOR, the user must specify the specified source compliance concentration (SCC) for each contaminant, on the 'TOR' Tab of the 'TOR Tabular and Graphical Output' Form. See Figure A-26.

**Source Compliance Concentration:** The Source Compliance Concentrations (SCC) is defined as the concentration of each contaminant, at the source well (i.e., the first well), that is acceptable for your site.

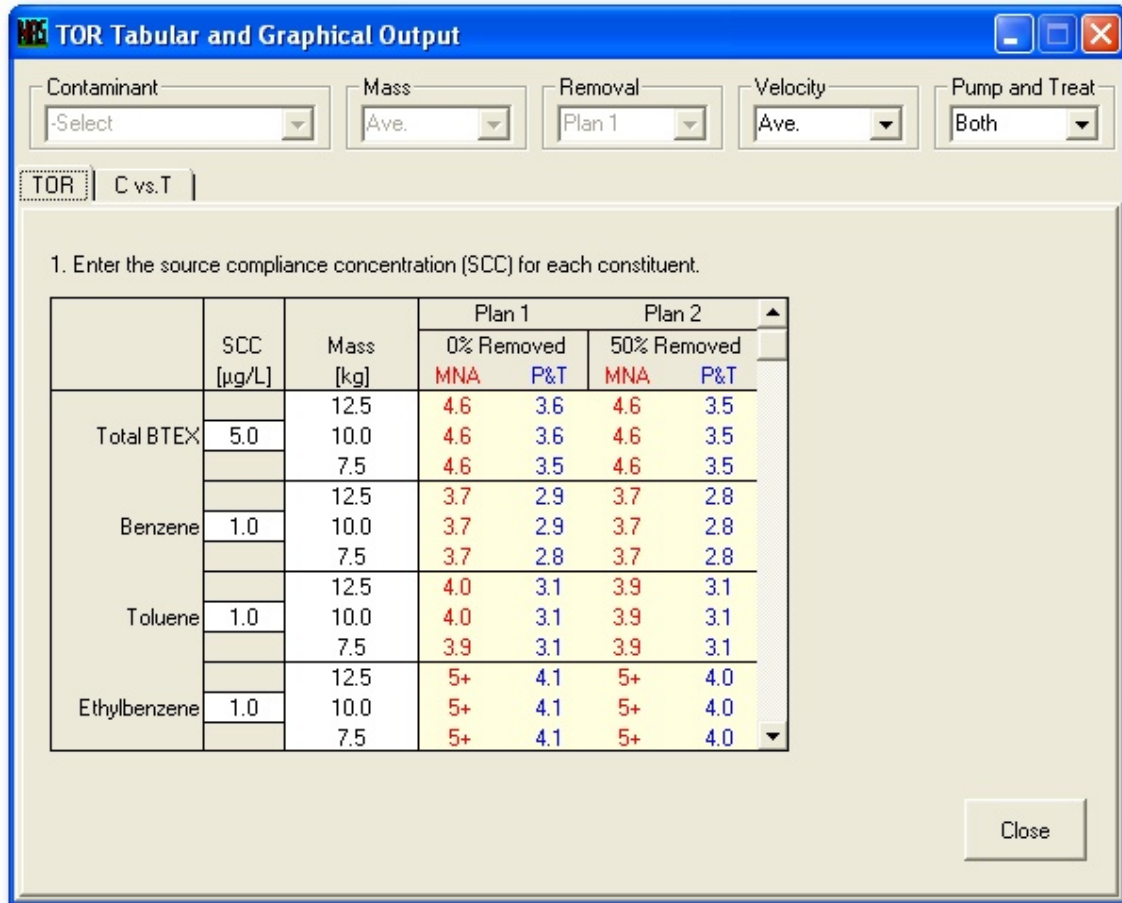


Figure A-26. TOR – Tabular Output

### Concentration vs time graph

NAS also offers a graphical representation of the TOR calculations based on the concentration versus time data contained in the associated \*.obs file. The graph can be viewed on the 'C vs. T' Tab of the 'TOR Tabular and Graphical Output' Form. See Figure A-27. A drop-down calendar is provided for the user to change the date of source reduction if different from the current concentration data set date. A checkbox allows NAS-predicted versus monitored well points to be plotted; this is particularly useful if more than one contaminant dataset is included in the simulation.

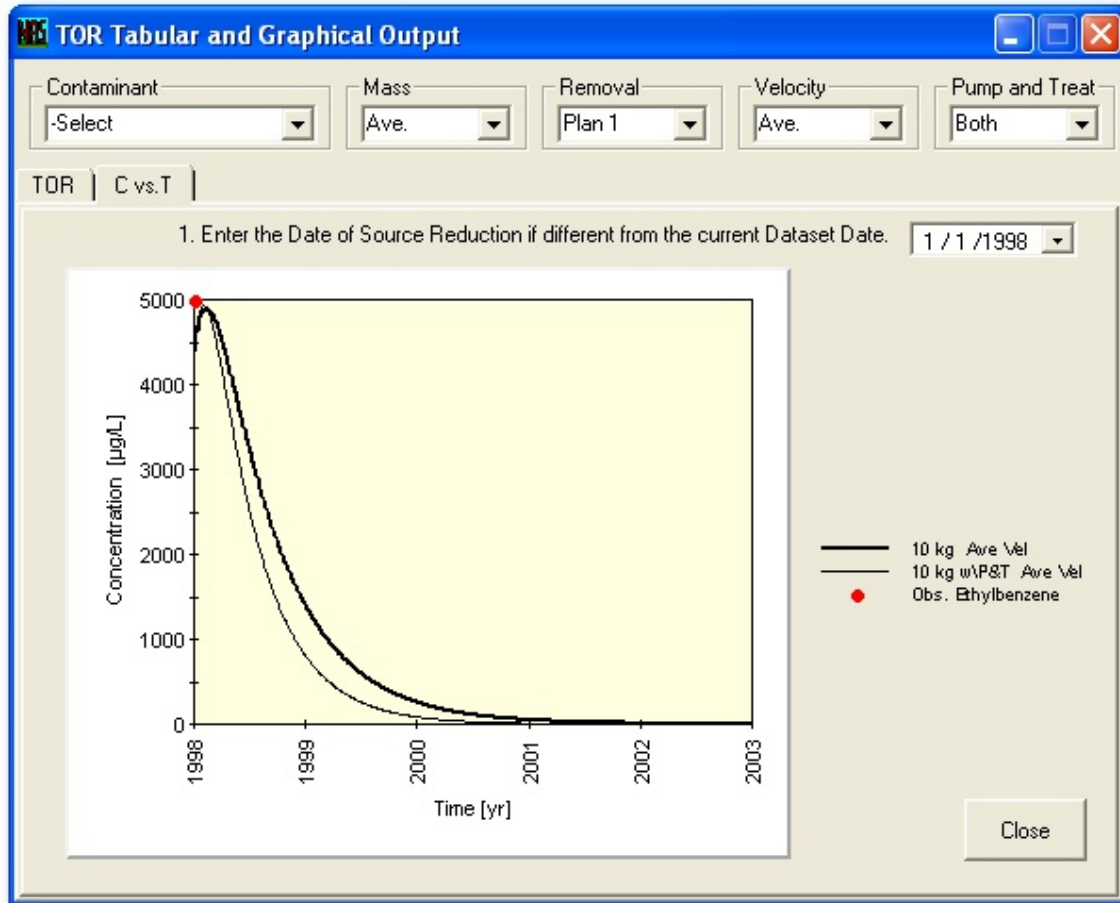


Figure A-27. TOR – Graphical Output – Concentration vs. Time

## Advanced Features

### Adjusting Redox Zonation Graphically

In addition to being able to manually adjust the redox conditions in the ‘Site Data – Redox Indicator Data’ tab, NAS gives the user the ability to manually adjust the redox zonation from the ‘Site Data Graphical Summary’ form. The user can hover the mouse over redox zone boundaries, and when the mouse cursor changed to a double-header arrow, the user may click-and-drag the boundary in either direction. This may be useful when contaminant and/or redox indicator data is limited and slightly adjusting the boundary may better fit the observed data, and suggest where additional monitoring may be beneficial. As the user adjust boundaries, the impact on NACs can be immediately seen, and related estimates will be automatically updated in visible forms (except the TOR estimates which would require the numerical model to be executed again).

## Managing Chronological Datasets

Contaminant and/or Redox Indicator data sets may be added to current projects either of two ways. One method was previously discussed in the NAS Main Menu section, by using the 'File -> Add Existing Project' menu item. This method is ideal if you already have NAS files made with the same monitoring profiles you wish to import, or if you wish to import a NAS file that already has multiple datasets in it. Another method for deleting sets, or sequentially creating new ones, in a current project is with the 'Add/Delete DataSet' buttons in the 'Contaminant Data' and 'Redox Indicator Data' tabs in the 'Site Data' form. To delete a data set, highlight it in the corresponding 'Cont. Datasets' or 'Redox Datasets' list, and then click the corresponding 'Delete DataSet' button. To add a data set, select your existing data set that most resembles the data set you wish to add (i.e., the set with the date, number of wells, well names, and distances that most closely matches the set you are adding), and click the corresponding 'Add DataSet' button. You will then be prompted to select a date for the new set from the drop-down calendar. NAS will create a new concentration profile chart have the same number of wells, well names, and well distances of the data set you copied, and you will just be required to fill in the concentration values. Individual wells may still be added or deleted by the usual method if so desired.

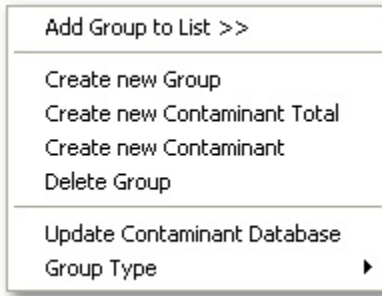
## Contaminant Database

Three types of items may be represented in the contaminant database: Contaminant Groups, Contaminant Totals, and Contaminants. The three items and how to edit existing ones or create new ones will be discussed in the following sections. NOTE: See 0 and 0 for additional information on required contaminant parameters and their definition and format.

Figure A-28 shows the menu list that is accessed by opposite-clicking in the left window (Database window) of the 'Contaminants' tab of the 'Site Data' form. If clicked over an item (such as a contaminant group in this figure), the first menu item will add that item to the user-specified source zone window on the left. The next four menu items are available in both the Database window and the Source window, with the first three of



these being self-explanatory. The fifth menu item ‘Delete’ will only be available when the user has clicked on an item, with the item name changing depending on which item the user may have clicked on. By clicking on the ‘Update Contaminant Database’ menu item, the user will revise the NAS internal contaminant database, with any changes being available to all future simulations of NAS.



**Figure A-28. Database Window Menu Items**

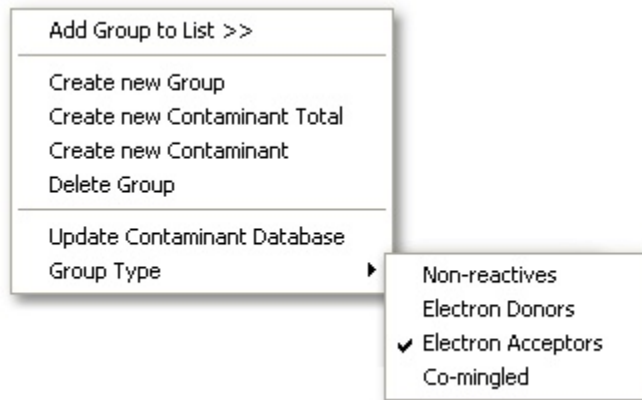
Figure A-29 shows the menu list that is accessed by opposite-clicking in the right window (User-specified source window) of the ‘Contaminants’ tab of the ‘Site Data’ form. The only menu items singular to this window are the two with the left-facing arrows. Clicking on the ‘Create New Group In Database’ menu saves a copy of the user-defined source group to the NAS database. Clicking on the ‘Update Group In Database’ menu revises a contaminant group in the database window with that of the same name in the source window.



**Figure A-29. Source Window Menu Items**

To create a new contaminant source, one should first create a contaminant group, then add only contaminant totals or contaminants under it. To create a new contaminant total, one should only add individual contaminants under it. To create a co-mingled source, one should first create a contaminant group, classify it as ‘Co-mingled’, and then up to one of each of the other groups may be created/added within it.

**Contaminant Group:** The contaminant group item is a collection of contaminant totals and/or individual contaminants. Figure A-30 is a view of the menu that becomes available when opposite-clicking on a contaminant group in the ‘Contaminants’ tab of the ‘Site Data’ form. The ‘Group Type’ submenu lists the types a group may be classified as. All contaminant totals and individual contaminants within a group will be classified as this type of contaminant. NOTE: If a group is classified as ‘Co-mingled’, it may then have, at the most, one of each other group (i.e., Non-reactives, Electron Donors, Electron Acceptors) in it.

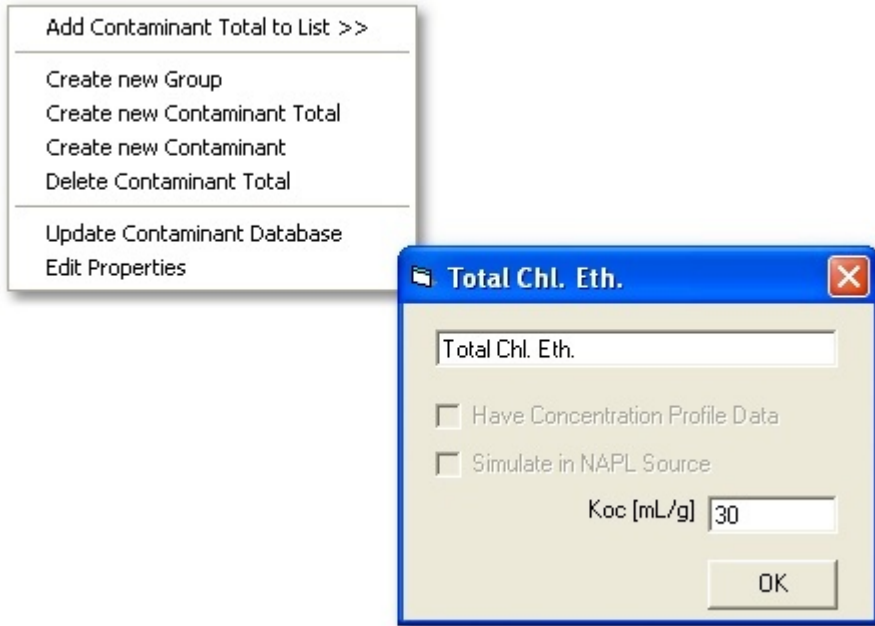


**Figure A-30. Contaminant Group Menu Items**

**Contaminant Total:** The contaminant total item is a collection of individual contaminants. Contaminant totals will not be explicitly simulated in NAS, in that the user will not be required to enter concentration profile data for the item. NAS will sum the concentrations of the individual contaminants within the contaminant total, and use that value for calculations. Figure A-31 is a view of the menu that becomes available when opposite-clicking on a contaminant total in the ‘Contaminants’ tab of the ‘Site Data’

form. The 'Edit Properties' submenu produces the properties box as shown. The only required property for a contaminant total is:

**Carbon Matter Partition Coefficient – Koc**



**Figure A-31. Contaminant Total Menu Items**

**Contaminant:** The contaminant item is an individual contaminant. Figure A-32 is a view of the menu that becomes available when opposite-clicking on a contaminant in the 'Contaminants' tab of the 'Site Data' form. The 'Edit Properties' submenu produces the properties box as shown. The user may use the checkboxes to specify if a concentration versus distance profile will be supplied, and if the contaminant will be simulated as a NAPL source constituent in the TOR simulation. The required properties for a contaminant are:

If 'Have Concentration Profile Data' or 'Simulate in NAPL Source' is true:

**Carbon Matter Partition Coefficient – Koc**

If 'Simulate in NAPL Source' is true:

**Mass Fraction**

**Solubility**

### Molecular Weight

If 'Simulate in NAPL Source' is true, and 'Group Type' is 'Electron Acceptors':

### Stoichiometric Factor

### Alternate Pathway (see next section)

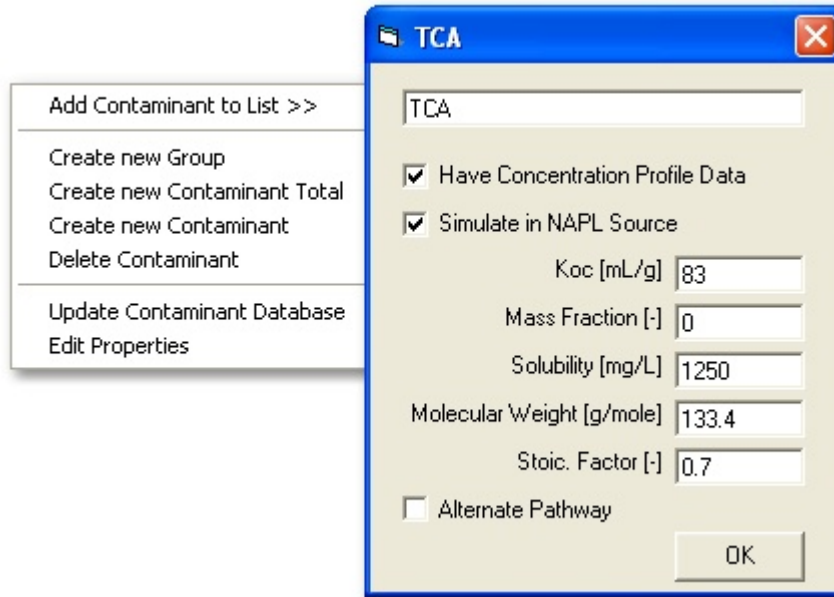


Figure A-32. Contaminant Menu Items

### Alternate Pathways:

If 'Simulate in NAPL Source' is true, and 'Group Type' is 'Electron Acceptors', then alternate reduction pathways may be specified. Figure A-33 is a view of the additional data that is required when the user selects the 'Alternate Pathway'. These are:

### Alternate Pathway Parent

### Contaminant Percent from Parent

Figure A-34 shown an example application of the alternate pathway function. The 'electron acceptors' contaminant group must be specified using a linear sequential pathway, such as that represented by Reductive Dechlorination in the figure. In this pathway, the parent may only go to one daughter product, with each daughter being the next parent in sequence. The alternate pathway function allows the user to specify additional child pathways from a parent, such as the abiotic degradation pathways shown in the figure.

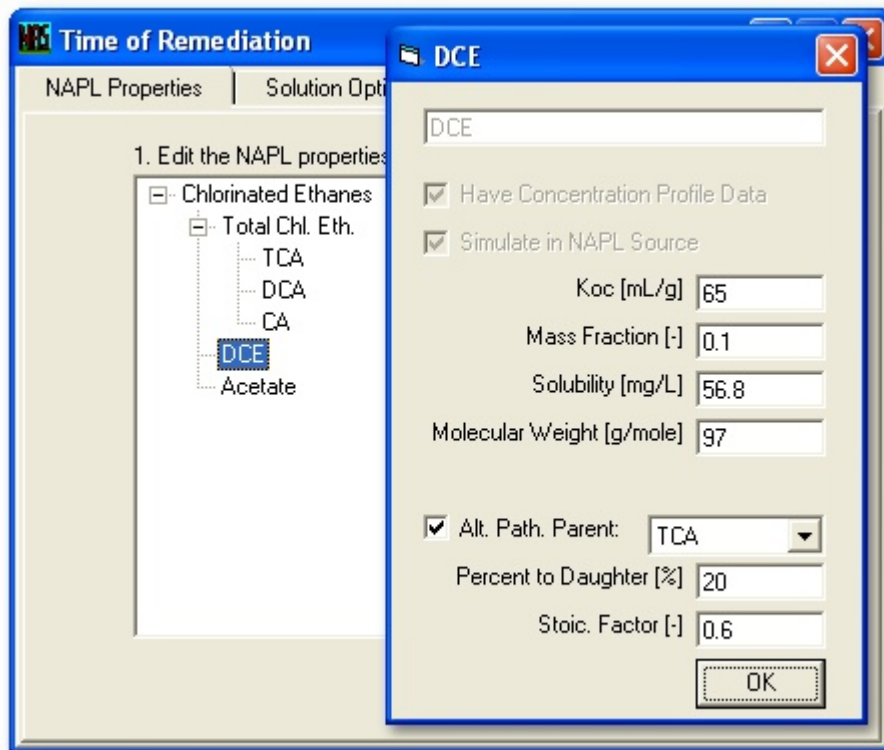


Figure A-33. Specifying an alternate reduction pathway

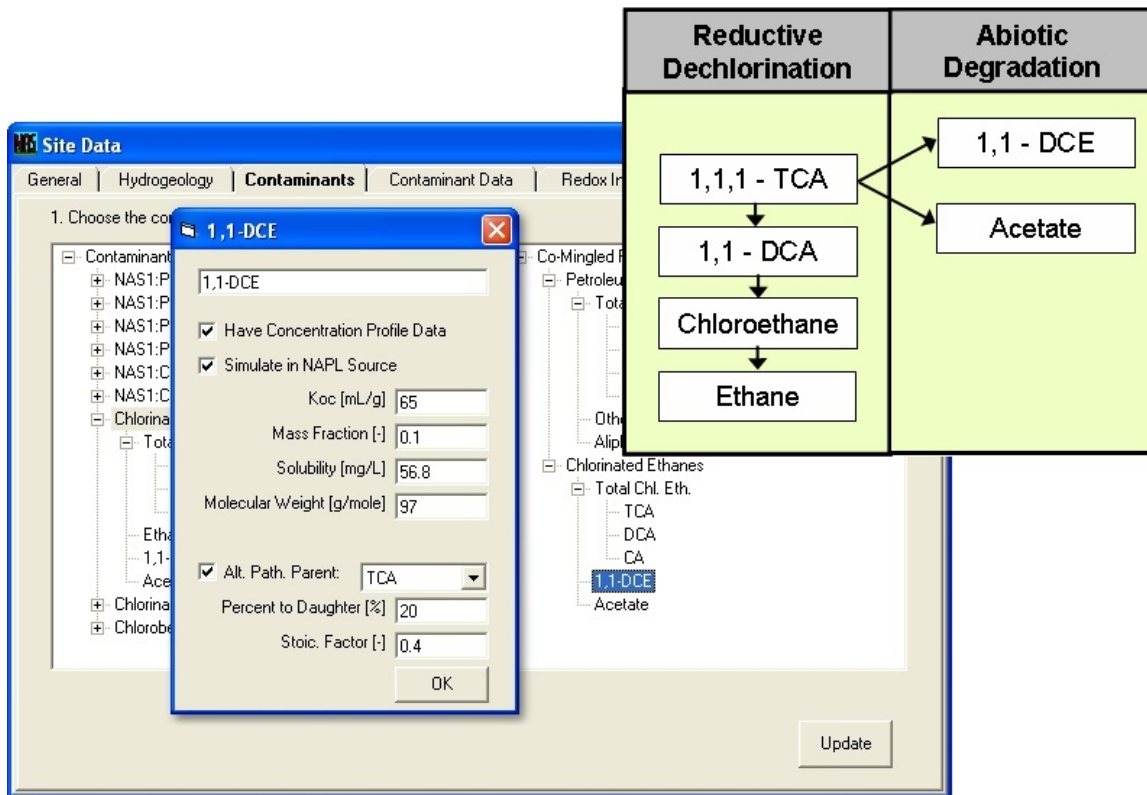


Figure A-34. Example of Alternate Pathway Application

## Reporting Features

### Report Generation

Clicking on the 'Print/Save' Button on the 'Data and Result Tabular Summary' Form converts the form into a Print Preview report capable of being formatted, saved, and printed. See Figure A-35. From the Print Preview, the following options are offered:

**Navigation:** The user can navigate through the data summary using either the Next/Previous navigation buttons, the Page Down/Page Up keyboard commands, or the scroll bar located to the left of the print preview.

**Save:** Clicking the Save button produces a standard windows save as dialog box enabling the user to save the Report in Excel file format.

**Print:** Clicking the Print button takes the user to a standard windows print dialog that allows the user to select the print range, select between various print options, and enter the print setup dialog. Once the user has selected the desired print range and options, the user may then choose to Print the selection.

**Setup:** Clicking the Setup button allows the user to simultaneously modify the print preview and options for the document sent to the printer. Among the options offered are margin widths, page orientation, custom headers/footers, and the on-screen zoom scale.

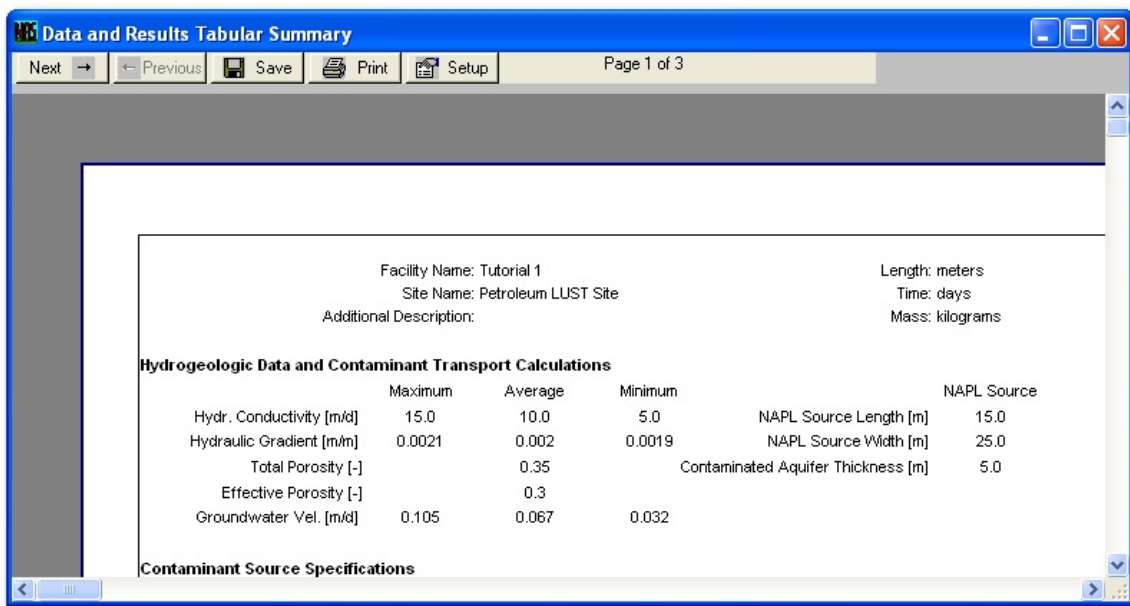


Figure A-35. Report Generator provided for Main Tabular Output

### Clipboard copy Tables

All tables in NAS have the capability of full Clipboard copy, for the purpose of pasting in reports. Select input tables in NAS also support pasting into them from the Clipboard (e.g copying and pasting large blocks of data from an excel file into the Contaminant Data profile table).

### Edit Graph Properties

All graphs in NAS, when opposite-clicked on, provide an editable properties dialog box. The user is given complete control to manage all visual aspects of the graph for reporting

purposes. An associated help file can be accessed by clicking on the 'Help' button on the bottom right of the properties box. See Figure A-36.

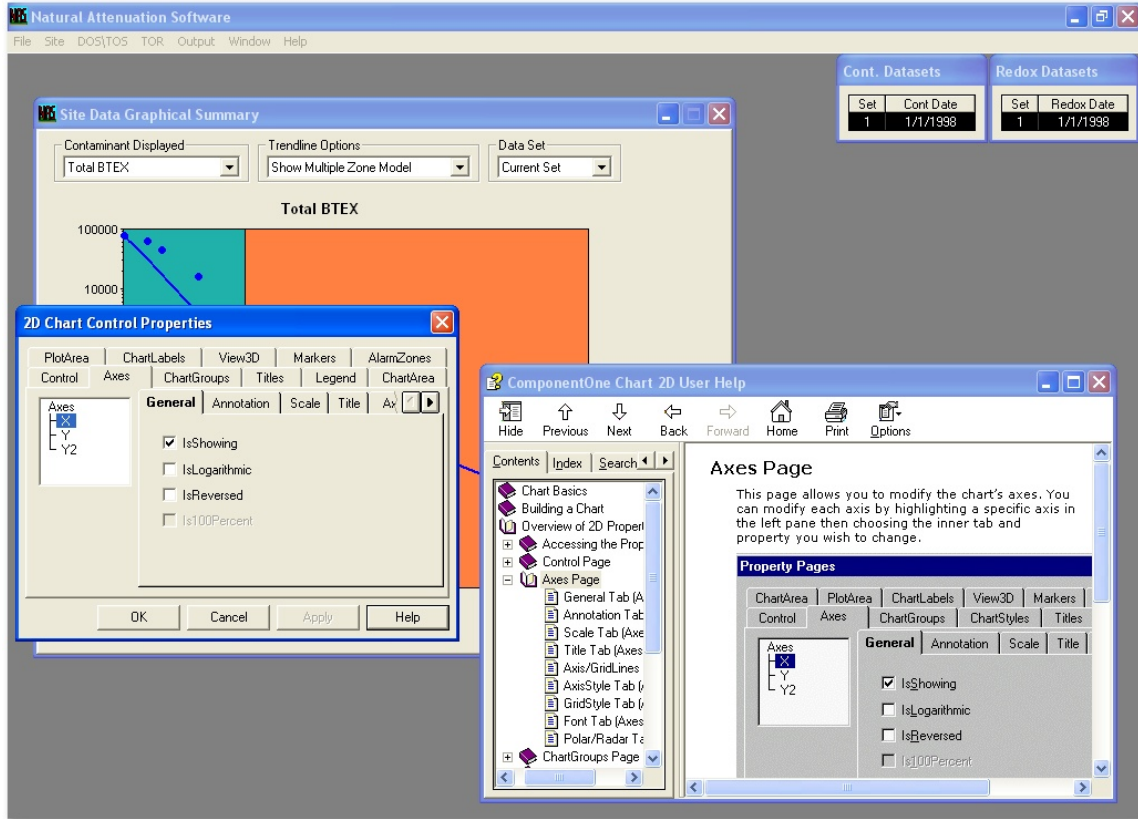


Figure A-36. Graph Properties Dialog Box and Associated Help Screen

## Save/Print Graphics

All graphs in NAS, when double-clicked on, provide a drop-down menu giving print and save options. Graphics can be printed in three different formats. Graphics can also be saved to either the Clipboard or a file in three different formats each. The 'Set Report Format' may be used to make the graphic more friendly for low-color or black-and-white reporting. See Figure A-37.



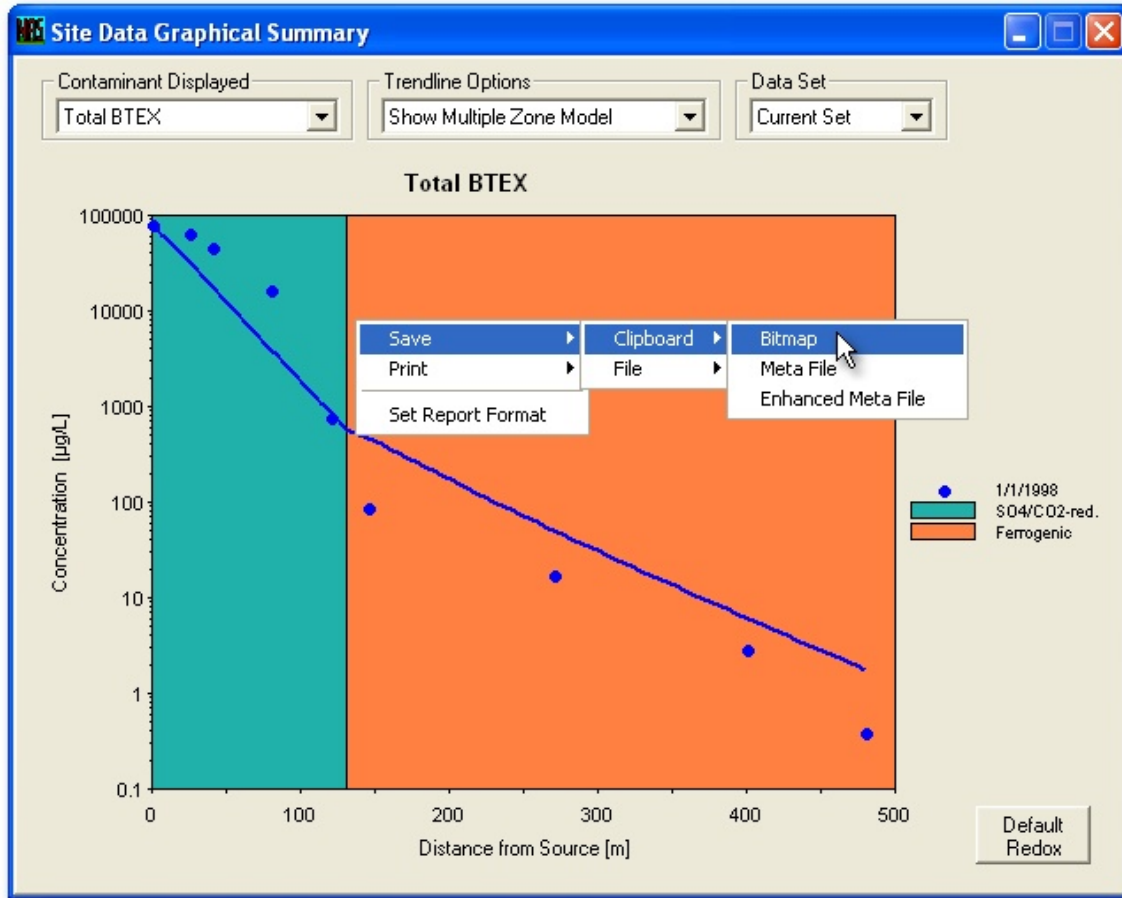


Figure A-37. Save/Print PopUp Menu provided for Graphs

## **APPENDICES**

## Appendix 1: \*.NAS File Structure

- 1      Record:      NASVER  
      Format:      None
  - NAS Version the file was compiled in.
  
- 2      Record:      Dummy input line  
      Format:      n/a
  - Blank line.
  
- 3      Record:      SDINPUT, TOSINPUT, TORINPUT  
      Format:      2I5, F5.0
  - SDINPUT is the flag to indicate completed input for the Site Data Module: =0, General Tab is complete; =1, Hydrogeology Tab is complete; =2, Contaminants Tab is complete; =3, Contaminant Data Tab is complete; =4, Redox Indicator Data Tab is complete;
  - TOSINPUT is the flag to indicate completed input for the Time of Stabilization Module: =0, POC has been saved; =1, RCCs have been saved;
  - TORINPUT is the flag to indicate completed input for the Time of Remediation Module: =1, Solution Options Tab is complete; =1.4, Solution Options Tab is complete and SCCs have been saved after Simulation Execution; =2, Pump and Treat Tab is complete;
  
- 4      Record:      Descriptive Text  
      Format:      None
  - \*\*\* Site Data Form \*\*\*

(Continue if SDINPUT >= 0)

- 5 Record: FACNAME  
Format: A50
- Facility Name.
- 6 Record: SITENAME  
Format: A50
- Site Name.
- 7 Record: ADDLDESC  
Format: A50
- Additional Description.
- 8 Record: LUNIT, TUNIT, MUNIT  
Format: 3A10
- LUNIT is the Length Unit: 'm' OR 'ft';
  - TUNIT is the Time Unit: 'd' OR 'yr';
  - MUNIT is the Mass Unit: 'kg' OR 'lb'.

(Continue if SDINPUT >= 1)

- 9 Record: KSUBHL, KSUBHB, KSUBHH  
Format: 3F10.0
- KSUBHL is the Hydraulic Conductivity - Minimum Estimate;
  - KSUBHB is the Hydraulic Conductivity - Best Estimate;
  - KSUBHH is the Hydraulic Conductivity - Maximum Estimate.
- 10 Record: HYGRADL, HYGRADB, HYGRADH  
Format: 3F10.0
- HYGRADL is the Hydraulic Gradient - Minimum Estimate;
  - HYGRADB is the Hydraulic Gradient - Best Estimate;
  - HYGRADH is the Hydraulic Gradient - Maximum Estimate.

11 Record: WPOCL, WPOCB, WPOCH  
Format: 3F10.0

- WPOCL is the Weight Percent Organic Carbon - Minimum Estimate;
- WPOCB is the Weight Percent Organic Carbon - Best Estimate;
- WPOCH is the Weight Percent Organic Carbon - Maximum Estimate.

12 Record: TPOR, EPOR, SZ, SY, SX  
Format: 5F10.0

- TPOR is the Total Porosity;
- EPOR is the Effective Porosity;
- SZ is the Contaminated Aquifer (Source) Thickness;
- SY is the Source Width;
- SX is the Source Length.

13 Record: Descriptive Text  
Format: None

- \*\*\* Contaminant Source \*\*\*

(Continue if SDINPUT >= 2)

14 Record: Descriptive Text  
Format: None

- \*\*\* Headers for Columnar Data \*\*\*

15 Record: CGNAME  
Format: A50

- Contaminant Group Name

16 Record: CGTYPE, CGNUM  
Format: 2I10

- CGTYPE is the Type of Contaminant Group: =0, Non-reactives; =1, Electron donors; =2, Electron acceptors; =3, Co-mingled;
- CGNUM: If CGTYPE=3 then CGNUM=Number of Contaminant Groups in Co-Mingled Group, else CGNUM=Number of Contaminants in Group.

(If CGTYPE = 3 then enter lines 16 – 17 CGNUM more times)

(Enter line 17 CGNUM times)

17 Record: CONTNAME, CONTMW, CONTSOL, CONTKOC, CONTFRAC, CONTTOT, CONTCD, CONTNPL, CONTGC, CONTDF, CONTDP

Format: A50, 4F10.0, 3I10, F10.0, I10, F10.0

- CONTNAME is the Contaminant Name;
- CONTMW is the Contaminant Molecular Weight;
- CONTSOL is the Contaminant Solubility;
- CONTKOC is the Contaminant Carbon Matter Partition Coefficient;
- CONTFRAC is the Contaminant Initial Mass Fraction in NAPL;
- CONTTOT specifies if the Contaminant is a Summation of Contaminants Flag: < 0, contaminant represents a summation of individual contaminants; = 0, contaminant is not represented within a total summed contaminant; > 0, contaminant is represented within a total summed contaminant, with the value representing the index of that total contaminant;
- CONTCD is the Contaminant Concentration Distribution Flag: = 0, the user has not provided a C vs.X profile for the contaminant; = 1, the user has provided a C vs.X profile for the contaminant;
- CONTNPL is the Contaminant in NAPL Source Flag: = 0, the contaminant is not included in the NAPL source in the TOR simulation; = 1, the contaminant is included in the NAPL source in the TOR simulation;

- CONTGC is the Contaminant Stoichiometric Factor to Daughter: If CGTYPE = 2, then CONTGC represents the stoichiometric factor relating degradation of the electron acceptor to its daughter product;
- CONTDF is the Contaminant Alternate Pathway Flag: = 0, contaminant does not represent an alternate pathway; < 0, contaminant represents an alternate pathway daughter product, with the absolute value representing the index of the parent contaminant;
- CONTDP specifies the Contaminant Percent from Parent: If CONTDF < 0, then CONTDP represents the Percent of mass (in aqueous phase concentration) of Parent, reserved for the production of this Daughter product.

18 Record: Descriptive Text

Format: None

- \*\*\* Contaminant and Redox Data \*\*\*

(Continue if SDINPUT >= 3)

19 Record: CONTDS, REDOXDS

Format: 2I10

- CONTDS is the Number of Contaminant Data Sets;
- REDOXDS is the Number of Redox Indicator Data Sets.

(Enter lines 20 – 21 CONTDS times)

20 Record: CDSDATE, CDSNUM

Format: A10, I10

- CDSDATE is the Date Contaminant Data Set was Sampled (Format: mm/dd/yyyy);
- CDSNUM is the Number of Wells in Contaminant Data Set.

(Enter line 21 CDSNUM times)

21 Record: CWNAME, CWDIST, CWCONT

Format: A15, 2F15.0

- CWNAME is the Contaminant Well Name;
- CWDIST is the Contaminant Well Distance from Source (First Well must be Source Well, i.e., Distance=0).
- CWCONT is the Contaminant Concentration in Well (ug/L) (NS=Not Sampled, BD=Below Detection). Enter CWCONT for each CGNUM with CONTCD = 1 and CONTTOT >= 0.

(Continue if SDINPUT >= 4)

(Enter line 22-24 REDOXDS times)

22 Record: RDSDATE, RDSNUM

Format: A10, I10

- RDSDATE is the Date Redox Indicator Data Set was Sampled (Format: mm/dd/yyyy);
- RDSNUM is the Number of Wells in Redox Indicator Data Set.

23 Record: RI(8)

Format: 8L2

- RI are the Flags for Redox Indicator Options: Oxygen, Nitrate, Mn(II), Iron(II), Sulfate, Sulfide, Methane, Hydrogen. Enter T to include the option in the simulation, enter F to omit. RI(1), RI(4), RI(5) will always be set to T.

(Enter line 24 RDSNUM times)

24 Record: RWNAME, RWDIST, RWCONT

Format: A15, 2F15.0



- RWNAME is the Redox Well Name;
- RWDIST is the Redox Well Distance from Source;
- RWCONT Redox Concentration in Well (mg/L, if Hydrogen then nM) (NS=Not Sampled, BD=Below Detection). Enter for each RI()=T

25 Record: Descriptive Text

Format: None

- \*\*\* TOS/DOS Form \*\*\*

(Continue if TOSINPUT >= 0)

26 Record: POC, TOSDATE

Format: F10.0, A10

- POC is the Distance from Source to Point of Compliance;
- TOSDATE is the Date Source Reduction was accomplished (Format: mm/dd/yyyy).

(Continue if TOSINPUT >= 1)

(In line 27, enter for each CGNUM with CONTCD = 1)

27 Record: RCC()

Format: ()F10.0

- Regulatory Compliance Concentration at the Point of Compliance (ug/L).

28 Record: Descriptive Text

Format: None

- \*\*\* TOR Form \*\*\*

(Continue if TORINPUT >= 1)

- 29 Record: NPLOPT, REMOPT, TORDATE  
Format: F10.0, A10
- NPLOPT is the NAPL Mass estimate option: Enter 0 for Best Estimate only; Enter 1 for Best, Maximum, and Minimum Estimates; Enter 2 for Best Estimate, and Percent(+/-) of Best Estimate;
  - REMOPT is the NAPL Source removal option: Enter 0 for no Mass Removal; Enter 1-3, for 1 to 3 different Mass Removal Plans;
  - TORDATE is the Date Source Emplaced or Reduction was accomplished (Format: mm/dd/yyyy).

- 30 Record: NPLMASS()  
Format: (F)10.0
- NPLMASS is the Estimated NAPL Mass: If NPLOPT=0-Enter Best Estimate; If NPLOPT=1-Enter Best, Maximum, and Minimum Estimates; If NPLOPT=2-Enter Best Estimate, and Percent(+/-) of Best Estimate.

(Enter line 31 if REMOPT > 0)

- 31 Record: NPLREM()  
Format: (F)10.0
- NPLREM is the Source Removal Plans: Enter Percent(%) Removal REMOPT times.

- 32 Record: PERLEN, VELRNG  
Format: F10.0, L10
- PERLEN is the Maximum length of TOR simulation time, in years;
  - VELRNG is the Flag to simulate range in velocities: Enter F to simulate Best Estimate velocity only; Enter T to simulate Minimum, Best Estimate, and Maximum velocities.

(Continue if TORINPUT >= 1.4)

(In line 33, enter for each CGNUM with CONTCD = 1 or CONTNPL = 1)

33 Record: SCC()

Format: ()F10.0

- SCC is the Compliance Concentration at the Source (ug/L).

(Continue if TORINPUT >= 2)

34 Record: PTMOD, PTAVSAT

Format: L2, F10.0

- PTMOD is the Pump and Treat flag: Enter T to simulate Pump and Treat to compare with MNA; Enter F to not simulate MNA only;
- PTAVSAT is the Average saturated thickness of aquifer. Enter if PTMOD = T.

(Enter lines 35-36 if PTMOD=T)

35 Record: PTOPT(3)

Format: 3L2

- PTOPT are the Pump and Treat Flags: PTOPT(1)-Flag for Pumping Well Distance from source; PTOPT(2)-Flag for Pumping Well Rate (<=PERLEN); PTOPT(3)-Flag for Pumping Well Duration. Enter T if parameter will be specified by user, enter F if parameter will be estimated by NAS.

(In line 36, enter for each PTOPT(=)T)

36 Record: PTUSER()

Format: ()F10.0

- PTUSER are the User-specified Pump and Treat parameters.

(Lines 37-40 always printed)

37 Record: Descriptive Text

Format: None

- \*\*\* Data/Results Output Format \*\*\*

38 Record: FRMEXP

Format: A100

- FRMEXP is the Page formatting for print/saved form of the 'Data and Results Table'.

39 Record: FRMHEAD

Format: A100

- FRMHEAD is the Text and format of headers on printed/saved form of the 'Data and Results Table'.

40 Record: FRMFOOT

Format: A100

- FRMFOOT is the Text and format of footers on printed/saved form of the 'Data and Results Table'.

## Appendix 2: NAS Contaminant Database File Structure

- 1      Record:      Descriptive Text, NUMCGS  
Location:      Column 1 - 2  
Format:      None, I10
- Descriptive Text is \*\*\* Number of Groups \*\*\*.
  - NUMCGS is the Number of Contaminant Groups in Database.
- 2      Record:      Descriptive Text  
Location:      Columns 1 - 11  
Format:      None
- Descriptive Text are Headers for Columnar Data (i.e., Contaminant  
MW(g/mole) SOL(mg/l) Koc(ml/g) NAPL frac Total  
Conc Data NAPL Source Stoic.Factor Alt. Path Daut.  
%).
- (Enter lines 3 – 6 NUMCGS times)
- 3      Record:      Dummy input line  
Location:      Columns ()  
Format:      n/a
- Blank line.
- 4      Record:      CGNAME  
Location:      Column 1  
Format:      A100
- CGNAME is the Contaminant Group Name.
- 5      Record:      Descriptive Text , CGTYPE, Descriptive Text ,CGNUM  
Location:      Columns 1 - 4

Format: 3A50, I10

- Descriptive Text is \*\*\* Type of Group \*\*\*.
- CGTYPE is the Type of Contaminant Group: = "Non-reactive" ; = "Electron Donors" ; = "Electron Acceptors" ; = "Co-mingled";
- Descriptive Text is \*\*\* Number of Contaminants in Groups \*\*\*.
- CGNUM: If CGTYPE="Co-mingled" then CGNUM=Number of Contaminant Groups in Co-Mingled Group, else CGNUM=Number of Contaminants in Group.

(if CGTYPE="Co-mingled" then Enter lines 3-6 CGNUM more times)

(Enter line 6, CGNUM times)

6 Record: CONTNAME, CONTMW, CONTSOL, CONTKOC,  
CONTFRAC, CONTTOT, CONTCD, CONTNPL, CONTGC, CONTDF, CONTDTP

Location: Columns 1 - 11

Format: A50, 4F10.0, 3I10, F10.0, I10, F10.0

- CONTNAME is the Contaminant Name;
- CONTMW is the Contaminant Molecular Weight;
- CONTSOL is the Contaminant Solubility;
- CONTKOC is the Contaminant Carbon Matter Partition Coefficient;
- CONTFRAC is the Contaminant Initial Mass Fraction in NAPL;
- CONTTOT is the Contaminant is a Summation of Contaminants Flag:  
< 0, contaminant represents a summation of individual contaminants;  
= 0, contaminant is not represented within a total summed  
contaminant; > 0, contaminant is represented within a total summed  
contaminant, with the value representing the index of that total  
contaminant;
- CONTCD is the Contaminant Concentration Distribution Flag: = 0, the  
user has not provided a C vs.X profile for the contaminant; = 1, the  
user has provided a C vs.X profile for the contaminant;

- CONTNPL is the Contaminant in NAPL Source Flag: = 0, the contaminant is not included in the NAPL source in the TOR simulation; = 1, the contaminant is included in the NAPL source in the TOR simulation;
- CONTGC is the Contaminant Stoichiometric Factor to Daughter: If CGTYPE = 2, then CONTGC represents the stoichiometric factor relating degradation of the electron acceptor to its daughter product;
- CONTDF is the Contaminant Alternate Pathway Flag: = 0, contaminant does not represent an alternate pathway; < 0, contaminant represents an alternate pathway daughter product, with the absolute value representing the index of the parent contaminant;
- CONTDP is the Contaminant Percent from Parent: If CONTDF < 0, then CONTDP represents the Percent of mass (in aqueous phase concentration) of Parent, reserved for the production of this Daughter product.

## Appendix 3: Determining Redox Conditions

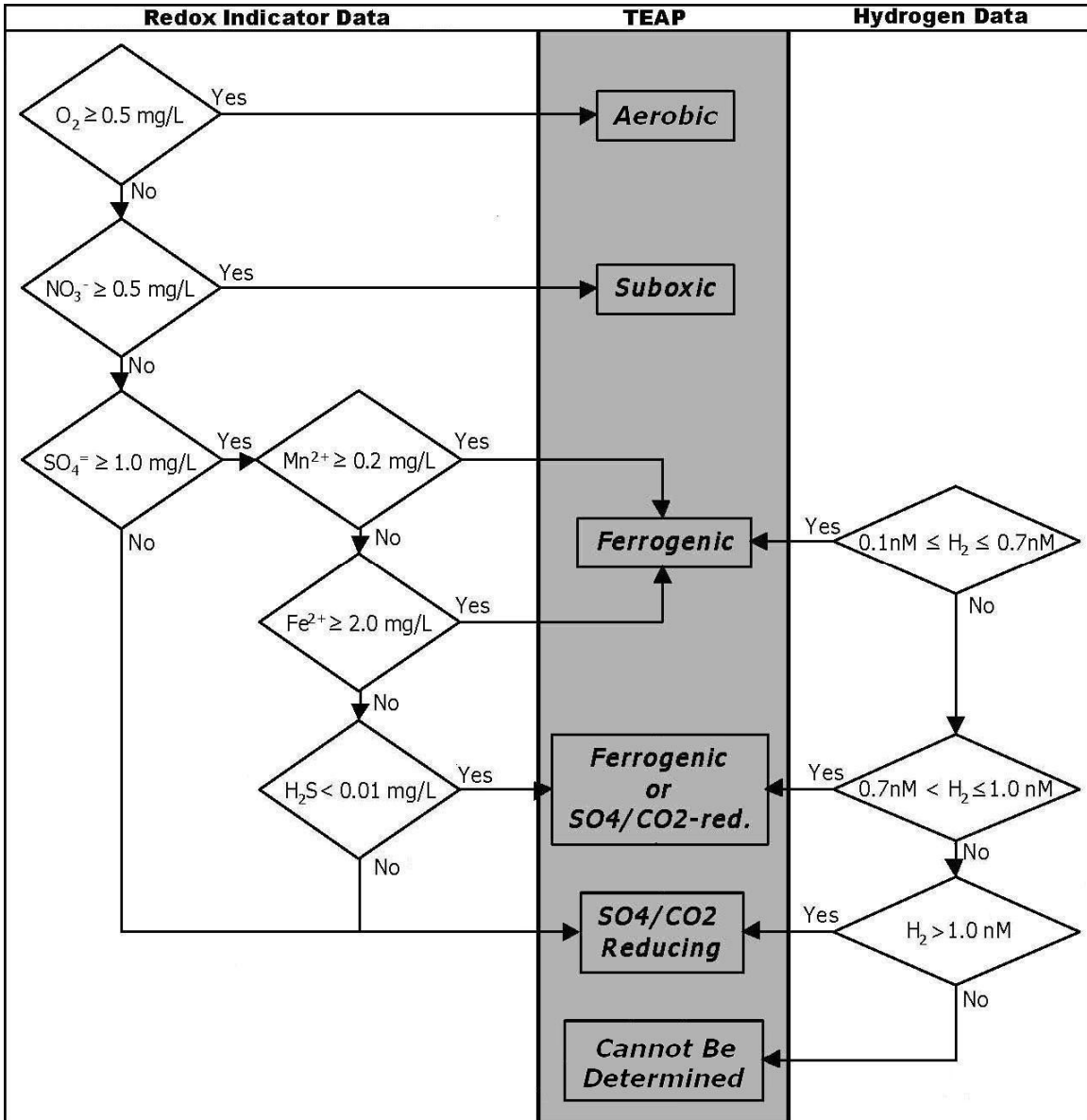


Figure A-38. Flow Chart for Determining Redox Conditions



## **Appendix B: SEAM3D v5.0 Input Instructions**

## SEAM3Dv5.0 INPUT INSTRUCTIONS

Program execution:

To properly run the combined MODFLOW/MT3DMS/SEAM3D executable, at the DOS command prompt, an argument flag must be typed following the program executable name.

1. To run MODFLOW, type: *SEAM3Dv5.0.exe mod*
2. To run MT3DMS or SEAM3D, type: *SEAM3Dv5.0.exe s3d*

The program will then begin execution asking for the appropriate MODFLOW / MT3DMS / SEAM3D Name File.

Major Changes to MT3DMS since v5.0:

1. The name-file procedure is now the only method to start a MT3DMS simulation run. A name-file specifies the names of most input and output files used in a model simulation. In addition, it controls the parts of the model program that are active, i.e., the “packages” that are used in the current simulation. As a result, the “TRNOP” array in the BTN input file is no longer used. However a dummy input line must still remain where the “TRNOP” is formerly specified.
2. The optional implicit matrix solver, the General Conjugate-Gradient (GCG) solver, must now be used in every simulation. In other words, the dispersion, sink/source and reaction terms are now always solved by the implicit finite-difference method, regardless of whether the advection term is solved by the implicit finite-difference method, the mixed Eulerian-Lagrangian methods, or the third-order TVD method.

For the complete input options for MODFLOW and MT3DMS please refer to the full documentation available from their respective websites. SEAM3D v5.0 incorporates:

MODFLOW v1.17.01

MT3DMS v5.2

## INPUT INSTRUCTIONS FOR THE BASIC TRANSPORT PACKAGE

Since the BTN package is needed for every simulation, this input file is always required.

### FOR EACH SIMULATION:

A1 Record: HEADNG(1)

Format: A80

- HEADNG(1) is the first line of any title or heading for the simulation run. The line should not be longer than 80 characters.

A2 Record: HEADNG(2)

Format: A80

- HEADNG(2) is the second line of any title or heading for the simulation run. The line should not be longer than 80 characters.

A3 Record: NLAY, NROW, NCOL, NPER, NCOMP, MCOMP

Format: 6I10

- NLAY is the total number of layers;
- NROW is the total number of rows;
- NCOL is the total number of columns;
- NPER is the total number of stress periods;
- NCOMP is the total number of chemical species included in the current simulation. For single-species simulation, set NCOMP=1;
- MCOMP is the total number of “mobile” species. MCOMP must be equal to or less than NCOMP. For single-species simulation, set MCOMP=1.

Note that “mobile species” are involved in both transport and reaction while “immobile” species equal to (NCOMP-MCOMP) are involved in reaction only. Also, for each species included in NCOMP, MT3DMS automatically tracks a sorbed or immobile counterpart if a

sorption isotherm or dual-domain mass transfer is specified through the Chemical Reaction Package. Thus, there is no need to define separate “immobile” species to simulate sorption or a dual-domain system. The ability to define separate immobile species is only intended for using MT3DMS with add-on reaction packages. **For this version of SEAM3D, NCOMP must equal NCOMP. Species must be entered in the following order:**

1. Nonbiodegradable tracers
2. Hydrocarbon substrates
3. Aqueous phase electron acceptors
4. Inorganic nutrients
5. Products
6. Daughters
7. Components related to RD Package (in this order)
  - a. PCE (if included in the simulation)
  - b. TCE
  - c. DCE
  - d. VC
  - e. Ethene
  - f. Chloride

A4 Record: TUNIT, LUNIT, MUNIT

Format: 3A4

- TUNIT is the name of unit for time, such as DAY or HOUR;
- LUNIT is the name of unit for length, such as FT or M;
- MUNIT is the name of unit for mass, such as LB or KG.

Note that these names are used for identification purposes only, and do not affect the model outcome.

A5 Record: Dummy input line

Format: n/a

- TRNOP is no longer used since MT3DMS v5.0. However, a dummy input line must still be specified in the input file. A blank line is acceptable.

A6 Record: LAYCON(NLAY)

Format: 40I2

- LAYCON is a 1D integer array indicating the type of model layers. Each value in the array corresponds to one model layer. Enter LAYCON in as many lines as necessary if  $NLAY > 40$ .
  - $LAYCON=0$ , the model layer is confined. The layer thickness  $DZ$  to be entered in a subsequent record will be used as the *saturated thickness* of the layer.
  - $LAYCON \neq 0$ , the model layer is either unconfined or convertible between confined and unconfined. The saturated thickness, as calculated by the flow model and saved in the flow-transport link file, will be read and used by the transport model. (Note that this type corresponds to the LAYCON values of 1, 2, and 3 of MODFLOW; however, there is no need to distinguish between these layer types in the transport simulation.)

A7 Array: DELR(NCOL)

Reader: RARRAY

- DELR is a 1D real array representing the cell width along rows ( $\Delta x$ ), in the direction of increasing column indices ( $j$ ). Specify one value for each column of the grid.

A8 Array: DELC(NROW)

Reader: RARRAY

- DELC is a 1D real array representing the cell width along columns ( $\Delta y$ ), in the direction of increasing row indices (i). Specify one value for each row of the grid.

A9    Array:        HTOP(NCOL,NROW)

Reader:        RARRAY

- HTOP is a 2D array defining the top elevation of all cells in the first (top) model layer, relative to the same datum as the hydraulic heads.
  - If the first model layer is unconfined, HTOP can be set most conveniently to a uniform elevation above the water table. Note that the concentrations for the cells in the first model layer are calculated at nodal points assumed to be midway between HTOP and the bottom of the first layer. Thus, HTOP should not be set much higher than the water table. Also note that the difference between HTOP and the bottom elevation of the first layer must be equal to the layer thickness DZ to be defined in the next record.
  - If the first model layer is confined, HTOP is equal to the bottom elevation of the confining unit overlying the first model layer.

A10   Array:        DZ(NCOL,NROW) (one array for each layer in the grid)

Reader:        RARRAY

- DZ is the thickness of all cells in each model layer. DZ is a three-dimensional (3D) array. The input to 3D arrays is handled as a series of two-dimensional arrays with one array for each layer, entered in the sequence of layer 1, 2, ..., NLAY. The thickness of the first layer must be equal to the difference between HTOP and its bottom elevation. When the grid is discretized into horizontal layers, HTOP for the first layer and DZ within each layer are uniform. However, if a vertically distorted grid is used, both HTOP and DZ may be variable for cells within the same layer.

- A11 Array: PRSITY(NCOL,NROW) (one array for each layer)  
 Reader: RARRAY
- PRSITY is the “effective” porosity of the porous medium in a single porosity system. Note that if a dual-porosity system is simulated (**not simulated in this version of SEAM3D**), PRSITY should be specified as the “mobile” porosity, i.e., the ratio of interconnected pore spaces filled with mobile waters over the bulk volume of the porous medium; the “immobile” porosity is defined through the Chemical Reaction Package.
- A12 Array: ICBUND(NCOL,NROW) (one array for each layer)  
 Reader: IARRAY
- ICBUND is an integer array specifying the boundary condition type (inactive, constant-concentration, or active) for every model cell. For multi-species simulation, ICBUND defines the boundary condition type *shared by all species*. Note that different species are allowed to have different constant-concentration conditions through an option in the Source and Sink Mixing Package.
    - ICBUND=0, the cell is an inactive concentration cell for all species. Note that no-flow or “dry” cells are automatically converted into inactive concentration cells. Furthermore, active cells in terms of flow can be treated as inactive concentration cells to minimize the area needed for transport simulation, as long as the solute transport is insignificant near those cells.
    - ICBUND<0, the cell is a constant-concentration cell *for all species*. The starting concentration of each species remains the same at the cell throughout the simulation. (To define different constant-concentration conditions for different species at the same cell location, refer to the Sink/Source Mixing Package.) Also note that unless explicitly defined as a constant-



concentration cell, a constant-head cell in the flow model is not treated as a constant-concentration cell.

- If ICBUND>0, the cell is an active (variable) concentration cell where the concentration value will be calculated.

(Enter A13 for each species)

A13 Array:       SCONC(NCOL,NROW) (one array for each layer)

Reader:       RARRAY

- SCONC is the starting concentration (initial condition) at the beginning of the simulation (unit:  $\text{ML}^{-3}$ ). For multispecies simulation, the starting concentration must be specified for all species, one species at a time.

A14 Record:     CINACT, THKMIN

Format:        2F10.0

- CINACT is the value for indicating an inactive concentration cell (ICBUND=0). Even if it is not anticipated to have inactive cells in the model, a value for CINACT still must be submitted.
- THKMIN is the minimum saturated thickness in a cell, expressed as the decimal fraction of the model layer thickness (DZ), below which the cell is considered inactive. The default value is 0.01 (i.e., 1% of the model layer thickness).

A15 Record:     IFMTCN, IFMTNP, IFMTRF, IFMTDP, SAVUCN

Format:        4I10, L10

- IFMTCN is a flag indicating whether the calculated *concentration* should be printed to the standard output text file and also serves as a printing-format code if it is printed.
- IFMTCN>0, concentration is printed in the wrap form.  
    <0, concentration is printed in the strip form.  
    =0, concentration is not printed.

- IFMTNP is a flag indicating whether the *number of particles in each cell* (integers) should be printed and also serves as a printing-format code if they are printed. The convention is the same as that used for IFMTCN.
- IFMTRF is a flag indicating whether the model-calculated *retardation factor* should be printed and also serves as a printing-format code if it is printed. The convention is the same as that used for IFMTCN.
- IFMTDP is a flag indicating whether the model-calculated, distance-weighted *dispersion coefficient* should be printed and also serves as a printing-format code if it is printed. The convention is the same as that used for IFMTCN.
- SAVUCN is a logical flag indicating whether the concentration solution should be saved in a default unformatted (binary) file named MT3Dnnn.UCN, where nnn is the species index number, for post-processing purposes or for use as the initial condition in a continuation run.
  - SAVUCN=T, the concentration of each species will be saved in the default file MT3Dnnn.UCN. In addition, the model spatial discretization information will be saved in another default file named MT3D.CNF, to be used in conjunction with MT3Dnnn.UCN for post-processing purposes.
  - SAVUCN=F, neither MT3Dnnn.UCN nor MT3D.CNF is created.

A16 Record: NPRS

Format: I10

- NPRS is a flag indicating the frequency of the output, and also indicating whether the output frequency is specified in terms of total elapsed simulation time or the transport step number. Note that what are actually printed or saved is controlled by the input values entered in the preceding record (Record A15).

NPRS>0, simulation results will be printed to the standard output text

file or saved to the unformatted concentration file at times as specified in record TIMPRS(NPRS) to be entered in the next record.

=0, simulation results will not be printed or saved except at the end of simulation.

<0, simulation results will be printed or saved whenever the number of transport steps is an even multiple of NPRS.

(Enter A17 only if NPRS > 0)

A17 Record: TIMPRS(NPRS)

Format: 8F10.0

- TIMPRS is the total elapsed time at which the simulation results are printed to the standard output text file or saved in the default unformatted (binary) concentration file MT3Dnnn.UCN. Note that if NPRS > 8, enter TIMPRS in as many lines as necessary.

A18 Record: NOBS, NPROBS

Format: 2I10

- NOBS is the number of observation points at which the concentration of each species will be saved at the specified frequency in the default MT3Dnnn.OBS where nnn is the species index number.
- NPROBS is an integer indicating how frequently the concentration at the specified observation points should be saved in the observation file MT3Dnnn.OBS. Concentrations are saved every NPROBS step.

(Enter A19 NOBS times if NOBS > 0)

A19 Record: KOBS, IOBS, JOBS

Format: 3I10

- KOBS, IOBS and JOBS are the cell indices (layer, row, column) in which the observation point or monitoring well is located and for which the concentration is to be printed at every transport step in file

MT3Dnnn.OBS. Enter one set of KOBS, IOBS, JOBS for each observation point.

A20 Record: CHKMAS, NPRMAS

Format: L10, I10

- CHKMAS is a logical flag indicating whether a one-line summary of mass balance information should be printed, for checking and post-processing purposes, in the default file MT3Dnnn.MAS, where nnn is the species index number.
  - CHKMAS=T, the mass balance information for each transport step will be saved in file MT3Dnnn.MAS;
  - CHKMAS=F, file MT3Dnnn.MAS is not created.
- NPRMAS is an integer indicating how frequently the mass budget information should be saved in the mass balance summary file MT3Dnnn.MAS. Mass budget information is saved every NPRMAS step.

FOR EACH STRESS PERIOD:

A21 Record: PERLEN, NSTP, TSMULT

Format: F10.0, I10, F10.0

- PERLEN is the length of the current stress period. If the flow solution is transient, PERLEN specified here must be equal to that specified for the flow model. If the flow solution is steady-state, PERLEN can be set to any desired length.
- NSTP is the number of time steps *for the transient flow solution* in the current stress period. If the flow solution is steady-state, NSTP=1.
- TSMULT is the multiplier for the length of successive time steps used in the transient flow solution; it is used only if NSTP>1.
  - TSMULT>0, the length of each flow time step within the current stress period is calculated using the geometric

progression as in MODFLOW. Note that both NSTP and TSMULT specified here must be identical to those specified in the flow model if the flow model is transient.

- TSMULT $\leq$ 0, the length of each flow time step within the current stress period is read from the record TSLNGH (see A22). This option is needed in case the length of time steps for the flow solution is not based on a geometric progression in a flow model, unlike MODFLOW.

(Enter A22 if TSMULT  $\leq$ 0)

A22 Record: TSLNGH(NSTP)

Format: 8F10.0

- TSLNGH provides the length of time steps for the flow solution in the current stress period. This record is needed only if the length of time steps for the flow solution is not based on a geometric progression. Enter TSLNGH in as many lines as necessary if NSTP $>$ 8.

A23 Record: DT0, MXSTRN, TTSMULT, TTSMAX

Format: F10.0, I10, 2F10.0

- DT0 is the user-specified transport stepsize within each time step of the flow solution. DT0 is interpreted differently depending on whether the solution option chosen is explicit or implicit:
  - For explicit solutions (i.e., the GCG solver is not used), the program will always calculate a maximum transport stepsize which meets the various stability criteria. Setting DT0 to zero causes the model-calculated transport stepsize to be used in the simulation. However, the model-calculated DT0 may not always be optimal. In this situation, DT0 should be adjusted to find a value that leads to the best results. If DT0 is given a value greater than the model-calculated stepsize, the model-

calculated stepsize, instead of the user-specified value, will be used in the simulation.

- For implicit solutions (i.e., the GCG solver is used), DT0 is the initial transport stepsize. If it is specified as zero, the model-calculated value of DT0, based on the user-specified Courant number in the Advection Package, will be used. The subsequent transport stepsize may increase or remain constant depending on the user-specified transport stepsize multiplier TTSMULT and the solution scheme for the advection term.
- MXSTRN is the maximum number of transport steps allowed within one time step of the flow solution. If the number of transport steps within a flow time step exceeds MXSTRN, the simulation is terminated.
- TTSMULT is the multiplier for successive transport steps within a flow time step, if the Generalized Conjugate Gradient (GCG) solver is used *and* the solution option for the advection term is the standard finite-difference method. A value between 1.0 and 2.0 is generally adequate. If the GCG package is not used, the transport solution is solved explicitly as in the original MT3D code, and TTSMULT is always set to 1.0 regardless of the user-specified input. Note that for the particle tracking based solution options and the 3<sup>rd</sup>-order TVD scheme, TTSMULT does not apply.
- TTSMAX is the maximum transport stepsize allowed when transport stepsize multiplier TTSMULT > 1.0. Setting TTSMAX=0 imposes no maximum limit.

## INPUT INSTRUCTIONS FOR THE ADVECTION PACKAGE

The input file is needed only if the Advection Package is used; however, this package is needed under almost all circumstances.

### FOR EACH SIMULATION:

B1    Record:        MIXELM, PERCEL, MXPART, NADVFD  
      Format:        I10, F10.0, 2I10

- MIXELM is an integer flag for the advection solution option (**only MIXELM =0 and -1 are supported by SEAM3D**).

MIXELM = 0, the standard finite difference method with upstream or central-in-space weighting, depending on the value of NADVFD;

= 1, the forward-tracking method of characteristics (MOC);

= 2, the backward-tracking modified method of characteristics (MMOC);

= 3, the hybrid method of characteristics (HMOC) with MOC or MMOC automatically and dynamically selected;

= -1, the third-order TVD scheme (ULTIMATE).

- PERCEL is the Courant number, i.e., the number of cells (or a fraction of a cell) advection will be allowed in any direction in one transport step.
  - For implicit finite-difference or particle tracking based schemes, there is no limit on PERCEL, but for accuracy reasons, it is generally not set much greater than one. Note, however, that the PERCEL limit is checked over the entire model grid. Thus, even if  $PERCEL > 1$ , advection may not be more than one cell's length at most model locations.
  - For the explicit finite-difference or the third-order TVD scheme, PERCEL is also a stability constraint, which must not

exceed one and will be automatically reset to one if a value greater than one is specified.

- MXPART is the maximum total number of moving particles allowed, and is used only when MIXELM= 1 or 3.
- NADVFD is an integer flag indicating which weighting scheme should be used; it is needed only when the advection term is solved using the implicit finite-difference method.

NADVFD =0 or 1, upstream weighting (default);  
=2, central-in-space weighting.

(Enter B2 if MIXELM=1, 2 or 3)

B2 Record: ITRACK, WD  
Format: I10, F10.0

- ITRACK is a flag indicating which particle tracking algorithm is selected for the Eulerian-Lagrangian methods.  
ITRACK =1, the first-order Euler algorithm is used;  
=2, the fourth-order Runge-Kutta algorithm is used; this option is computationally demanding and may be needed only when PERCEL is set greater than one.  
=3, the hybrid 1<sup>st</sup> and 4<sup>th</sup> order algorithm is used; the Runge-Kutta algorithm is used in sink/source cells and the cells next to sinks/sources while the Euler algorithm is used elsewhere.
- WD is a concentration weighting factor between 0.5 and 1. It is used for operator splitting in the particle tracking based methods. The value of 0.5 is generally adequate. The value of WD may be adjusted to achieve better mass balance. Generally, it can be increased toward 1.0 as advection becomes more dominant.

(Enter B3 if MIXELM=1 or 3)

B3 Record: DCEPS, NPLANE, NPL, NPH, NPMIN, NPMAX



Format: F10.0, 5I10

- DCEPS is a small Relative Cell Concentration Gradient below which advective transport is considered negligible. A value around  $10^{-5}$  is generally adequate.
- NPLANE is a flag indicating whether the random or fixed pattern is selected for initial placement of moving particles.
  - NPLANE=0, the random pattern is selected for initial placement. Particles are distributed randomly in both the horizontal and vertical directions by calling a random number generator. This option is usually preferred and leads to smaller mass balance discrepancy in nonuniform or diverging/converging flow fields.
  - NPLANE>0, the fixed pattern is selected for initial placement. The value of NPLANE serves as the number of vertical “planes” on which initial particles are placed within each cell block. The fixed pattern may work better than the random pattern only in relatively uniform flow fields. For two-dimensional simulations in plan view, set NPLANE=1. For cross sectional or three-dimensional simulations, NPLANE=2 is normally adequate. Increase NPLANE if more resolution in the vertical direction is desired.
- NPL is number of initial particles per cell to be placed at cells where the Relative Cell Concentration Gradient is less than or equal to DCEPS. Generally, NPL can be set to zero since advection is considered insignificant when the Relative Cell Concentration Gradient is less than or equal to DCEPS. Setting NPL equal to NPH causes a uniform number of particles to be placed in every cell over the entire grid (i.e., the uniform approach).
- NPH is number of initial particles per cell to be placed at cells where the Relative Cell Concentration Gradient is greater than DCEPS. The selection of NPH depends on the nature of the flow field and also the

computer memory limitation. Generally, use a smaller number in relatively uniform flow fields and a larger number in relatively nonuniform flow fields. However, values exceeding 16 in two-dimensional simulation or 32 in three-dimensional simulation are rarely necessary. If the random pattern is chosen, NPH particles are randomly distributed within the cell block. If the fixed pattern is chosen, NPH is divided by NPLANE to yield the number of particles to be placed per vertical plane, which is rounded to one of the predefined fixed pattern values.

- NPMIN is the minimum number of particles allowed per cell. If the number of particles in a cell at the end of a transport step is fewer than NPMIN, new particles are inserted into that cell to maintain a sufficient number of particles. NPMIN can be set to zero in relatively uniform flow fields, and a number greater than zero in diverging/converging flow fields. Generally, a value between zero and four is adequate.
- NPMAX is the maximum number of particles allowed per cell. If the number of particles in a cell exceeds NPMAX, all particles are removed from that cell and replaced by a new set of particles equal to NPH to maintain mass balance. Generally, NPMAX can be set to approximately twice of NPH.

(Enter B4 if MIXELM=2, or 3)

B4 Record: INTERP, NLSINK, NPSINK

Format: 3I10

- INTERP is a flag indicating the concentration interpolation method for use in the MMOC scheme. Currently, only linear interpolation is implemented. Enter INTERP=1.
- NLSINK is a flag indicating whether the random or fixed pattern is selected for initial placement of particles to approximate sink cells in

the MMOC scheme. The convention is the same as that for NPLANE. It is generally adequate to set NLSINK equivalent to NPLANE.

- NPSINK is the number of particles used to approximate sink cells in the MMOC scheme. The convention is the same as that for NPH. It is generally adequate to set NPSINK equivalent to NPH.

(Enter B5 if MIXELM=3)

B5 Record: DCHMOC

Format: F10.0

- DCHMOC is the critical Relative Concentration Gradient for controlling the selective use of either MOC or MMOC in the HMOC solution scheme.

The MOC solution is selected at cells where the Relative Concentration Gradient is greater than DCHMOC;

The MMOC solution is selected at cells where the Relative Concentration Gradient is less than or equal to DCHMOC.

## INPUT INSTRUCTIONS FOR THE DISPERSION PACKAGE

The input file is needed only if the Dispersion Package is used in the simulation.

### FOR EACH SIMULATION:

- C0    Record:        One or more optional keywords.  
      Format:        [Free]
- The only keyword currently supported is [MultiDiffusion], case insensitive. The keyword must be specified in an input line with the \$ sign in the first column. The keyword input record is optional.
- C1    Array:        AL(NCOL,NROW) (One array for each layer).  
      Reader:       RARRAY
- AL is the longitudinal dispersivity,  $\alpha_L$ , for every cell of the model grid (unit: L).
- C2    Array:        TRPT(NLAY)  
      Reader:       RARRAY
- TRPT is a 1D real array defining the ratio of the horizontal transverse dispersivity,  $\alpha_{TH}$ , to the longitudinal dispersivity,  $\alpha_L$ . Each value in the array corresponds to one model layer. Some recent field studies suggest that TRPT is generally not greater than 0.1.
- C3    Array:        TRPV(NLAY)  
      Reader:       RARRAY
- TRPV is the ratio of the vertical transverse dispersivity,  $\alpha_{TV}$ , to the longitudinal dispersivity,  $\alpha_L$ . Each value in the array corresponds to one model layer. Some recent field studies suggest that TRPT is generally not greater than 0.01.

Set TRPV equal to TRPT to use the standard isotropic dispersion mode. Otherwise, the modified isotropic dispersion model is used.

*If no keyword is defined:*

C4 Array: DMCOEF(NLAY)

Reader: RARRAY

- DMCOEF is the effective molecular diffusion coefficient (unit:  $L^2 T^{-1}$ ). Set DMCOEF=0 if the effect of molecular diffusion is considered unimportant. Each value in the array corresponds to one model layer.  
*Enter one array for all solute components.*

*If keyword [MultiDiffusion] is defined:*

C4 Array: DMCOEF(NCOL,NROW) (One array for each layer)

Reader: RARRAY

- DMCOEF is the effective molecular diffusion coefficient (unit:  $L^2 T^{-1}$ ). Set DMCOEF=0 if the effect of molecular diffusion is considered unimportant. Each value in the array corresponds to one model cell.  
*Repeat the input for each mobile components.*

## INPUT INSTRUCTIONS FOR THE SINK & SOURCE MIXING PACKAGE

The input file is needed if any sink or source option is used in the flow model, including the constant-head or general-head-dependent boundary conditions. The classification of the sink/source types used in MT3DMS is the same as that used by MODFLOW (McDonald and Harbaugh, 1988).

### FOR EACH SIMULATION:

D1 Record: Dummy input line

Format: n/a

- These logical flags are no longer needed as the status of various flow sink/source packages is obtained by MT3DMS through the Flow-Transport Link File produced by MODFLOW. However, a dummy input line must still be specified in the input file. A blank line is acceptable.

D2 Record: MXSS, ISSGOUT

Format: 2I10

- MXSS is the maximum number of all point sinks and sources included in the flow model. Point sinks and sources include constant-head cells, wells, drains, rivers, and general-head-dependent boundary cells. Recharge and evapotranspiration are treated as areally distributed sinks and sources; thus, they should not be counted as point sinks and sources. MXSS should be set close to the actual number of total point sinks and sources in the flow model to minimize the computer memory allocated to store sinks and sources.
- ISSGOUT is the unit number for an optional output file to save the calculated flux-averaged composite concentrations at multi-node wells. The name of the output file must be specified through the Name File as in "DATA ISSGOUT FileName".

FOR EACH STRESS PERIOD:

(Enter D3 if FRCH=T)

D3 Record: INCRCH

Format: I10

- INCRCH is a flag indicating whether an array containing the concentration of recharge flux for each species will be read for the current stress period.

If INCRCH  $\geq 0$ , an array containing the concentration of recharge flux for each species will be read.

$< 0$ , the concentration of recharge flux will be reused from the last stress period. If INCRCH  $< 0$  is specified for the first stress period, by default, the concentration of positive recharge flux (source) is set equal to zero and that of negative recharge flux (sink) to the aquifer concentration.

(Enter D4 for each species if FRCH=T and INCRCH  $\geq 0$ )

D4 Array: CRCH(NCOL,NROW)

Reader: RARRAY

- CRCH is the concentration of recharge flux for a particular species. If the recharge flux is positive, it acts as a source whose concentration can be specified as desired. If the recharge flux is negative, it acts as a sink (discharge) whose concentration is always set equal to the concentration of groundwater at the cell where discharge occurs. Note that the location and flow rate of recharge/discharge are obtained from the flow model directly through the unformatted flow-transport link file.

(Enter D5 if FEVT=T)

D5 Record: INCEVT

Format: I10

- INCEVT is a flag indicating whether an array containing the concentration of evapotranspiration flux for each species will be read for the current stress period.

If INCEVT  $\geq 0$ , an array containing the concentration of

evapotranspiration flux for each species will be read.

$< 0$ , the concentration of evapotranspiration flux for each species will be reused from the last stress period. If INCEVT  $< 0$  is specified for the first stress period, by default, the concentration of negative evapotranspiration flux (sink) is set to the aquifer concentration, while the concentration of positive evapotranspiration flux (source) is set to zero.

(Enter D6 for each species if FEVT=T and INCEVT  $\geq 0$ )

D6 Array: CEVT(NCOL,NROW)

Reader: RARRAY

- CEVT is the concentration of evapotranspiration flux for a particular species. Evapotranspiration is the only type of sink whose concentration may be specified externally. Note that the concentration of a sink cannot be greater than that of the aquifer at the sink cell. Thus, if the sink concentration is specified greater than that of the aquifer, it is automatically set equal to the concentration of the aquifer. Also note that the location and flow rate of evapotranspiration are obtained from the flow model directly through the unformatted flow-transport link file.

D7 Record: NSS

Format: I10



- NSS is the number of point *sources* whose concentrations need to be specified. By default, unspecified point sources are assumed to have zero concentration. (The concentration of point *sinks* is always set equal to the concentration of groundwater at the sink location.) Note that in MT3DMS, point sources are generalized to include not only those associated with a flow rate in the flow model, but also those independent of the flow solution. This type of “mass-loading” sources may be used to include contaminant sources which have minimal effects on the hydraulics of the flow field.

(Enter D8 NSS times if NSS>0)

D8 Record: KSS, ISS, JSS, CSS, ISSTYPE, (CSSMS(n), n=1, NCOMP)

Format: 3I10, F10.0, I10, [free]

- KSS, ISS, JSS are the cell indices (layer, row, column) of the point source for which a concentration needs to be specified for each species.
- CSS is the specified source concentration or mass-loading rate, depending on the value of ISSTYPE, in a single-species simulation,. (For a multi-species simulation, CSS is not used, but a dummy value still needs to be entered here.)

Note that for most types of sources, CSS is interpreted as the source concentration with the unit of mass per unit volume ( $ML^{-3}$ ), which, when multiplied by its corresponding flow rate ( $L^3 T^{-1}$ ) from the flow model, yields the mass-loading rate ( $MT^{-1}$ ) of the source.

For a special type of sources (ISSTYPE=15), CSS is taken directly as the mass-loading rate ( $MT^{-1}$ ) of the source so that no flow rate is required from the flow model.

Furthermore, if the source is specified as a constant-concentration cell (ISSTYPE=-1), the specified value of CSS is assigned directly as the concentration of the designated cell. If the designated cell is also

associated with a sink/source term in the flow model, the flow rate is not used.

- ISSTYPE is an integer indicating the type of the point source as listed below:

ISSTYPE = 1, constant-head cell;

= 2, well;

= 3, drain (note that in MODFLOW conventions, a drain is always a sink, thus, the concentration for drains cannot be specified if the flow solution is from MODFLOW);

= 4, river (or stream);

= 5, general-head-dependent boundary cell;

= 15, mass-loading source(**not simulated in this version of SEAM3D**);

= -1, constant-concentration cell.

**(NEW CODES ARE SIMULATED – SEE MT3DMS MANUAL)**

- (CSSMS(n), n=1, NCOMP) defines the concentrations of a point source for multispecies simulation with NCOMP>1. In a multispecies simulation, it is necessary to define the concentrations of *all species* associated with a point source. As an example, if a chemical of a certain species is injected into a multispecies system, the concentration of that species is assigned a value greater than zero while the concentrations of all other species are assigned zero. CSSMS(n) can be entered in free format, separated by a comma or space between values.

Several important notes on assigning concentration for the constant-concentration condition (ISSTYPE = -1) are listed below:

- (a) The constant-concentration condition defined in this input file takes precedence to that defined in the Basic Transport Package input file.

- (b) In a multiple stress period simulation, a constant-concentration cell, once defined, will remain a constant-concentration cell in the duration of the simulation, but its concentration value can be specified to vary in different stress periods.
- (c) In a multispecies simulation, if it is only necessary to define different constant-concentration conditions for selected species at the same cell location, specify the desired concentrations for those species, and assign a *negative* value for all other species. The negative value is a flag used by MT3DMS to skip assigning the constant-concentration condition for the designated species.

Since version 5.2, users can specify the input concentration of an injection well (ISSTYPE=2), i.e., CSS or CSSMS, as a negative integer code (IC). The absolute value of the integer code is the single cell location indicator of the extraction well whose output concentration is used as the input concentration for the injection well. For an extraction well located at layer K, row I, and column J, IC is computed as,  $IC = NCOL * NROW * (K - 1) + NCOL * (I - 1) + J$ , where NCOL and NROW are the total numbers of columns and rows.

## INPUT INSTRUCTIONS FOR THE CHEMICAL REACTION PACKAGE

The input file is needed only if chemical reactions are simulated. In addition, the option for modeling transport in a dual-domain system is specified through this file.

### FOR EACH SIMULATION:

E1    Record:        ISOTHM, IREACT, IRCTOP, IGETSC  
      Format:        4I10

- ISOTHM is a flag indicating which type of sorption (or dual-domain mass transfer) is simulated:

ISOTHM =0, no sorption is simulated;  
         =1, Linear isotherm (equilibrium-controlled);  
         =2, Freundlich isotherm (equilibrium-controlled);  
         =3, Langmuir isotherm (equilibrium-controlled);  
         =4, First-order kinetic sorption (nonequilibrium);  
         =5, Dual-domain mass transfer (without sorption);  
         =6, Dual-domain mass transfer (with sorption) (**not simulated in this version of SEAM3D**).

- IREACT is a flag indicating which type of kinetic rate reaction is simulated:

IREACT =0, no kinetic rate reaction is simulated;  
         =1, first-order irreversible reaction.  
         =100, zeroth-order reaction (decay or production).

Note that this reaction package is not intended for modeling chemical reactions between species. An add-on reaction package developed specifically for that purpose may be used.

- IRCTOP is an integer flag indicating how reaction variables are entered:

IRCTOP  $\geq 2$ , all reaction variables are specified as 3D arrays on a

cell-by-cell basis.

<2, all reaction variables are specified as a 1D array with each value in the array corresponding to a single layer.

This option is mainly for retaining compatibility with the previous versions of MT3D.

- IGETSC is an integer flag indicating whether the initial concentration for the nonequilibrium sorbed or immobile phase of all species should be read when nonequilibrium sorption (ISOTHM=4) or dual-domain mass transfer (ISOTHM=5 or 6) is simulated:

IGETSC=0, the initial concentration for the sorbed or immobile phase is not read. By default, the sorbed phase is assumed to be in equilibrium with the dissolved phase (ISOTHM=4), and the immobile domain is assumed to have zero concentration (ISOTHM=5 or 6).

>0, the initial concentration for the sorbed phase or immobile liquid phase of all species will be read.

(Enter E2A if ISOTHM=1, 2, 3, 4 or 6; but not 5)

E2A Array: RHOB(NCOL,NROW) (one array for each layer)

Reader: RARRAY

- RHOB is the bulk density of the aquifer medium (unit:  $\text{ML}^{-3}$ ).

(Enter E2B if ISOTHM=5 or 6)

E2B Array: PRSITY2(NCOL,NROW) (one array for each layer) (**not simulated in this version of SEAM3D**)

Reader: RARRAY

- PRSITY2 is the porosity of the immobile domain, i.e., the ratio of pore spaces filled with immobile fluids over the bulk volume of the aquifer medium, when the simulation is intended to represent a dual-domain system.

(Enter E2C for each species if IGETSC>0)

E2C Array: SRCONC(NCOL,NROW) (one array for each layer)

Reader: RARRAY

- SRCONC is the user-specified initial concentration for the sorbed phase of a particular species if ISOTHM= 4 (unit:  $\text{MM}^{-1}$ ). Note that for equilibrium-controlled sorption, the initial concentration for the sorbed phase cannot be specified. SRCONC is the user-specified initial concentration for the immobile liquid phase if ISOTHM=5 or 6 (unit:  $\text{ML}^{-3}$ ).

(Enter E3 for each species if ISOTHM>0)

E3 Array: SP1(NCOL,NROW) (one array for each layer)

Reader: RARRAY

- SP1 is the first sorption parameter. The use of SP1 depends on the type of sorption selected (i.e., the value of ISOTHM):

For linear sorption (ISOTHM=1) and nonequilibrium

sorption (ISOTHM=4), SP1 is the distribution coefficient ( $K_d$ ) (unit:  $\text{L}^3 \text{M}^{-1}$ ).

For Freundlich sorption (ISOTHM=2), SP1 is the Freundlich equilibrium constant ( $K_f$ ) (the unit depends on the Freundlich exponent  $a$ ).

For Langmuir sorption (ISOTHM=3), SP1 is the Langmuir equilibrium constant ( $K_l$ ) (unit:  $\text{L}^3 \text{M}^{-1}$ ).

For dual-domain mass transfer without *sorption* (ISOTHM=5), SP1 is not used, but still must be entered.

For dual-domain mass transfer with sorption (ISOTHM=6), SP1 is Also the distribution coefficient ( $K_d$ ) (unit:  $\text{L}^3 \text{M}^{-1}$ ).

(Enter E4 for each species if ISOTHM>0)

E4 Array: SP2(NCOL,NROW) (one array for each layer)

Reader: RARRAY

- SP2 is the second sorption or dual-domain model parameter. The use of SP2 depends on the type of sorption or dual-domain model selected: For linear sorption (ISOTHM=1), SP2 is read but not used. For Freundlich sorption (ISOTHM=2), SP2 is the Freundlich exponent  $a$ . For Langmuir sorption (ISOTHM=3), SP2 is the total concentration of the sorption sites available ( $\bar{S}$ ) (unit:  $\text{MM}^{-1}$ ). For nonequilibrium sorption (ISOTHM=4), SP2 is the first-order mass transfer rate between the dissolved and sorbed phases (unit:  $\text{T}^{-1}$ ). For dual-domain mass transfer (ISOTHM=5 or 6), SP2 is the first-order mass transfer rate between the two domains (unit:  $\text{T}^{-1}$ ).

(Enter E5 for each species if IREACT>0)

E5    Array:        RC1(NCOL, NROW) (one array for each layer)

Reader:        RARRAY

- If IREACT=1 (first-order kinetic reactions), RC1 is the first-order rate coefficient for the dissolved (liquid) phase (unit:  $\text{T}^{-1}$ ). If a dual-domain system is simulated, the reaction rates for the liquid phase in the mobile and immobile domains are assumed to be equal.
- If IREACT=100 (zeroth-order decay or production), RC1 is the zeroth-order rate coefficient for the dissolved (liquid) phase (unit:  $\text{ML}^{-3}\text{T}^{-1}$ ) (*positive for decay and negative for production*). If a dual-domain system is simulated, the rate coefficients for the liquid phase in the mobile and immobile domains are assumed equal.

(Enter E6 for each species if IREACT>0)

E6    Array:        RC2(NCOL, NROW) (one array for each layer)

Reader:        RARRAY

- If IREACT=1 (first-order kinetic reactions),

RC2 is the first-order rate coefficient for the sorbed (solid) phase (unit:  $T^{-1}$ ). If a dual-domain system is simulated, the rate coefficients for the sorbed phase in the mobile and immobile domains are assumed equal.

- If IREACT=100 (zeroth-order decay or production),

RC2 is the zeroth-order rate coefficient for the sorbed (solid) phase (unit:  $MM^{-1}T^{-1}$ ) (*positive for decay and negative for production*). If a dual-domain system is simulated, the rate coefficients for the sorbed phase in the mobile and immobile domains are assumed equal.



## INPUT INSTRUCTIONS FOR THE GENERALIZED CONJUGATE GRADIENT PACKAGE

The input file is needed only if the GCG solver is used for implicit solution schemes. This package is a new addition in MT3DMS

### FOR EACH SIMULATION:

F1 Record: MXITER, ITER1, ISOLVE, NCRS

Format: Free

- MXITER is the maximum number of outer iterations; it should be set to an integer greater than one only when a nonlinear sorption isotherm is included in simulation.
- ITER1 is the maximum number of inner iterations; a value of 30-50 should be adequate for most problems.
- ISOLVE is the type of preconditioners to be used with the Lanczos/ORTHOMIN acceleration scheme:
  - = 1, Jacobi
  - = 2, SSOR
  - = 3, Modified Incomplete Cholesky (MIC) (MIC usually converges faster, but it needs significantly more memory)
- NCRS is an integer flag for treatment of dispersion tensor cross terms:
  - = 0, lump all dispersion cross terms to the right-hand-side (approximate but highly efficient).
  - = 1, include full dispersion tensor (memory intensive).

F2 Record: ACCL, CCLOSE, IPRGCG

Format: Free

- ACCL is the relaxation factor for the SSOR option; a value of 1.0 is generally adequate.

- CCLOSE is the convergence criterion in terms of relative concentration; a real value between  $10^{-4}$  and  $10^{-6}$  is generally adequate.
- IPRGCG is the interval for printing the maximum concentration changes for each iteration. Set IPRGCG to zero as default for printing at the end of each stress period.

## INPUT INSTRUCTIONS FOR THE BIODEGRADATION PACKAGE

This input file must be created only if the Biodegradation Package is specified in the Basic Transport Package; i.e., TRNOPT(6) is set to "T". Input is read on unit 11.

### FOR EACH SIMULATION:

F1 Record: NTRAC, NHCAR, NNUTR, NDAUT

Format: 4I10

- NTRAC is the total number of non-biodegradable tracers:  
 $0 \leq \text{NTRAC} \leq 5$ .
- NHCAR is the total number of biodegradable substrates:  
 $0 \leq \text{NHCAR} \leq 8$ .
- NNUTR is the total number of inorganic nutrients:  
 $0 \leq \text{NNUTR} \leq 5$ .
- NDAUT is the total number of daughter products:  
 $0 \leq \text{NDAUT} \leq \text{NHCAR}$ .

F2 Record: STOCHOPT

Format: L2

- Flag for spatial variability option for maximum specific rate of substrate utilization. Enter T to allow the parameter to vary in space; enter F for constant value.

F3 Record: CLNOPT(6)

Format: 6L2

- Flags for TEAP options: aerobes, NO<sub>3</sub> reducers, Mn(IV) reducers, Fe(III) reducers, SO<sub>4</sub> reducers, methanogens. Enter T to include the TEAP in the simulation; enter F to omit.

F4 Record: ENDOPT(4)  
Format: 4L2

- Flags for product options: NxOy, Mn(II), Fe(II), H2S. Enter T to include the product in the simulation; enter F to omit. Note that ENDOPT(5) for CH4 is not entered here since it is automatically set from CLNOPT(6) for methanogens.

F5 Record: Descriptive Text  
Format: None

- “Hydrocarbon Minimum Concentrations”.

F6 Record: AHMIN(NHCAR)  
Format: F10.0

- Minimum concentrations: Enter AHMIN on a separate line for each hydrocarbon.

F7 Record: Descriptive Text  
Format: None

- “EA Starting and Minimum Concentrations”.

(Enter lines F8 and F9 if the number of solid phase electron acceptors > 0)

F8 Array: SEOLD (NCOL,NROW,NLAY,NSLID)  
Reader: RARRAY

- Starting concentrations: Enter SEOLD(NCOL,NROW) on a separate line for each layer (inner loop) and for each solid phase electron acceptor (outer loop). The solid phase electron acceptors are read in the following order: Fe(III), Mn(IV). NSLID is the total number of solid phase electron acceptors (calculated automatically from the TEAP options).

F9 Record: SEMIN(NSLID)

- Format: F10.0
- Minimum concentrations: Enter SEMIN after SEOLD(NCOL,NROW) for each solid phase electron acceptor.
- F10 Record: AEMIN(NELEC)  
Format: F10.0
- Minimum concentrations: Enter AEMIN on a separate line for each electron acceptor.
- F11 Record: Descriptive Text  
Format: None
- “Nutrient Minimum Concentrations”.
- (Enter line F12 if the number of nutrients > 0)
- F12 Record: ANMIN(NNUTR)  
Format: F10.0
- Minimum concentrations: Enter ANMIN on a separate line for each nutrient.
- F13 Record: Descriptive Text  
Format: None
- “Biomass Starting Concentrations”.
- F14 Array: XMOLD (NCOL,NROW,NLAY,NCLNY)  
Reader: RARRAY
- Starting concentrations: Enter XMOLD(NCOL,NROW) on a separate line for each layer (inner loop) and for each microbial population (outer loop). NCLNY is the total number of microbial populations in the simulation.
- F15 Record: XMMIN

- Format: F10.0
- Minimum conc. For all microbial populations: Enter XMMIN after the last entry of XMOLD(NCOL,NROW) for the final microbial population. Note: only one value for XMMIN is entered, and it applies to all microbial populations.
- F16 Record: NITER  
Format: I10
- Number of biodegradation time steps per transport time step.
- F17 Record: KSCR,ISCR,JSCR  
Format: 3I10
- Layer, row, and column indices for screen output.
- F18 Record: Descriptive Text  
Format: None
- “Electron Acceptor Inhibition Terms”.
- (Enter lines F19 and F20 if the total number of EA processes (including methanogenesis) > 1)
- F19 Record: Descriptive Text  
Format: None
- “Inhibition of [inhibitee]” Enter this line prior to each inhibitor process.
- F20 Record: AKINH(NINH,NINH)  
Format: F10.0
- Electron acceptor inhibition coefficient: Enter AKINH(lj, lk) for each inhibitor lk (inner loop) of electron acceptor process lj (outer loop). Note that electron acceptor process lj will require entry of (lj - 1)

inhibitors. NINH = the total number of electron acceptor processes minus one.

**Example 1: Simulate aerobes and NO<sub>3</sub> reducers (NINH = 1)**

Line 1: "Inhibition of NO<sub>3</sub>"  
Line 2: AKINH(1,1) -- coef. of O<sub>2</sub> inhibition of NO<sub>3</sub>

**Example 2: Simulate aerobes, Fe(III), SO<sub>4</sub> reducers, and methanogens (NINH = 3)**

Line 1: "Inhibition of Fe(III)"  
Line 2: AKINH(1,1) -- coef. of O<sub>2</sub> inhibition of Fe(III)  
  
Line 3: "Inhibition of SO<sub>4</sub> "  
Line 4: AKINH(2,1) -- coef. of O<sub>2</sub> inhibition of SO<sub>4</sub>  
Line 5: AKINH(2,2) -- coef. of Fe(III) inhibition of SO<sub>4</sub>  
  
Line 6: "Inhibition of methanogenesis"  
Line 7: AKINH(3,1) -- coef. of O<sub>2</sub> inhib. of methanogenesis  
Line 8: AKINH(3,2) -- coef. of Fe(III) inhib. of methanogenesis  
Line 9: AKINH(3,3) -- coef. of SO<sub>4</sub> inhib. of methanogenesis

F21 Record: Descriptive Text

Format: None

- "Elec. Acc. Product Generation Coefs".

(Enter line F22 if NENDE > 0)

F22 Record: ENDE(NENDE)

Format: F10.0

- Electron acceptor product generation coefficient: Enter ENDE on a separate line NENDE times. NENDE is the number of products from

the electron acceptors (specified in ENDOPT of the basic transport package), excluding methanogenesis.

F23 Record: Descriptive Text  
Format: None

- “Methane Generation Coefficients”.

(Enter line F24 if methanogenesis is simulated)

F24 Record: ENDH(NHCAR)  
Format: F10.0

- Methane generation coefficients: Enter ENDH on a separate line E24 for each hydrocarbon.

F25 Record: Descriptive Text  
Format: None

- “Daughter Generation Coefficients”.

(Enter line F26 if NDAUT >0)

F26 Record: ENDD(NDAUT)  
Format: F10.0

- Daughter generation coefficients: Enter ENDD on a separate line F26 for each daughter product.

F27 Record: Descriptive Text  
Format: None

- “Electron Acceptor Use Coefficients”.

(Enter lines F28 and F29 for each electron acceptor process, excluding methanogenesis)

F28 Record: Descriptive Text  
Format: None



- “Use of [Electron Acceptor, .e.g., O2]” Enter this line prior to each electron acceptor process.

F29 Record: AGAM(NHCAR,NEATOT)

Format: F10.0

- Use coefficients: Enter AGAM on a separate line for each hydrocarbon (inner loop) and for electron acceptor (outer loop). Electron acceptor loop is read in the following order: O2, NO3, Fe(III), Mn(IV), SO4 (i.e., from highest to lowest energy). NEATOT is the total number of electron acceptors simulated. Lines are not read for electron acceptors that are not included in the simulation.

F30 Record: Descriptive Text

Format: None

- “Nutrient Use Coefficients.

(Enter line F31 if NNUTR > 0)

F30.5 Record: Descriptive Text

Format: None

- CURRENTLY UNASSIGNED

F31 Record: APSI(NHCAR,NNUTR)

Format: F10.0

- Nutrient use coefficients: Enter APSI on a separate line F31 for each hydrocarbon (inner loop) and for each nutrient (outer loop). Insert a descriptive text line (F30.4) at the beginning of each nutrient loop.

(Enter lines F32 through F43 for each microbial population (i.e., NCLNY times): microbial populations are read in the order of highest to lowest energy)

F32 Record: Descriptive Text

- Format: None
- Microbial Population Name, e.g., “Aerobes”.
- F33 Record: Descriptive Text  
Format: None
- “Death Rate”.
- F34 Record: XKD(NCLNY)  
Format: F10.0
- First order decay rate for the microbial population  
XKD < 0 death rate calculated by model (recommended)  
XKD = 0 no microbial death  
XKD > 0 death rate is constant at the specified value.
- F35 Record: Descriptive Text  
Format: None
- “Half Saturation Constants”.
- F36 Record: AKHALFH(NHCAR,NLI,NCLNY)  
Format: F10.0
- Hydrocarbon half saturation constant: Enter AKHALFH on a separate line for each electron acceptor utilized by the current microbial population (inner loop) and for each hydrocarbon (outer loop). NLI is the number of electron acceptors utilized by the current microbial population:  
NLI = 2 for NO<sub>3</sub> reducers  
NLI = 1 for all other populations.
- (Do not enter line F37 for Fe(III) or Mn(IV) reducers)
- F37 Record: AKHALFE(NLI,NCLNY)

Format: F10.0

- Electron acceptor half saturation constant: Enter AKHALFE on a separate line for each electron acceptor utilized by the current microbial population.

(Enter line F38 if NNUTR > 0)

F38 Record: AKHALFN(NNUTR,NLI,NCLNY)

Format: F10.0

- Nutrient half saturation constant: Enter AKHALFN on a separate line F38 for each electron acceptor utilized by the current microbial population (inner loop) and for each nutrient (outer loop).

F39 Record: Descriptive Text

Format: None

- “Maximum Specific Utilization Rate”.

(Enter line F40 if STOCHOPT(1) is”.true.” -- see line F2)

F40 Record: VSPMAX(NCOL,NROW,NLAY,NHCAR,NLI,NCLNY)

Format: F10.0

- Maximum specific rate of substrate utilization: Enter VSPMAX(NCOL, NROW) on a separate line for each layer (inner loop), each electron acceptor utilized by the current microbial population (middle loop), and for each hydrocarbon (outer loop).

(Enter line F41 if STOCHOPT(1) is”.false.” -- see line F2)

F41 Record: VSPMAX(NHCAR,NLI,NCLNY)

Format: F10.0

- Maximum specific rate of substrate utilization: Enter VSPMAX on a separate line for each electron acceptor utilized by the current microbial population (inner loop) and for each hydrocarbon (outer loop).

F42 Record: Descriptive Text

Format: None

- “Yield Coefficients”.

F43 Record: YIELD(NHCAR,NLI,NCLNY)

Format: F10.0

- Yield coefficients: Enter YIELD on a separate line F43 for each electron acceptor utilized by the current microbial population (inner loop) and for each hydrocarbon (outer loop).

## INPUT INSTRUCTIONS FOR THE REDUCTIVE DECHLORINATION PACKAGE

This input file must be created only if the Reductive Dechlorination Package is specified in the Basic Transport Package; i.e., TRNOPT(9) is set to "T". Input is read on unit 14. In order to simulate Reductive Dechlorination, the Biodegradation Package must also be simulated; i.e., TRNOPT(6) is set to "T".

### FOR EACH SIMULATION:

- I1     Record:     PCEOPT  
       Format:     L2  
                   Flag for PCE option. Enter T to include PCE in the simulation; enter F to omit PCE. Note: SEAM3D uses PCEOPT to calculate the number of chlorinated constituents in the simulation (NCHLO)  
                   NCHLO = 6 if PCEOPT = T  
                   NCHLO = 5 if PCEOPT = F.
- I2     Record:     Descriptive Text  
       Format:     None  
                   • "Chlorinated Compound Minimum Concs."
- I3     Record:     ACPMIN(NCHLO)  
       Format:     F10.0  
                   • Minimum concentrations: Enter ACPMIN on a separate line I3 for each chlorinated constituent.
- I4     Record:     Descriptive Text  
       Format:     None  
                   • "Biomass Starting Concentrations"

- I5     Record:     YMOLD(NCOL,NROW,NLAY,NCLNC)  
        Format:     RARRAY
- Starting concentrations: Enter YMOLD(ncol, nrow) on a separate line I5 for each layer (inner loop) and for each microbial population (outer loop). NCLNC is the total number of microbial populations for reductive dechlorination, and SEAM3D sets NCLNC = 2..
- I6     Record:     YMMIN  
        Format:     F10.0
- Minimum conc. for both microbial populations: Enter YMMIN after the last entry of YMOLD(ncol, nrow) for the final microbial population. Note: only one value for YMMIN is entered, and it applies to both microbial populations.
- I7     Record:     Descriptive Text  
        Format:     None
- “Yield Coefficients”
- I8     Record:     YIELD(NCHLO-2)  
        Format:     F10.0
- Yield coefficients: Enter YIELDC on a separate line for the chlorinated ethenes PCE (only if PCEOPT = T), TCE, DCE, and VC. Note: there is no yield coefficient for Ethene or Chloride.
- I9     Record:     Descriptive Text  
        Format:     None
- “Chlorinated Ethene Inhibition Terms”.
- I10    Record:     Descriptive Text  
        Format:     None

- “Inhibition of [inhibitee]” Enter this line prior to each chlorinated ethene that is inhibited.

I11 Record: AKINHC(NCHLO-2,NCHINH)

Format: F10.0

- Chlorinated ethene inhibition coefficient: Enter AKINHC(lc, lk) on a separate line for each inhibitor lk (inner loop) of chlorinated ethene lc (outer loop). Note that chlorinated ethene lc will require entry of NCHINH inhibitors. NCHINH = NTEAP+NCHLO-3, where NTEAP equals the total number of electron acceptor processes, excluding methanogenesis.

**Example 1: Simulate aerobes, NO<sub>3</sub> and Fe(III) reducers, and methanogens with PCEOPT = F; therefore, (NTEAP=3, NCHLO=5, NCHINH = 5)**

Line 1: “Inhibition of TCE”  
 Line 2: AKINHC(1,1) – coef. of O<sub>2</sub> inhibition of TCE  
 Line 3: AKINHC(1,2) – coef. of NO<sub>3</sub> inhibition of TCE  
 Line 4: AKINHC(1,3) – coef. of Fe(III) inhibition of TCE

Line 5: “Inhibition of DCE”  
 Line 6: AKINHC(2,1) – coef. of O<sub>2</sub> inhibition of DCE  
 Line 7: AKINHC(2,2) – coef. of NO<sub>3</sub> inhibition of DCE  
 Line 8: AKINHC(2,3) – coef. of Fe(III) inhibition of DCE  
 Line 9: AKINHC(2,4) – coef. of TCE inhibition of DCE

Line 10: “Inhibition of VC”  
 Line 11: AKINHC(3,1) – coef. of O<sub>2</sub> inhibition of VC  
 Line 12: AKINHC(3,2) – coef. of NO<sub>3</sub> inhibition of VC  
 Line 13: AKINHC(3,3) – coef. of Fe(III) inhibition of VC  
 Line 14: AKINHC(3,4) – coef. of TCE inhibition of VC  
 Line 15: AKINHC(3,5) – coef. of DCE inhibition of VC

F12 Record: Descriptive Text

Format: None

- “Chlorinated Ethene Stoichiometric Factors”.

I13 Record: STOICH(NCHLO-2,3)

Format: F10.0

- Stoichiometric factor relating degradation of chlorinated ethenes to daughter products Enter STOICH(lc, ld) on a separate line for each daughter product ld (inner loop) of chlorinated ethene lc (outer loop) as follows: NOTE: Set STOICH for DCE to Ethene equal to zero.

**Example 2: For PCEOPT = T, (note: omit lines 2 and 3 if PCEOPT = F)**

Line 1: “Stoichiometric Factors”  
Line 2: STOICH(1,1) – coef. for PCE -> TCE  
Line 3: STOICH(1,2) – coef. for PCE -> Chloride  
Line 4: STOICH(2,1) – coef. for TCE -> DCE  
Line 5: STOICH(2,2) – coef. for TCE -> Chloride  
Line 6: STOICH(3,1) – coef. for DCE -> VC  
Line 7: STOICH(3,2) – coef. for DCE -> Chloride  
Line 8: STOICH(3,3) – coef. for DCE -> Ethene  
Line 9: STOICH(4,1) – coef. for VC -> Ethene  
Line 10: STOICH(4,2) – coef. for VC -> Chloride

I14 Record: Descriptive Text

Format: None

- “Half saturation constants for reductive dechlorination”

I15 Record: AKHALFC(NCHLO-2)

Format: F10.0

- Chlorinated ethene half saturation constant: Enter AKHALFC on a separate line for the chlorinated ethenes PCE (only if PCEOPT = T),



TCE, DCE, and VC. Note: there is no half saturation constant for Ethene or Chloride.

I16 Record: Descriptive Text

Format: None

- “Maximum specific rate of reductive dechlorination”

I17 Record: VSPMXA(NCHLO-2)

Format: F10.0

- Maximum specific rate of reductive dechlorination: Enter VSPMXA on a separate line I17 for the chlorinated ethenes PCE (only if PCEOPT = T), TCE, DCE, and VC. Note: there is no maximum specific rate constant for Ethene or Chloride.

I18 Record: Descriptive Text

Format: None

- “Death Rate”

I19 Record: YKD(NCLNC)

Format: F10.0

- First order decay rate for the chlorinated ethene microbial populations. Enter YKD on a separate line I19 for each microbial population. NCLNC is the total number of microbial populations for reductive dechlorination, and SEAM3D sets NCLNC = 2.  
YKD < 0 death rate calculated by model (recommended)  
YKD = 0 no microbial death  
YKD > 0 death rate is constant at the specified value.

(Enter lines I20 to I29 for each microbial population specified in the BIO package: NCLNY microbial populations will be read in the order of highest to lowest energy)

- I20 Record: Descriptive Text  
Format: None
- Microbial Population Name, e.g., “Aerobes”
- I21 Record: Descriptive Text  
Format: None
- “Half Saturation Constants”
- I22 Record: AKHALFD(NDOX)  
Format: F10.0
- Half saturation constant for direct oxidation: Enter AKHALFD on a separate line I22 for each chlorinated ethene (i.e., DCE and VC) that can undergo direct oxidation. NDOX is the number of chlorinated ethenes that can undergo direct oxidation, and  $NDOX = 2$ .
- I23 Record: Descriptive Text  
Format: None
- “Maximum specific rate of direct oxidation”
- I24 Record: VSPMXD(NDOX)  
Format: F10.0
- Maximum specific rate of direct oxidation: Enter VSPMXD on a separate line for each chlorinated ethene (i.e., DCE and VC) that can undergo direct oxidation.

(Enter lines I25 through I26 under the methanogenic population if methanogenesis is simulated)

- I25 Record: Descriptive Text  
Format: None
- “Methane generation coefficients”

I26 Record: ENDC(NDOX)

Format: F10.0

- Methane generation coefficients: Enter ENDC on a separate line for each chlorinated ethene (i.e., DCE and VC) that can undergo direct oxidation

I27 Record: Descriptive Text

Format: None

- “Electron Acceptor Use Coefficients”

(Enter lines I28 through I29 for each electron acceptor process, excluding methanogenesis)

I28 Record: Descriptive Text

Format: None

- “Use of [Electron Acceptor, e.g., O<sub>2</sub>]” Enter this line prior to each electron acceptor process.

I29 Record: AGAMC(NDOX,NEATOT)

Format: F10.0

Use coefficients: Enter AGAMC on a separate line I29 for each chlorinated ethene (i.e., DCE and VC) that can undergo direct oxidation (inner loop) and for electron acceptor (outer loop). Electron acceptor loop is read in the following order: O<sub>2</sub>, NO<sub>3</sub>, Fe(III), Mn(IV), SO<sub>4</sub> (i.e., from highest to lowest energy). NEATOT is the total number of electron acceptors simulated. Lines are not read for electron acceptors that are not included in the simulation.

## INPUT INSTRUCTIONS FOR THE COMETABOLISM PACKAGE

This input file must be created only if the Reductive Dechlorination Package is specified in the Basic Transport Package; i.e., TRNOPT(9) is set to "T". Input is read on unit 14. In order to simulate Reductive Dechlorination, the Biodegradation Package must also be simulated; i.e., TRNOPT(6) is set to "T".

### FOR EACH SIMULATION:

- H1    Record:        RDPOPT(3)  
      Format:        3L2
- Flag to indicate if any recalcitrant compounds are specified in the RDP. Enter T to indicate that recalcitrant is included in the RDP; enter F if not.  
      RDPOPT(1) for TCE  
      RDPOPT(2) for cisDCE  
      RDPOPT(3) for VC
- H2    Record:        NRCOM, NRCOMNC  
      Format:        2I10
- NRCOM is the number of total simulated recalcitrant compounds subject to cometabolism
  - NRCOMNC is the number of recalcitrants not specified using the RDP. Note that  $NRCOMNC = NCCOM$  if all  $RDPOPT(1-3) = F$ ;  $NRCOMNC < NCCOM$  if any  $RDPOPT(1-3) = T$ .
- H3    Record:        Descriptive Text  
      Format:        None
- "Recalcitrant Compound Minimum Concs."
- H4    Record:        ARMIN(NRCOM)

- Format: F10.0
- Minimum concentrations: Enter ARMIN on a separate line for each recalcitrant compound.
- H5 Record: Descriptive Text  
Format: None
- “Enzyme half saturation constants for recalcitrant compound”
- H6 Record: AKHALFR(NRCOM)  
Format: F10.0
- Recalcitrant compound enzyme half saturation constant. Enter AKHALFR on a separate line for each recalcitrant compound.
- H7 Record: Descriptive Text  
Format: None
- “Maximum specific rate of cometabolism”
- H8 Record: VSPMAXR(NRCOM)  
Format: F10.0
- Maximum specific rate of cometabolism: Enter VSPMAXR on a separate line for each recalcitrant compound.
- H9 Record: Descriptive Text  
Format: None
- “Enzyme half saturation constants for growth substrate”
- H10 Record: AKENZS  
Format: F10.0
- Enzyme half saturation constants for growth substrate.
- H11 Record: Descriptive Text

- Format: None
- “Haldine constant for growth substrate”
- H12 Record: AKHALS  
Format: F10.0
- Haldine constant for growth substrate.
- H13 Record: Descriptive Text  
Format: None
- “Death Rate”
- H14 Record: AKHALS  
Format: F10.0
- First order decay rate for the cometabolizing aerobic population.
- H15 Record: Descriptive Text  
Format: None
- “Fraction of aerobic population active towards cometabolism”
- H16 Record: RFA  
Format: F10.0
- Initial fraction of aerobic population active towards cometabolism.
- H17 Record: Descriptive Text  
Format: None
- “Transformation capacity for growth”
- H18 Record: TRCAP(NRCOM)  
Format: F10.0
- Transformation capacity: Enter TRCAP on a separate line for each recalcitrant compound.



## INPUT INSTRUCTIONS FOR THE NAPL DISSOLUTION PACKAGE

This input file must be created only if the NAPL Dissolution Package is specified in the Basic Transport Package; i.e., TRNOPT(7) is set to "T". Input is read on unit 12. In order to simulate NAPL dissolution, the Biodegradation Package must also be simulated; i.e., TRNOPT(6) is set to "T".

### FOR EACH SIMULATION:

- G1    Record:        NTDIS, NHDIS, NCDIS, NRDIS,MAXDIS  
      Format:        4I10
- NTDIS is the total number of non-biodegradable tracers in the NAPL:  
 $0 \leq \text{NTDIS} \leq \text{NTRAC}$ .
  - NHDIS is the total number of biodegradable substrates in the NAPL:  
 $0 \leq \text{NHDIS} \leq \text{NHCAR}$ .
  - NCDIS is the total number of chlorinated ethenes in the NAPL:  
Only PCE, TCE, and DCE are allowed to exist in the NAPL, thus  
( $0 \leq \text{NCDIS} \leq 3$  if PCEOPT = T)  
( $0 \leq \text{NCDIS} \leq 2$  if PCEOPT = F).
  - NRDIS is the total number of recalcitrants in the NAPL:  
Enter the number of recalcitrants in the NAPL that are not specified using NCDIS.
  - MAXDIS is the maximum number of NAPL nodes specified during any stress period
- G2    Record:        Descriptive Text  
      Format:        None
- "Solubility"
- G3    Record:        SOLUBT(NTDIS)



- Format: F10.0
- Tracer Solubility: Enter SOLUBT on a separate line NTDIS times.
- G4 Record: SOLUBH(NHDIS)  
Format: F10.0
- Hydrocarbon Solubility: Enter SOLUBH on a separate line NHDIS times.
- G5 Record: SOLUBC(NCDIS)  
Format: F10.0
- Chlorinated Ethene Solubility: Enter SOLUBC on a separate line NCDIS times.
- G6 Record: SOLUBR(NRDIS)  
Format: F10.0
- Recalcitrant Solubility: Enter SOLUBR on a separate line NRDIS times.
- G7 Record: Descriptive Text  
Format: None
- “Molecular Weight”
- G8 Record: WTMOLT(NTDIS)  
Format: F10.0
- Tracer Molecular Weight: Enter WTMOLT on a separate line NTDIS times.
- G9 Record: WTMOLH(NHDIS)  
Format: F10.0
- Hydrocarbon Molecular Weight: Enter WTMOLH on a separate line NHDIS times.

G10 Record: WTMOLC(NCDIS)

Format: F10.0

- Chlorinated Ethene Molecular Weight: Enter WTMOLC on a separate line NCDIS times.

G11 Record: WTMOLR(NRDIS)

Format: F10.0

- Recalcitrant Molecular Weight: Enter WTMOLR on a separate line NRDIS times.

G12 Record: WTMOLI

Format: F10.0

- Inert fraction molecular weight. Enter WTMOLI one time.

FOR EACH STRESS PERIOD:

G13 Record: MXDIS

Format: I10

- Number of nodes where NAPL parameters are specified for the current stress period. If MXDIS < 0, NAPL Parameters from the preceding stress period will be reused.

(if MXDIS > 0, then enter line G14 MXDIS times)

G14 Record: KK, II, JJ, DIFALP, SINERT,  
FRAX(NTDIS+NHDIS+NCDIS+NRDIS), FLMASS

Format: 3I10,3F10.0,I10

- KK is the layer number of node containing NAPL mass.
- II is the row number of node containing NAPL mass.

- JJ is the column number of node containing NAPL mass. DIFALP is the NAPL Dissolution rate [T-1] in node. If DIFALP < 0, NAPL Dissolution rate from the preceding stress period will be used.
- SINERT is the initial soil concentration of NAPL [M M-1] in the node at the beginning of the stress period. If SINERT < 0, model calculated soil concentration in this node at the end of the preceding stress period will be used
- FRAX is the initial mass fraction of species in NAPL: Enter FRAX for each NTDIS, NHDIS, NCDIS ,and NRDIS. If FRAX < 0, model calculated mass fraction of species from the preceding stress period will be used
- FLMASS is the flag to specify if additional NAPL mass loading or removal at the end of the current stress period. If FLMASS = 0 (or blank), no additional mass is loaded or removed. If FLMASS >0 then additional mass is loaded. If FLMASS < 0 then additional mass is removed.

(if FLMASS > 0, then enter line G15)

G15 Record: MASLOAD  
Format: F10.0

- Mass rate of additional NAPL mass loading during the current period [M T-1].

(if FLMASS < 0, then enter line G16)

G116 Record: MASREM(NTDIS+NHDIS+NCDIS+NRDIS)  
Format: F10.0

- Percent of NAPL mass removed during the current period [%].Enter MASREM for each NTDIS, NHDIS, NCDIS, and NRDIS.

## PHYTOREMEDIATION PACKAGE INPUT INSTRUCTIONS

Input to the Phytoremediation (PUP) Package is read from the file that is type "PUP". All non-array parameters are free format if the word FREE is specified in item 4 of the Basic Package input file; otherwise, the non-array parameters have 10-character fields.

### FOR EACH SIMULATION

1. Record:    FRCF            FTSCF            ISOTHMP

Format:    2L2, I10

- FRCF is a logical flag for simulating root sorption;
- FTSCF is a logical flag for simulating transpiration.
- ISOTHMP is a flag indicating which type of plant uptake is simulated:  
ISOTHMP =1, Linear isotherm (equilibrium-controlled);  
          =2, Freundlich isotherm (equilibrium-controlled);  
          =3, Langmuir isotherm (equilibrium-controlled);

(Enter 2 if FRCF=T)

2. Array:    RHOBR(NCOL,NROW)(one array for each layer)

Reader:    RARRAY

- RHOBR is the bulk density of the root medium (unit: ML-3 ).

(Enter 3 for each species if ISOTHMP>1)

3 Array:    SP1P(NCOL,NROW) (one array for each layer)

Reader:    RARRAY

SP1P is the first plant uptake parameter. The use of SP1P depends on the type of plant uptake selected (i.e., the value of ISOTHMP):

For Freundlich plant uptake (ISOTHMP=2), SP1P is the Freundlich exponent a.

For Langmuir plant uptake (ISOTHMP=3), SP1P is the Langmuir equilibrium constant (Kl) (unit: L3 M-1 ).

(Enter 4 for each species if ISOTHMP>2)

4 Array: SP2P(NCOL,NROW) (one array for each layer)

Reader: RARRAY

SP2P is the second plant uptake parameter. The use of SP2P depends on the type of plant uptake:

For Langmuir plant uptake (ISOTHMP=3), SP2P is the total concentration of the plant uptake sites available ( ) (unit: MM-1 ).

### FOR EACH STRESS PERIOD

(Enter 5 through 8 if FRCF=T)

5. Record: INSURF                      INEXDP                      INRCF

Format: 3I10

- INSURF--is the PUP/ET surface (SURF) read flag.
  - If INSURF  $\geq 0$ , an array containing the PUP/ET surface elevation (SURF) will be read.
  - If INSURF  $< 0$ , the PUP/ET surface from the preceding stress period will be reused.
- INEXDP--is the extinction depth (EXDP) read flag.
  - If INEXDP  $\geq 0$ , an array containing the extinction depth (EXDP) will be read.
  - If INEXDP  $< 0$ , the extinction depth from the preceding stress period will be reused.
- INRCF--is the root concentration factor (RCF) read flag.
  - If INRCF  $\geq 0$ , an array containing the root concentration factor (RCF) will be read for each species.
  - If INRCF  $< 0$ , the root concentration factors from the preceding stress period will be reused.

(Enter 6 if INSURF  $\geq 0$ )

6. Array: SURF(NCOL,NROW)(one array for each layer)  
Reader: RARRAY
- SURF--is the elevation of the PUP/ET surface.

(Enter 7 if INEXDP  $\geq$  0)

7. Array: EXDP(NCOL,NROW)(one array for each layer)  
Reader: RARRAY
- EXDP--is the PUP/ET root extinction depth.

(Enter 8 for each species if INRCF  $\geq$  0)

8. Array: RCF(NCOL,NROW)  
Reader: RARRAY
- RCF--is the root concentration factor.

(Enter 9 through 10 if FTSCF=T)

9. Record: INTSCF  
Format: 1I10
- INTSCF--is the transpiration concentration factor (TSCF) read flag.
    - If INTSCF  $\geq$  0, an array containing the transpiration concentration factor (TSCF) will be read for each species.
    - If INTSCF  $<$  0, the transpiration concentration factors from the preceding stress period will be reused.

(Enter 10 for each species if INRCF  $\geq$  0)

10. Array: TSCF(NCOL,NROW)  
Reader: RARRAY
- TSCF--is the transpiration concentration factor.

END INPUT

RCF Notes:

- RCF must be between 0.0 and 1.0. Thus if the RCF is specified as less than 0.0 it will be set to 0.0 by the program. Correspondingly, if the RCF specified is greater than 1.0 it will be set to 1.0 by the program.
- PUP/ET parameters (PUP/ET surface and root extinction depth) are specified in two-dimensional arrays, SURF and EXDP, with one value for each vertical column. Accordingly, PUP/ET is calculated for one cell in each vertical column. IEVT (the layer indicator array code from the EVT package) determines for which cell/layer in the column PUP/ET will be calculated (See EVT input file).
- If root sorption is simulated, the first retardation factors displayed in the standard output file represent retardation values without the root sorption effect. Following retardation factor arrays represent the total values(including root sorption) recalculated for each stress period.

#### TSCF Notes:

- TSCF must be between 0.0 and 1.0. Thus if the TSCF is specified as less than 0.0 it will be set to 0.0 by the program. Correspondingly, if the TSCF specified is greater than 1.0 it will be set to 1.0 by the program.
- If the Source/Sink Mixing Package (SSM) is also used, TSCF must be coordinated with CEVT from SSM. Either TSCF or CEVT must be set to zero for all grid locations where EVTR is less than or equal to zero (i.e., where EVTR indicates that water is exiting the model). If this is not done, the same mass may be removed from the model domain twice and mass balance errors will occur.
- TSCF only has meaning if the evapotranspirative water flux (EVTR) is negative, indicating that water is being drawn out of the aquifer. If EVTR is positive for a cell with non-zero TSCF, the program will terminate and an error message will be generated.
- SEAM3D assumes evaporation is insignificant in cells and for stress periods where phytoremediation is active. If this is not true, model results will be less accurate.
- The location and flow rate of discharge is obtained from the flow model directly through the unformatted flow-transport link file.