

A GIS TECHNIQUE FOR ESTIMATING NATURAL ATTENUATION RATES AND MASS BALANCES

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ABSTRACT: Regulatory approval of monitored natural attenuation (MNA) as a component for site remediation often requires a demonstration that contaminant mass has decreased significantly over time. Successful approval of MNA also typically requires an estimate of past and future natural attenuation rates. Calculation of electron acceptor and/or donor mass budgets is also useful in establishing the potential effectiveness of MNA. In this paper we present the application of the GIS program (TINMASS) for quantifying and visualizing contaminant and electron acceptor/donor mass-in-place. TINMASS uses a triangulated irregular network (TIN) to interpolate dissolved contaminant mass between monitoring points. The technique is best suited to sites where the plume has reached a steady-state, and the existing network of monitoring wells includes points located at or outside the perimeter of the plume, both horizontally and vertically. Natural attenuation rates can be estimated from the slope of the line formed by a log-linear plot of contaminant mass versus time. We present an example application illustrating use of the method for mass-balance analysis of sequential decay of trichloroethene. A second example is presented illustrating use of the method for evaluating fuel hydrocarbon degradation by quantifying masses of biodegradation end products.

INTRODUCTION

In April 1999, the U.S. Environmental Protection Agency (EPA) issued a policy directive regarding the use of MNA at Superfund, RCRA corrective action, and underground storage tank sites (OSWER Directive 9200.4-17P). The directive described lines of evidence that are typically investigated for determining the adequacy of MNA as a site remedy. One line of evidence is historical groundwater and/or soil data that demonstrate a meaningful trend of decreasing contaminant mass and/or concentration over time (EPA, 1999). Another line of evidence is hydrogeologic and geochemical data that demonstrate indirectly the types and rates of natural attenuation processes that are active at a site. In most cases, biodegradation is recognized as the most important natural attenuation process (for organic contaminants). As such, MNA evaluations are typically designed to estimate natural biodegradation rates. Rate estimates are used in analytical and/or numerical models to predict the time required to attain cleanup standards under a MNA remediation scenario.

Establishing a decreasing trend in contaminant mass is sometimes difficult because it can require multiple sampling events over several years, as well as a monitoring network that is sufficient to define the limits of the plume vertically and horizontally. Even at sites where the monitoring network is adequate, synthesis and interpretation of historical groundwater monitoring data can be

complicated by temporal and spatial variation. For example, declining trends may be evident in some wells, but absent in others. Even if multiple wells at a site show decreasing concentration trends, the local persistence of contamination can sometimes jeopardize the approval of MNA as a site remedy.

A variety of methods are available for estimating site-specific intrinsic biodegradation rates, most of which have been described in existing EPA guidance manuals (Wiedemeier et al., 1998; EPA, 1998). The conservative tracer normalization (dilution-correction) and Buscheck and Alcantar (1995) methods are two of the more commonly employed techniques for estimating biodegradation rates. Both of these techniques require the installation of a series of monitoring points distributed along a linear transect that extends from the contaminant source to downgradient, along the length of the plume. An alternative approach to estimating attenuation/biodegradation rates is to quantify the contaminant mass-in-place trend over time (Dupont et al., 1997).

In this paper we describe the development and application of TINMASS, a simple GIS tool for visualizing natural attenuation trends and estimating natural attenuation rates. TINMASS provides a means for estimating past and present contaminant mass-in-place, as well an effective graphical framework for visualizing mass reduction trends. Unlike the normalization and Buscheck and Alcantar (1995) methods, TINMASS does not require the placement of wells along a linear transect extending from source to downgradient. Not only can the method be used to estimate mass loss trends for the contaminant, it can also be used to estimate increases in the mass of inorganic end-products (e.g., Fe^{II} , H_2S , and CH_4), thereby facilitating a mass balance analysis. In addition, the method allows for specification of spatial variation in porosity and aquifer thickness.

DESCRIPTION OF TINMASS

TINMASS is a MapInfo® for Windows application that can be used to calculate the mass of a dissolved constituent in groundwater based on water quality data contained in a database (e.g., Microsoft Excel® or Access®). Input data for TINMASS include the following parameters at each sample location: (1) aquifer or interval thickness; (2) concentration of the constituent or chemical; and (3) porosity. Coordinates of each sample are taken directly from the MapInfo® object representing the sample location. An example input parameter window for TINMASS is shown in Figure 1.

Computational Technique. A triangulated irregular network (TIN) algorithm is used to interpolate constituent mass between monitoring points. The technique is a simple numerical integration approach commonly used to estimate volumes in civil engineering applications. In the first step, an optimum network of triangles connecting all sample locations is generated using the Dulauney Triangulation procedure. Dulauney Triangulation connects points to form a network of triangles that have as nearly equal angles at their vertices as possible. The procedure was based on an algorithm described by Watson (1982).

In the second step, an estimate of the mass of dissolved contaminant within each triangle is determined based on the assumption that aqueous concentration (C_w), porosity (n), and aquifer/interval thickness (b) vary linearly

between the sample locations. The dissolved mass within the aquifer bounded horizontally by each triangle is determined by:

$$M_w = \int_{\text{area}} nC_w b(dx dy)$$

where n , C_w , and b vary linearly across the triangle. Details on the interpolation and integration may be found in Istok (1989). The total mass of dissolved constituent in the aquifer unit equals the sum of the mass from each triangle.

Running TINMASS will create a TIN network as a MapInfo® table and calculate mass in units of pounds or kilograms. Data from the model run (input data fields or values entered, number of nodes, TIN triangles generated, and total mass) are stored in another MapInfo® summary table indexed by a Run ID. The Run ID may be used as an identifier of the contaminant and the sampling period. Thus, results from multiple periods and different chemicals may be summarized in one summary table. This approach supports the determination of temporal mass-in-place trends.

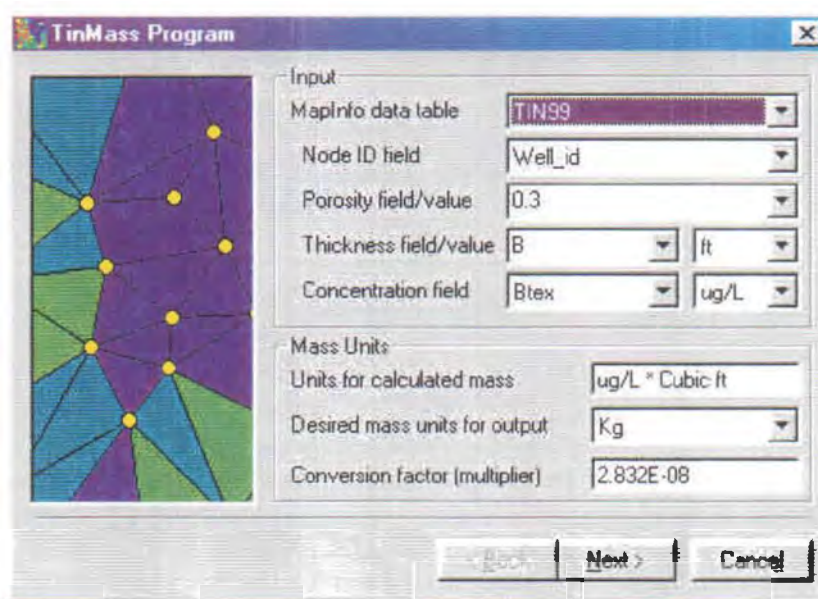


FIGURE 1. Example input parameter window for TINMASS.

Practical Use and Limitations. Mass-in-place estimates computed by TINMASS can be used to estimate site-specific natural attenuation rates at sites where sufficient historical data are available, and the existing monitoring network has defined the vertical and horizontal limits of the plume. The natural attenuation rate can be approximated as the slope of an exponential regression on a log-linear plot of mass vs. time. When using TINMASS for this purpose it is important to use a consistent set of monitoring locations across time. Even if the number of available data points increased during the relevant period, the same set of points should be used in order to limit the extent to which spatial/temporal variability will bias the rate estimate.

Use of TINMASS for estimating natural attenuation rates is best suited to sites where the plume is receding or has reached a steady-state condition. The method is not suitable for sites where a significant portion of the contamination occurs outside the existing monitoring network. At such sites it would not be possible to prove that temporal mass reductions were caused by attenuation (and not due to plume migration beyond the TIN network).

TINMASS can estimate mass-in-place of a constituent in a variably thick aquifer or within a discrete interval of an aquifer (depending on the layout of the monitoring network). In order to estimate mass-in-place in three dimensions, it is sometimes appropriate to estimate mass-in-place for separate layers (monitoring depth zones) and sum the results.

Because concentrations typically decrease in an exponential manner away from the source, the linear interpolation used in this procedure has a tendency to overestimate mass-in-place. The potential for overestimation decreases as the number of monitoring points in the TIN network increases. It should be noted that TINMASS only examines mass trends for the dissolved phase. Where present, non-aqueous phase liquids (NAPLs) will usually account for a dominant portion of the total mass, but estimation of NAPL mass is subject to a very high level of uncertainty. If undetected, NAPL presence may cause misinterpretation of mass removed versus mass-in-place trends. Despite the uncertainty of the mass estimate for a given sampling event, the uncertainty is relatively constant over time when using TINMASS to assess mass-in-place trends for dissolved plumes (assuming that the network is constant through time). Consequently, the natural attenuation rate estimate for dissolved plume mass is not significantly affected by errors associated with each individual mass estimate.

EXAMPLE APPLICATIONS

Example A. Natural attenuation is treating a portion of the dissolved chlorinated solvent plume beneath the Sanitary Landfill (SLF) at the U.S. DOE Savannah River Site (WSRC, 1997). Much of the trichloroethene (TCE) in the plume has been reductively dechlorinated to *cis*-1,2-dichloroethene (DCE) and vinyl chloride (VC). An abundance of dissolved organic carbon is the likely reductant supporting dechlorination. The landfill was capped in 1997, and a horizontal well biosparging system is now being operated to treat the groundwater contamination. A modeling analysis was recently completed to evaluate the performance of natural attenuation for eliminating the residual contamination that escapes the biosparging treatment zone. Estimation of site-specific natural biodegradation rates was the first step in the natural attenuation modeling process. TINMASS was used to specify a TIN network within the plume, and to quantify the dissolved mass for TCE, DCE, and VC over time (see Figure 2). A uniform porosity of 20% was specified as an input parameter. The unit thickness for each point was specified as the difference between the water level and a datum elevation. Although the monitoring network consisted of multi-level wells screened at three depths, all the wells were pooled together for this analysis since the aquifer formation and contaminant distribution are relatively homogeneous

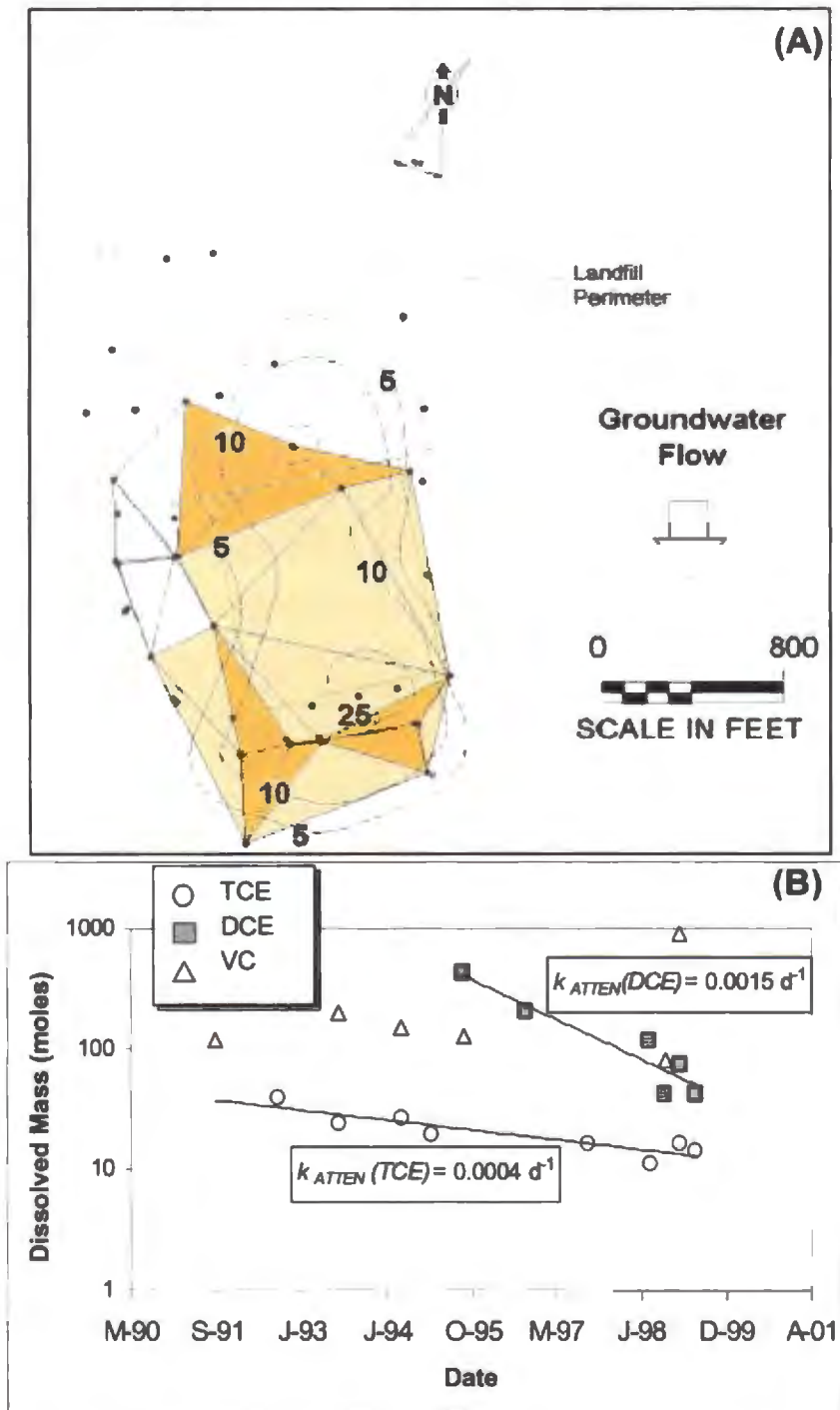


FIGURE 2. (A) Configuration of 1993 TCE plume ($\mu\text{g/L}$) and TIN network used to estimate dissolved chloroethene mass at the Savannah River Site SLF. Shading in TIN triangles is user-specified, and represents different mass per volume quantities (values not shown). (B) Time series plots of dissolved mass for TCE, DCE, and VC.

over the interval (approximately 18 meters).

As illustrated in Figure 2, the TIN network covered reasonably well the configuration of the TCE plume at the SLF. TINMASS was used to estimate dissolved masses for TCE, DCE, and VC. The TINMASS estimates (kilograms) were converted to moles to allow a mass balance assessment of the sequential decay of TCE over time (under anaerobic conditions, one mole of TCE decays to one mole of DCE, and one mole of DCE decays to one mole of VC). The data were plotted on a log-linear graph, and decay coefficients were approximated as the slope of an exponential regression of the data (see Figure 2). From this analysis, the estimated first-order biodegradation rate is 0.15 yr^{-1} TCE, and 0.55 yr^{-1} for DCE. Fewer data were available for the DCE rate estimate since laboratory analysis for this constituent did not commence until 1995. Note that these rates apply to the attenuation of the whole plume, without regard for spatial variability in redox conditions.

Additional TINMASS analyses were performed to estimate biodegradation rates for aerobic and anaerobic zones (data not shown). In general, the anaerobic regions coincide with the footprint of the landfill perimeter, and aerobic zones occur outside the landfill perimeter. Mass estimates from TINMASS suggest that the DCE biodegradation rate is 0.44 yr^{-1} in the anaerobic zone, and 0.66 yr^{-1} in the aerobic zone. The mass of VC appeared to show a net increase directly underneath the landfill cap during the period analyzed, and the rate of VC accumulation in the anaerobic zone was consistent with the rate of DCE mass decay. In the aerobic zone downgradient of the landfill, the VC biodegradation rate estimated from TINMASS is 0.29 yr^{-1} .

The data in Figure 2B suggest that TCE and DCE are attenuating at the SLF. Sufficient data are available to suggest that the TCE has degraded as a first order trend. There is more scatter in the DCE trend, which likely reflects spatial variability in the processes and conditions affecting DCE degradation.

Example B. During the 1980s, a jet fuel (JP-4) release introduced hydrocarbon contamination into a shallow aquifer beneath a confidential site in the Northeastern U.S. Sampling performed during the early 1990s detected benzene, toluene, ethylbenzene, and xylene (BTEX), and naphthalene in the site groundwater. More recent sampling events have confirmed that benzene and naphthalene are the only two contaminants present at concentrations above clean-up levels. Other straight-chain and branched hydrocarbons typical of JP-4 are also present in the groundwater. These have not been differentiated, and are characterized only as total petroleum hydrocarbon (TPH). The residual light non-aqueous phase liquid (LNAPL) that was present in the 1990s likely still remains in certain locations.

In addition to declining constituent concentrations, evidence of natural attenuation includes the accumulation of biodegradation end-products (e.g., H_2S , CH_4 , and Fe^{II}). TINMASS was used to estimate mass removed and attenuation rates for the various contaminants. The mass of dissolved H_2S , CH_4 , and Fe^{II} was also estimated with TINMASS, and these data were used with stoichiometric relationships to estimate the potential amount of biodegradation associated with

each biodegradation end product. Biodegradation rates were also estimated by the method of Buscheck and Alcantar (1995) for the purpose of comparison with the rates estimates from the mass-in-place calculations. The results of these analyses are summarized in Table 1.

TABLE 1. Summary of dissolved mass-in-place and associated natural attenuation rate estimates for groundwater constituents at JP-4 site.

	Attenuation Rate by TINMASS (yr ⁻¹)	Degradation Rate by Buscheck and Alcantar (yr ⁻¹)	Mass Removed 1996 – 2000 (kg)	Mass Produced by 2000 (kg)	Possible Incurred Biodegradation Based on Stoichiometry ¹ (kg)
BTEX	0.40	3.8	20	--	203
Benz	0.40	3.0	6	--	209
Naph	0.26	2.4	49	--	215
TPH	0.88	0.7	1050	--	184
Fe^{II}	--	--	--	184	--
H₂S	--	--	--	120	--
CH₄	--	--	--	98	--

1. Stoichiometric relationships presented by Wiedemeier et al. (1998) were used to calculate the amount of biodegradation possible – assuming no microbial growth - for the observed masses of accumulated biodegradation end products. Octane was used as a surrogate for TPH.

As shown in Table 1, application of TINMASS allowed an estimate of the dissolved mass of BTEX, naphthalene, and TPH degraded during the period of 1996 to 2000. This analysis indicates that TPH represents the greatest fraction removed during this period. By comparison, the masses of BTEX and naphthalene removed were significantly smaller. This finding is not surprising given that BTEX and naphthalene together represent less than 5% by weight of typical virgin JP-4.

The attenuation rates estimated from the TINMASS calculations for BTEX, benzene, and naphthalene are within the range normally reported for biodegradation of these compounds in aquifers. However, these estimates likely underestimate the actual rate of intrinsic biodegradation since this did not account for contributions from source dissolution. During the period of 1996 to 2000, additional BTEX and naphthalene likely was introduced into the groundwater by dissolution from the LNAPL source. If source dissolution ~~was~~ had not occurred, plume attenuation (and mass removal) would have been more rapid. Contributions from source dissolution likely explain, in part, the differences in the rate estimates between the TINMASS method and the method of Buscheck and Alcantar. The Buscheck and Alcantar method focuses on biodegradation in the plume, while the TINMASS method applies to both source and plume. As shown in Table 1, rates estimated with the Buscheck and Alcantar method are nearly an order of magnitude faster than attenuation rate estimates derived from the TINMASS calculations (with the exception of TPH). Others have noted, however, that the method by Buscheck and Alcantar is prone to overestimating the rate of biodegradation (McNab and Doohar, 1998). As such, we conclude

that the attenuation rate estimated by TINMASS method is a conservative approximation to the biodegradation rate.

The last column in Table 1 provides an estimate of the mass of each constituent that could have been degraded if all the H₂S, CH₄, and Fe^{II} observed was due to the biodegradation of that constituent. These data suggest that at least a portion of the observed mass removed from 1996 to 2000 can be attributed to biodegradation under ferrogenic, sulfidogenic, and methanogenic conditions. Comparison of the mass removal estimates for BTEX, naphthalene, and TPH with their calculated potential incurred biodegradation provides insight as to the principal electron donors driving the accumulation of H₂S, CH₄, and Fe^{II}. This comparison suggests that the biodegradation of benzene, BTEX, and naphthalene alone during 1996 to 2000 does not account for all the H₂S, CH₄, and Fe^{II} that has accumulated. It follows that biodegradation of the TPH has contributed to a significant portion of the H₂S, CH₄, and Fe^{II} that have accumulated.

SUMMARY

The software programs BIOSCREEN (Newell et al., 1996) and BIOCHLOR (Aziz et al., 2000) provide a variety of tools for analyzing natural attenuation, including an ability to estimate contaminant mass-in-place and mass biodegraded. Although TINMASS is not an alternative to these powerful tools, it offers a unique capability to estimate dissolved contaminant mass across a variably contaminated domain. Unlike BIOSCREEN and BIOCHLOR, TINMASS is not limited to symmetrical and homogeneous model domains, and does not employ transport equations or flow parameters. Instead, TINMASS focuses primarily on the trends in empirical data. TINMASS allows users to estimate dissolved mass across formations of variable porosity, variable thickness, and variable contaminant distribution. It also provides a simple framework for integrating historical mass-in-place trends across multiple monitoring points.

In this paper, mass-in-place calculations were used to estimating site-specific attenuation rates and assess mass balances between biodegradation parent compounds and daughter products. These applications suggest that TINMASS is a useful tool for natural attenuation analysis. Additional evaluation at other sites is needed to further examine the use of this method for estimating site-specific natural attenuation rates.

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