

# Natural Attenuation Software (NAS): a computer program for estimating remediation times of contaminated groundwater

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## 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.

*Keywords: monitored natural attenuation, groundwater remediation, petroleum hydrocarbons, chlorinated ethenes.*

## 1 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 [1,2]. 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.

## 2 Natural attenuation processes

### 2.1 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:

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

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

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

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

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

Eqn (3) may be expressed in terms of the one-dimensional natural attenuation capacity (NAC) model Chapelle and Bradley [3]. 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:

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



### 2.2 Redox processes in groundwater systems

The most common terminal electron-accepting processes (TEAPs) in groundwater systems are  $O_2$ ,  $NO_3^-$ ,  $Mn(IV)$ ,  $Fe(III)$ ,  $SO_4^{2-}$ , and  $CO_2$  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* [4]. Dissolved  $H_2$ , may also be an effective indicator of ambient redox processes. Under anaerobic conditions,  $H_2$  is produced by fermentive microorganisms metabolizing organic matter and then utilized by respirative microorganisms in TEAPs, with each process having a different affinity for  $H_2$  uptake Lovley and Goodwin [5]. See fig. 1 for a flowchart for determining TEAP zonation in groundwater systems.

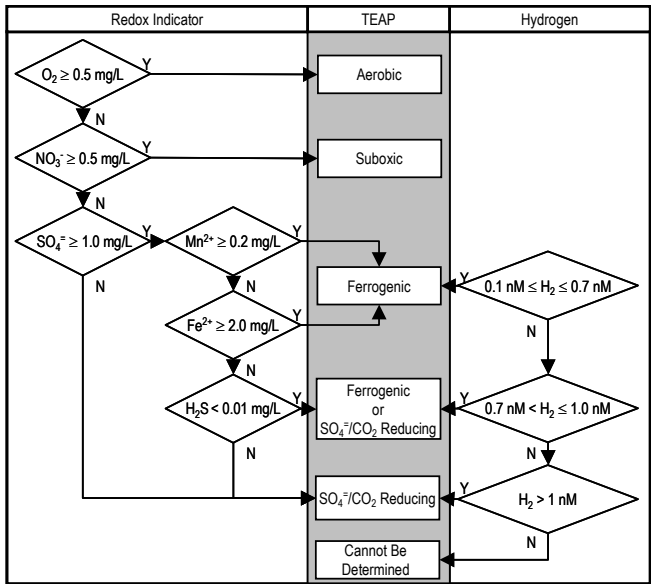


Figure 1: Flowchart showing how NAS determines redox condition.

### 2.3 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.

## 2.4 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.

## 2.5 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* [6]. 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:

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

## 2.6 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* [7]. 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:

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

## 2.7 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 [8,9]. The NAPL dissolution term for the solute-transport, mass-balance equation is:

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



### 3 Natural Attenuation Software

A flowchart describing how the NAS software can be used to address TOR questions is shown in fig. 2. NAS requires detailed site information about hydrogeology, contaminant concentrations, and redox conditions before the analysis can proceed. See table 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 required for a plume extent to contract to regulatory limits. A numerical solution estimates the time required for NAPL contaminants in the source area to attenuate to a predetermined target source concentration. NAS then analytically estimates 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.

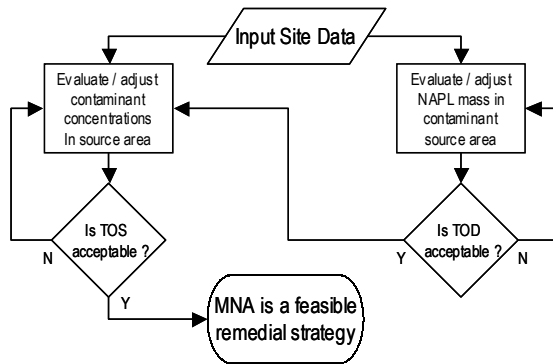


Figure 2: Flowchart showing how NAS can be applied to TOR problems.

Table 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	$M_N, S_X, S_Y, S_Z, J_i^m, C_i^{EA}, SCC$	TOD, $S_N$
	NAPL mass removal options	
TOS	No additional data needed	TOS

#### 3.1 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 [3]. Employing the steady-state solution to eqn (1) on the plume centerline and expressing in terms of the one-dimensional NAC model yields:

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

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

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

**3.2 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 TOR 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 eqn (1), and instead require a quantitative, numerical approximation. NAS uses the numerical model SEAM3D (Sequential Electron Acceptor Model, 3 Dimensional) Waddill and Widdowson [9,10], to estimate the TOD. SEAM3D consists of a series of modules, including the parent code MT3DMS Zheng and Wang [11], 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.

**3.3 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 eqn (1). For the case of a semi-infinite aquifer with a constant source, a time-dependent, two-dimensional solution is given by Domenico [12]:

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

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 eqn (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:

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

#### 4 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. Fig. 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 [13,14].

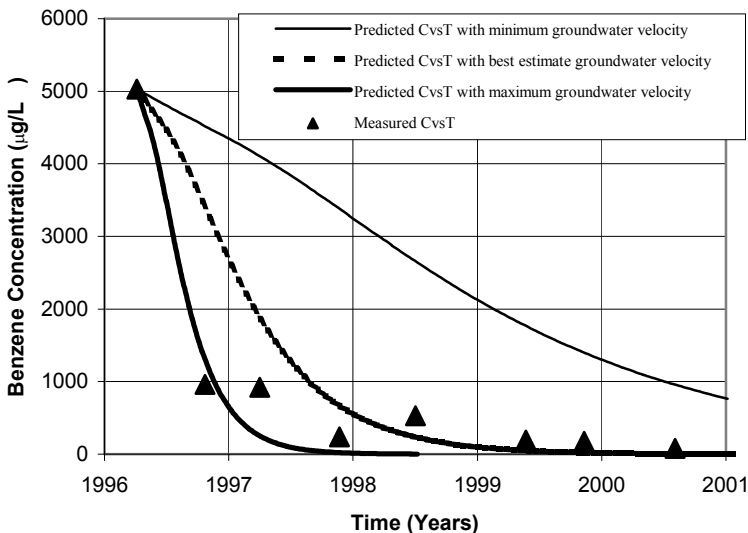


Figure 3: Measured versus NAS-predicted concentration changes at MW-8.

## 5 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.

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## Notation

$D$ = 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 <sup>3</sup> ]	$K$ = Hydraulic Conductivity [L/T]
$\bar{K}_{x,le}^e$ = effective half saturation constant for electron acceptor [M/L <sup>3</sup> ]	$i$ = Hydraulic Gradient [L/L]
$I_{le,li}$ = inhibition function (defined by?)	$n_e$ = effective porosity [-]
$R_{sink,le}^{bio,EA}$ = biodegradation sink term to account for the reduction of a chlorinated ethene [M/L <sup>3</sup> T]	$f_{oc}$ = fraction organic carbon [-]
$M_y$ = microbial biomass concentration [M/L <sup>3</sup> ]	$T_a$ = 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 <sup>3</sup> ]	$M_N$ = NAPL mass [M]
$\bar{K}_{lc}^e$ = effective half saturation constant [M/L <sup>3</sup> ]	$S_X$ = 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 <sup>3</sup> T]	$S_Z$ = Source thickness [L]
$l_s$ = 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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