Environmental Laboratory

**US Army Corps of Engineers**®
Engineer Research and
Development Center

*Environmental Quality and Installations Research Program*

# Proof-of-Concept Application of Tier 2 Modeling Approach within the Training Range Environmental Evaluation and Characterization System

Mark S. Dortch, Billy E. Johnson, Jeffrey A. Gerald, Zhonglong Zhang, and Andrew P. Simmons

August 2011

# Proof-of-Concept Application of Tier 2 Modeling Approach within the Training Range Environmental Evaluation and Characterization System

Mark S. Dortch, Billy E. Johnson, Jeffrey A. Gerald, Zhonglong Zhang, and Andrew P. Simmons

*Environmental Laboratory*
*U.S. Army Engineer Research and Development Center*
*3909 Halls Ferry Road*
*Vicksburg, MS 39180-6199*

Final report

**Abstract:** The Training Range Environmental Evaluation and Characterization System (TREECS) is being developed for the Army to forecast the fate of and risk from munitions constituents (MCs), such as high explosives (HE), within and transported from firing/training ranges to surface water and groundwater. The overall objective is to provide environmental specialists with tools to assess the potential for migration of MCs into surface water and groundwater systems and to assess range management strategies to protect human and environmental health. Tier 1 consists of screening-level methods that assume highly conservative, steady-state MC loading and fate. Tier 1 requires minimal data input and can be easily and quickly applied by environmental staff. If MC concentrations predicted with Tier 1 exceed protective health benchmarks at receptor locations, then further evaluation with Tier 2 is recommended to obtain more definitive results.

Tier 2 provides time-varying analyses since it does not make the highly conservative assumptions of steady-state (time-invariant) conditions with no MC loss or degradation as used for Tier 1. Tier 2 solves mass balance equations for both solid and non-solid phase MC with dissolution. MC residue loadings to the range soil can vary from year to year based on munitions use; thus, media concentrations computed with Tier 2 should be closer to those expected under actual conditions. Media concentrations will also reflect time phasing associated with time-varying MC loading conditions and transport arrival times, which can be greatly extended for the vadose zone and groundwater. Having time as a dimension in the analysis provides a powerful tool for examining range management strategies to promote attenuation of media concentrations.

This report describes the proof-of-concept application of the prototype TREECS Tier 2 modeling approach and provides recommendations for final implementation and use of those methods.

# Contents

# Figures and Tables

## Figures

## Tables

# Preface

# Unit Conversion Factors

| Multiply | By | To Obtain |
|---|---:|---|
| cubic feet | 0.02831685 | cubic meters |
| degrees Fahrenheit | (F-32)/1.8 | degrees Celsius |
| feet | 0.3048 | meters |
| miles (U.S. statute) | 1,609.347 | meters |
| pounds mass | 453.59 | Grams |
| English tons | 907.2 | kilograms |
| slugs | 14.59390 | kilograms |
| square feet | 0.09290304 | square meters |

# List of Acronyms/Abbreviations

| | |
|---|---|
| AEC | Army Environmental Command |
| AMC | Antecedent moisture content for SCS curve number run-off method |
| AOI | area of interest |
| CMS | Contaminant Model for Streams |
| CN | SCS curve number for runoff calculations |
| DoD | Department of Defence |
| EL | Environmental Laboratory |
| EPED | Environmental Processes and Effects Division |
| ERDC | Engineer Research and Development Center |
| FRAMES | Framework for Risk Analysis in Multimedia Environmental Systems |
| HGCT | Hydro-Geo-Characteristics Toolkit |
| HE | high explosives |
| $KClO_4$ | potassium perchlorate |
| MC | munitions constituents |
| MEPAS | Multimedia Environmental Pollutant Assessment System |
| MW | molecular weight |
| ORAP | Operational Range Assessment Program |
| PET | Potential evapotranspiration |
| Plus-SG | Plus operator for Surface water and Groundwater |
| POC | Proof-of-concept (application) |
| RDX | Research Department Explosive, a high explosive |
| RECOVERY | Contaminant fate and transport model for surface water and sediments |
| RMUS | DoD Range and Munitions Use Subcommittee |
| R-Project | Free-ware statistical software package for doing sensitivity analysis |
| SAFRs | small arms firing ranges |
| SCS | Soil Conservation Service |
| SWAT | Soil and Water Assessment Tool (watershed model) |
| S/U | sensitivity and uncertainty |
| TNT | tri-nitro-toluene, a high explosive |
| TREECS | Training Range Environmental Evaluation and Characterization System |
| TSS | total suspended solids concentration |
| USLE | Universal Soil Loss Equation |
| VB | Visual Basic programming language |
| VM | Visual Minteq equilibrium chemistry model |
| WFF | water flux file used in FRAMES |
| WSS | Web Soil Survey Web-based tool |
| 3D | three-dimensional |

# 1    Introduction

## Background

The Training Range Environmental Evaluation and Characterization System (TREECS) is being developed for the Army with varying levels of capability to forecast the fate of munitions constituents (MCs), such as high explosives (HE) and metals, within and transported from firing/training ranges to surface water and groundwater. The overall purpose is to provide environmental specialists with tools to assess the potential for MC migration into surface water and groundwater systems and to assess range management strategies to ensure protection of human health and the environment. In addition to the Army, these tools could potentially be used by other services within the Department of Defense (DoD).

TREECS will be accessible from the World Wide Web and will initially have two tiers for assessments. Tier 1 will be screening-level methods that require minimal data input requirements and can be easily and quickly applied to assess the potential for MC migration into surface water and/or groundwater at concentrations exceeding protective health benchmarks at receptors' locations. Assumptions, such as steady-state conditions, are made to provide conservative or worst case estimates for potential receptor media concentrations under Tier 1. If a potential concern is indicated by a Tier 1 analysis, then there would be cause to proceed to Tier 2 to obtain a more definitive assessment. The formulations for the Tier 1 modeling approach are presented by Dortch et al. (2009).

Tier 2 assessment methods will require more detailed site data, and will require more knowledge and skill to apply, but can be applied by local environmental staff that have a moderate understanding of multi-media fate and transport. The Tier 2 approach will allow time-varying analyses of both the solid and non-solid phases of MCs with dissolution. A time-varying analysis should provide more accurate predictions with generally lower concentrations due to mediating effects of transport phasing and dampening. The Tier 2 modeling approach is described by Dortch et al. (2011). Tiers 1 and 2 focus on contaminant stressors and human and ecological health end point metrics.

## Scope

This report describes a proof-of-concept (POC) application of the prototype Tier 2 modeling approach and provides recommendations for its implementation and use. The POC application was required to evaluate the reasonableness of the approach, to learn what was missing, to learn how to obtain various input data and to determine what parts needed revision. Additionally, the Tier 2 POC application results are compared with those from Tier 1 to gain a better understanding of the differences provided by the two methods and the added benefits of using Tier 2 over Tier 1.

The details of the Tier 2 modeling approach are not repeated in this report, but they can be found in the report by Dortch et al. (2011). The Tier 2 POC application was not intended to validate the accuracy of the models as that will be done later through various applications to field study sites with observed data.

There was a requirement to conduct the POC application for an Army installation that had been categorized as *inconclusive* under Phase I of the Army's Operational Range Assessment Program (ORAP). Ranges categorized as *inconclusive* require a follow-up Phase II assessment that involves quantitative assessment including field sampling to determine if there is an off-range migration that may pose an unacceptable risk to human health or the environment. Pilot studies of several installations are presently being conducted under Phase II ORAP to lay the foundation for assessing the remainder of *inconclusive* sites. Fort A. P. Hill is one of those installations being evaluated as a pilot study, and it was chosen for this POC application. Fort A. P. Hill was also used for the POC application of Tier 1 as reported by Dortch et al. (2010).

One of the primary goals of developing TREECS is to provide cost-effective tools that can rapidly facilitate a better understanding of each site when conducting ORAP Phase II. TREECS Tier 1 and Tier 2 application results could show that some ranges presently categorized as *inconclusive* should be removed from that category and placed in the *unlikely* category, while other results could show that some ranges in the *inconclusive* category require closer attention or higher priority than others.

The terminology "protective health benchmark" is used throughout this report. This terminology, as used here, refers to the surface water, sediment, and groundwater screening value concentrations that have been developed

by the DoD Range and Munitions Use Subcommittee (RMUS). These screening values were developed so that all services would have a consistent list. Range sampling data would be compared to the appropriate media screening values presented here to determine if further range assessment is appropriate. MC concentrations less than these conservative screening values will be considered to have no adverse impacts on human health and/or the environment, and therefore, would not require any further action. Sampling data with MC concentrations exceeding these screening values do not necessarily indicate the presence of an unacceptable risk, or the necessity for cleanup or other mitigation measures. Results above these conservative screening values indicate that a more detailed evaluation of the existing data is required. These DoD screening values have been stored within the database that is used in TREECS to evaluate media concentrations.

The DoD screening values are not the only threshold values that can be used for evaluating potential impacts of media constituent concentrations. If appropriate State or local regulatory standards are more stringent, they take precedence and should be used on a site-specific basis. Also, other situations may require a different threshold to compare data to. Assessors should always be aware of site-specific conditions before they finalize conclusions.

It is noted that the ecological benchmarks for metals in water reported in this report are for a hardness of 100 mg/L. This is because the benchmark database values are for 100 mg/L hardness, and the feature to adjust the metal benchmarks to local site hardness values had not been added to TREECS at the time this work was performed. Media concentrations are compared to benchmarks in this report for illustrative purposes and are not intended to guide decisions for further investigations or actions regarding potential environmental health concerns.

# 2 Approach

The general approach for this study consisted of selection of a study site and application of a preliminary version of the Tier 2 formulations to that site as described in this report.

## Site selection and description

Fort A.P. Hill was selected as the study site for the POC application for both Tier 1 and Tier 2. The reasons for selecting Fort A.P. Hill included the following.

- Fort A.P. Hill was selected for pilot study under Phase II ORAP.
- Fort A.P. Hill had numerous firings per year for both HE and small arms.
- Site characterization information from various sites had already been collected.
- Comprehensive range-use information with quantity of rounds fired for each munitions type for the period 2000-2006 had already been collected.
- Notable potential receptor locations were identified outside the installation in close proximity to the installation boundary.

As described by EA Engineering Science and Technology, Inc. (EA, Inc. 2006), Fort A.P. Hill occupies 75,794 acres in the eastern portion of Caroline County, Virginia. Bisected by U.S. Route 301, the installation is located approximately 20 miles southeast of Fredericksburg, Virginia. Fort A.P. Hill was established as an Army training facility in 1941 for use in troop and artillery training on land purchased by the federal government. Today, Fort A.P. Hill is a training and maneuver center focused on providing realistic joint and combined arms training. The installation is used year-round for military training of both active and reserve troops of the Army, Navy, Marines, and Air Force, as well as other government agencies. Fort A.P. Hill currently conducts training in 128 training areas. There are 98 firing ranges and three impact areas. Other information regarding this installation as well as the ORAP Phase I assessment can be found in the EA report (2006). Other site descriptions and characterizations required for the modeling are discussed in the sections of this report that pertain to those characterizations.

## Modeling approach

Following the development of the Tier 2 modeling approach (Dortch et al. 2011), the soil model formulations were coded into a Visual Basic (VB) program for application to Fort A.P. Hill. The export flux output from the soil model for leaching was linked to the inputs for the Multimedia Environmental Pollutant Assessment System (MEPAS) vadose zone model, and the export fluxes for rainfall ejected runoff, soil erosion, and solid phase particle erosion were linked to the inputs for the RECOVERY surface water model, which was used to model White Lake on Beverly Run. In addition to the RECOVERY model, the Contaminant Model for Streams (CMS) was also tested during this study as discussed in Chapter 6. The MEPAS vadose zone model fed into the MEPAS aquifer model. The MEPAS and RECOVERY models are described by Dortch et al. (2011), and all reside within the Adaptive Risk Assessment Modeling System (ARAMS™), which can be accessed from http://el.erdc.usace.army.mil/arams/arams.html. The Tier 2 soil model was also added to ARAMS to facilitate model linkages and to expedite the application procedure prior to final software development in TREECS. The Tier 2 soil model was also programmed into a spreadsheet to provide a means of verifying the correctness of the VB coded soil model.

Initial POC testing for Tier 2 was conducted within ARAMS. However, early in the study the TREECS development had proceeded enough that it was possible to do most of the POC application work within TREECS rather than ARAMS.

The first step in the modeling application was to establish the area of interest (AOI). This step is fully explained by Dortch et al. (2010) and is not repeated here. The same AOI is used for the Tier 2 POC application as was used for the Tier 1 application. The AOI consisted of the main impact area of the ranges. Next it was necessary to estimate the amount of MC mass residue deposited onto the AOI on an annual basis. Range firing records were used for this task as described by Dortch et al. (2010). The same MC mass residue loading rates used in the Tier 1 POC application were used in the Tier 2 POC application except that the loadings extended over a finite period of time rather than being constant indefinitely or steady-state. Two loading periods were assessed, 7-years and 60-years duration. Also, some variation in the metal loadings was used in the present study as discussed later in this report.

The next step was to set up the inputs for the Tier 2 soil fate and export model. This step required estimating the hydrologic variables used in the input and discussed by Dortch et al. (2010). However, the methods for estimating erosion and hydrology (runoff, infiltration, etc.) were refined since the Tier 1 study was done. Thus, the results for Tier 2 are different from the original Tier 1 results due to differences in erosion and infiltration rates. Subsequently Tier 1 results were refined as described in this report, and Tier 2 was verified to yield the same results as Tier 1 given the same hydrology and other inputs. Many of the Tier 2 model inputs are identical to those used in the Tier 1 POC application as discussed in Chapter 4 of this report.

After setting up model inputs, the models were run, and the computed concentrations of MCs for surface water, sediment, and groundwater were compared with health benchmarks. All of the inputs and how they were estimated are described in Chapter 4 of this report, and model output is described in Chapter 5. Sensitivity modeling and other tests are discussed in Chapter 6.

# 3 MC Residual Mass Loadings

The same MCs evaluated in the Tier 1 POC application were evaluated in the Tier 2 application. These constituents included: the high explosives RDX and TNT, lead, copper, and potassium perchlorate ($KClO_4$). The methods for estimating the annual loadings of each of these MC are described by Dortch et al. (2010). The estimated annual loadings are shown in Table 1.

Table 1. Estimated annual MC loadings from Dortch et al. (2010).

| MC | Loading, g/yr |
|---|---|
| TNT | 60,729 |
| RDX | 15,201 |
| Lead | 50,000,000 |
| Copper | 30,000,000 |
| Potassium perchlorate | 74 |

Note: Loading durations of 7 and 60 years were tested.

It is useful to maintain the loading rates as used in the Tier 1 application for this study, so that results from the two modeling approaches can be compared. Thus, the loading rate of each MC constituent was held constant over time for a finite time duration. Loading durations of 7 and 60 years were evaluated. The 7-year period is consistent with the length of the records used to identify the munitions use. The 60-year period is more consistent with the length of time this range has been used. As discussed in Chapter 6, time-varying loading rates were also modeled to explore the effect on dampening and attenuation of receiving media concentrations.

The ORAP Phase I report on Fort A.P. Hill (EA, Inc. 2006) stated that approximately 22,000,000 small arms rounds are fired per year. An examination of range firing records indicated that this value should have been the total number of small arms rounds fired over the 7-year period from 2000 to 2006. If a value of 22,000,000 rounds per year is used, this amount translates into 50,000,000 and 30,000,000 g/yr of lead and copper loading, respectively, deposited into the small arms firing ranges (SAFRs). A mass of 50,000,000 grams is 55 English tons, which is a considerably large amount of lead deposited each year. The reported value of 22,000,000 rounds per year is used initially for the Tier 2 POC

application since it was used in the Tier 1 POC application, but it is recognized that this amount is probably inflated by a factor of 7. Therefore, 1/7th of the lead and copper loading rates shown in Table 1 are also used for application comparisons.

# 4    Site Characterization and Model Inputs

Various site characteristics and other inputs must be determined or estimated to apply the TREECS Tier 2 models. These data fit into the general categories of site dimensions and physical characteristics, soil characteristics, hydrologic characteristics, fate/transport parameters, and chemical-specific properties. Each of the required variables within these categories and the methods for estimating them are discussed below. Some of these inputs are only briefly discussed since the same values were used for the Tier 1 POC application and are discussed more fully by Dortch et al. (2010).

## Site dimensions and physical characteristics

The AOI dimensions (length and width) and area must be determined for model input. For the Tier 1 and Tier 2 soil fate and export models, the AOI dimensions and area do not affect the export fluxes, but the area does affect the computed AOI soil concentration of MC residue, and the dimensions can affect aquifer concentrations. The thickness of the surface soil layer containing MC residue drops out of the equations for the Tier 1 soil model, so it is not required for Tier 1. For the Tier 2 soil model, the soil layer thickness must be defined, and it does affect export fluxes and soil concentrations. This is a variable that should be varied for sensitivity. The default value is 0.4 m (Dortch et al. 2011), but values of 0.2, 0.4, and 0.8 m were evaluated (see Chapter 6, "Additional Testing").

The aquifer concentrations computed by the MEPAS aquifer model can be affected by the AOI dimensions. The AOI surface area affects the amount of infiltration flow rate, which affects aquifer concentrations. The length and width of the AOI also can affect aquifer concentrations, especially when the receptor well is located in close proximity to the AOI. The AOI width $W_f$ is the AOI dimension that is perpendicular to the groundwater flow. The AOI length $L_f$ is the AOI dimension that is parallel to the groundwater flow. Aquifer concentrations are affected by the AOI dimensions when the receptor well's downstream longitudinal distance is less than approximately 10 times $W_f$. The downstream longitudinal distance of the well is measured from the AOI center, or at $L_f/2$. As a rule of thumb, the well should not be closer than 1.5 $L_f$ from the AOI center to properly apply the results of the MEPAS aquifer model. The user is required to enter $L_f$ and $W_f$ for the AOI,

but the AOI does not have to be rectangular or a parallelogram. For a polygon, the two dimensions should be the farthest lateral and longitudinal extent of the polygon when viewing it relative to the groundwater flow direction. Thus, the AOI area is not the product of $W_f$ and $L_f$, rather it is the area of the polygon.

Deciding the AOI shape and dimensions can be quite difficult even for a single impact area since impact areas are rather large and heterogeneous. At Fort A.P. Hill, there are three dudded impact areas, all of which are located south of U.S. Route 301. Figure 1 shows the general location of the three impact areas although they tend to run together. These areas are at the center of the wagon wheel of firing ranges and downrange of the small arms ranges and the direct and indirect firing points. These areas receive each type of live-fire munitions and pyrotechnics. It is noted that projectiles fired from SAFRs rarely fall in the central impact area, since each of those ranges usually have backstop berms within each range to stop the projectiles. Thus, these backstop berms can be source areas or AOIs.
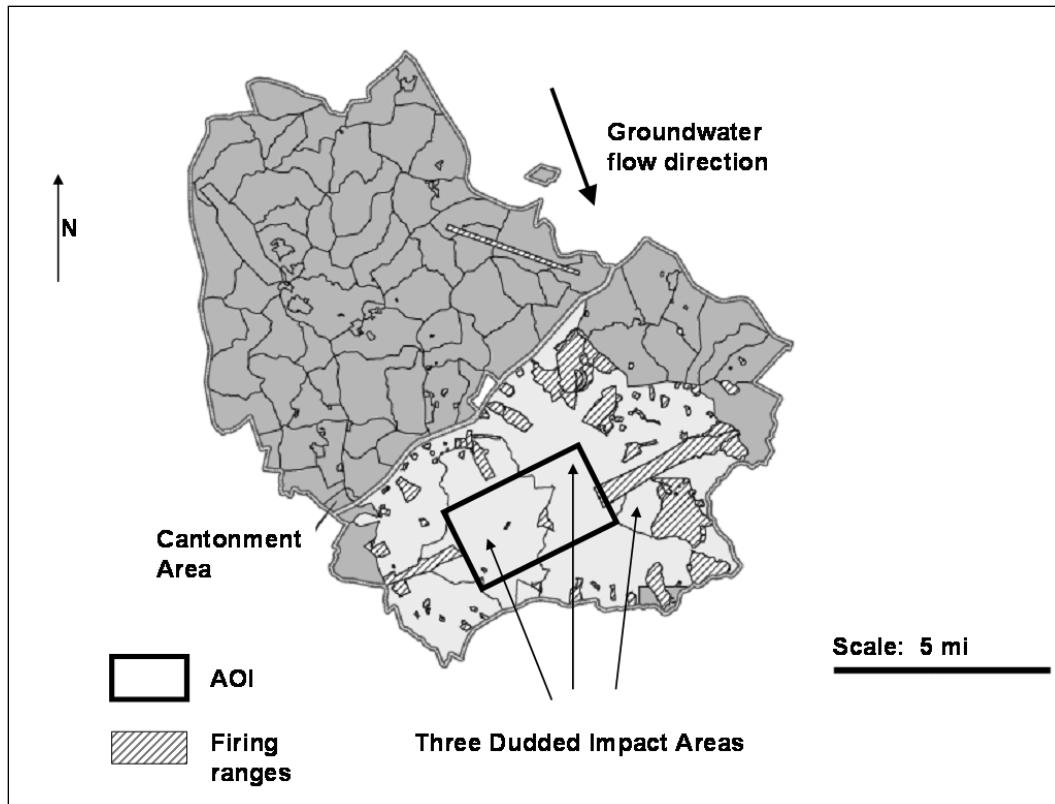


Figure 1. Fort A.P. Hill impact areas and delineated AOI (modified from EA, 2006)

For Fort A.P. Hill, the primary impact area, and thus the AOI, was depicted by examination of supplementary information (Army Environmental Command (AEC) 2009) and aerial views from Google Earth™. A single AOI was assessed as shown in Figure 1. The orientation of the AOI shown in Figure 1 was based on the general direction of groundwater flow indicated in the Phase I ORAP report (EA, Inc. 2006). The dimensions $W_f$ and $L_f$ were estimated to be 4,715 and 2,285 m, respectively. A rectangular shape was assumed to simplify calculation of AOI surface area, which is a required model input. The AOI surface area is 10,773,775 m².

The initial solid phase and non-solid phase MC concentration in soil must also be specified for the Tier 2 soil model. It was assumed that these concentrations are zero for this application, and the default input values are also zero. However, the user can change these values to reflect measured initial values stemming from past range activity and to reflect background concentrations, such as for metals that occur naturally in the environment.

A distance must be specified from the center of the AOI to each receptor groundwater well of interest. The nearest receptor well relative to the AOI is about 4,000 m down-gradient based on maps in the Phase I ORAP report (EA, Inc. 2006). Thus, one well location of 4,000 m was considered in the analysis, the same as for the Tier 1 POC application. Other well locations could be considered if deemed necessary. The receptor well was assumed to be along the centerline of the groundwater MC plume and near the water table surface, which results in highest well concentrations of MCs as predicted by the MEPAS aquifer model. Other well locations at greater depth or off the plume centerline can be considered; however, inputting other than zero for these two inputs will produce less conservative results with this model as explained in the section titled "Aquifer model" below.

A representative water body was required to assess surface water and sediment impacts. As in the Tier 1 POC application, White Lake, which is on Beverly Run, was selected for study. This lake is one of the closest water bodies relative to the AOI, and Beverly Run starts near the center of the AOI. White Lake is a small run-of-the-stream lake. The length of the lake appears to be on the order of 1500 m with a width of roughly 50 m, resulting in a surface area of 75,000 m². The mean depth was assumed to be 1 m, and the average annual flow through the lake was assumed to be 47,304,000 m³/yr. This flow rate was based on an assumed average flow

velocity of 0.1 ft/sec. With these lake dimensions and flow, the average residence time of water in the lake is 0.0016 year, or slightly more than half a day. Surface water flow-through rates can also be estimated from the catchment basin area that drains into the surface waters. Thus, the average annual runoff to the lake (i.e., the average annual flow through the lake) can be estimated from the product of the catchment basin area and the estimated average annual runoff depth. However, it is recognized that groundwater discharges can also contribute to lake inflow.

## Soil characteristics

Web Soil Survey[1] (WSS) was used to estimate some of the soil characteristics for the Fort A.P. Hill main impact area, i.e., the AOI. The soil classifications and their respective areas were provided by WSS, and an area-weighted-average was used to characterize the AOI. The soil texture is characterized as sandy loam, which is comprised of 65, 25, and 10 percent sand, silt, and clay, respectively. These soils are considered well drained and fall into hydrologic soil group B.

The sandy loam soil texture has a dry soil bulk density of 1.48 $g/cm^3$, a porosity of 44 percent, a field capacity of 17.5 percent, and a saturated hydraulic conductivity of 0.622 m/day. The value for saturated hydraulic conductivity is lower than the value used in the Tier 1 POC analysis, but it is considered more commensurate for the site soil texture per guidance in the TREECS Hydro-Geo-Characteristics Toolkit (HGCT). The soil surface organic matter content is 1.2 percent. This organic matter content translates into a fraction of organic carbon of approximately 0.007. The soil pH is about 5.5. These same values for soil characteristics were used for the Tier 1 POC application, except for the saturated hydraulic conductivity.

Soil characteristics are needed for the soil, the vadose zone, and the aquifer models. To expedite this application, the same soil characteristics were assumed for all three models. However, in most applications, the soil properties are different for these three zones and should be specified accordingly.

---

[1] http://websoilsurvey.nrcs.usda.gov/app/WebSoilSurvey.aspx

## Hydrologic characteristics

The Tier 2 soil model requires the long-term average annual rates for total precipitation, rainfall, infiltration, and soil erosion and the long-term average number of rainfall events per year. Some improvements and revisions were made to the hydrologic computations as discussed in Appendix C, which changed the input conditions used for the Tier 2 POC application compared with the original Tier 1 POC application.

Hydrologic computations were based on daily precipitation and daily average and maximum air temperature data from the Washington DC National Airport for the period 1970 – 1995. The average annual total precipitation for the 25-year period is 0.994 m/yr. The average annual rainfall is 0.923 m/yr, which occurred for an average of 99 rainfall events per year. For a curve number (CN) of 79, the average annual runoff depth for the 25-year period is 0.306 m/yr, which is much higher than the value of 0.067 m/yr computed previously during the Tier 1 POC application. The average annual evapotranspiration for the 25-year period is 0.453 m/yr, yielding an average annual infiltration rate of 0.201 m/yr, compared with 0.161 m/yr computed for the Tier 1 POC application.

The Tier 2 soil model also requires specification of the fraction of annual water infiltration flow rate and mass flux that goes into soil interflow. No interflow was assumed for the Tier 2 POC application since the soil saturated hydraulic conductivity is much greater than the infiltration rate.

The soil loss due to erosion was computed to be 1.457 tons/acre-yr (0.000221 m/yr) based on the Universal Soil Loss Equation (USLE) as described by Dortch et al. (2010). This erosion rate includes use of a sediment delivery ratio (SDR) of 0.2 for this site. The factors used in the USLE for Tier 2 were: R = 225, K = 0.24, L = 400 ft, S = 0.06, C = 0.1, and P = 1. These factors are the same as those used for Tier 1 except for L and S. The LS factor for the L and S stated above is 1.335, which is much less than the unrealistically high LS factor of 10 used in Tier 1. Also, the SDR was set to 1 for computing erosion in the Tier 1 POC application. For these reasons, a much higher and unrealistic erosion rate of 54 tons/acre-yr was obtained for the Tier 1 POC application.

The Darcy velocity used for the Tier 1 POC application was 16 cm/day, which was based on a groundwater gradient of 0.14 and saturated hydraulic conductivity of 1.12 m/day. The average ground surface slope for the site

was computed to be 0.06 based on a digital elevation map (DEM) that was downloaded from the WorldWide Web. This slope was assumed for the water table gradient. With this slope and the improved estimate of saturated hydraulic conductivity of 0.622 m/day, the Darcy velocity was computed to be 3.73 cm/day. It is noted that aquifer hydraulic conductivity can be quite different from conductivity of surface soils, but they were assumed to be the same in this study.

## Fate and transport parameters

Most of the estimated fate/transport parameters used in the Tier 1 POC application were also used for the Tier 2 POC application except as noted above. This section summarizes specification of these parameters for each model.

### Soil model

The Tier 2 soil model has six fate/transport related parameters: the soil-water distribution (or partition) coefficient $K_d$ for soil (L/kg); the soil detachability due to rainfall, $a$ (kg/L); the soil exchange layer thickness, $d_e$ (m), associated with rainfall ejection of pore water; the decay/degradation rate of liquid (water) phase constituent, $\lambda_l$ (yr$^{-1}$); the decay/degradation rate of adsorbed (particulate) phase constituent, $\lambda_a$ (yr$^{-1}$); and the initial mean diameter of solid phase constituent residue particles, $d_i$ (μm). Values used for each of these parameters are summarized below. Additionally, the average annual soil temperature is required, which was set to 13.5 $^o$C, the average annual air temperature plus one degree (Dortch et al. 2011).

The $K_d$ (soil) values for RDX, TNT, and potassium perchlorate were determined to be 0.13, 0.31, and 4E-10 L/kg, respectively, during the Tier 1 POC application (Dortch et al. 2010). The soil $K_d$ values used for lead and copper were 597 and 92 L/kg, respectively. Sorption partitioning coefficients for the two metals could be higher in reality, but the value for lead is consistent with values measured for lead in various soil types by Larson et al. (2005). It is recognized that sorption partitioning for metals is highly variable and depends on local soil-water chemistry and surface complexation.

The two rainfall ejection parameters $d_e$ and $a$ were set to 0.005 m and 0.4 kg/L, respectively, the same values as for the Tier 1 POC application. Both decay rates were set to zero for conservatism. Zero decay rates are

also consistent with the Tier 1 POC application since the Tier 1 models assume no decay.

Studies by Pennington et al. (2005) and Taylor et al. (2004) indicate that the typical size of HE particles is on the order of about 1 cm. Analysis of the Pennington data revealed that 49 percent of the particle mass for explosives was greater than 12.5 mm on average for all rounds analyzed. The Taylor data indicated about the same size on average for the mass residue captured for an 81-mm mortar round. Thus, the initial, average solid phase particle size ($d_i$) for RDX and TNT was set to 12,000 µm. The initial solid phase particle sizes for lead and copper were set to 500 and 5,000 µm, respectively, based on information provided by Larson et al. (2005) for silty sand B soil. Initial MC particle size should be varied for sensitivity since it is not easily known or determined and can depend on a number of factors, such as type of munitions and the energy yield for high explosives and the type of soil fired into and the distance between firing and impact points for small arms. Potassium perchlorate is considered to be water miscible due to its high solubility, and it very rapidly transfers to the non-solid phase; thus, initial particle size is not important and is not a required input.

Two additional parameter inputs are required by the Tier 2 soil model. One of the parameters declares whether spherically or cylindrically shaped solid phase particles are considered for dissolution. The other parameter declares whether or not to consider solid phase particle erosion. For the baseline Tier 2 POC application, spherical particles were assumed with no solid phase particle erosion. The effects of assuming cylindrical particles and allowing solid phase particle erosion were evaluated with sensitivity tests as discussed in Chapter 6.

Several chemical properties of each MC are also required, but these variables are discussed in the section on chemical-specific properties below.

**Vadose zone model**

The input parameters required for the MEPAS vadose model are discussed by Dortch et al. (2011). Values used for the Tier 2 POC application are discussed below.

Output from the soil model that is passed to the vadose zone model includes: the AOI dimensions, $W_f$ and $L_f$; water percolation flow rate due to

infiltration from soil (recharge into vadose zone); and MC mass flux versus time due to leaching from soil to the vadose zone. The water percolation flow rate is the product of the AOI surface area and infiltration rate $q_w$ in this application since there is no interflow. The MC mass flux depends on results from the soil model and can vary accordingly for each run.

Soil composition for the vadose zone must be specified. Composition was set the same as the surface soil, which is a sandy loam soil texture composed of 65, 25, and 10 percent sand, silt, and clay, respectively. The soil organic matter content was set to 1.2 percent, and the percent of iron plus aluminum was set to zero due to lack of information and for conservatism. This input for iron and aluminum is considered the oxyhydroxide forms outside of the clays and they are used in the MEPAS vadose zone and aquifer models to estimate adsorption partitioning between water and soil of aqueous phase metals. A value of zero is more conservative, as this reduces adsorption resulting in more mobility for metals. Additionally, input of typical values for soil iron and aluminum had no effect on the computed partition coefficient of the two metals for this soil. The percent for sand was reduced from 65 to 63.8, since the percentage of all components must sum to 100 percent for the MEPAS vadose and aquifer models. The soil pH was set to 5.5. Likewise, soil total porosity, dry bulk density, field capacity, and saturated hydraulic conductivity were set to values discussed within the "Soil characteristics" section above, which are 44 percent, 1.48 g/cm$^3$, 17.5 percent, and 0.62 m/day, respectively.

The thickness of the vadose zone, i.e., depth to groundwater, must be specified. A value of 6.1 m (20 ft) was used based on Fort A.P. Hill site information (EA, Inc. 2006). The vertical dispersivity is required and can be estimated as 0.01 times the thickness of the vadose zone. In this case the dispersivity was set to 0.061 m or 6.1 cm.

The half-life in the vadose zone must be specified for each MC. A very large value of 1.0 E20 years was set for each MC initially to represent no decay/degradation to allow comparison to Tier 1 results.

The vadose zone soil-water partition coefficient ($K_d$) for each constituent was set to the same values used for the soil model as discussed above. The water solubility limit for each MC is also required, but this variable is discussed in the section on chemical-specific properties below.

**Aquifer model**

The output from the vadose zone model that is passed to the MEPAS aquifer model includes water and MC fluxes from the vadose zone to aquifer as discussed by Dortch et al. (2011). The soil composition for the aquifer model was set to the same values as those used for the vadose zone and soil models. The soil characteristics of pH, total porosity, and dry bulk density were also set to the same values as those for the soil and vadose zone models.

The effective porosity was set to 41 percent, which is representative of sandy loam soil as per guidance in the HGCT. This input parameter is not required for the other models and is used in aquifer transport to allow for dead end pore spaces. The percentage of constituent flux entering the aquifer from the vadose zone must also be specified and was set to 100 percent. Any losses due to interflow are taken into account in the soil model.

Other fate/transport parameters required by the aquifer model include the receptor well location(s), the three dispersivities (m), the aquifer thickness (m), and the Darcy velocity. The three dispersivities, which were computed by the model interface, were 400, 132, and 1 m for the longitudinal, transverse, and vertical directions, respectively, based on the well location. As previously stated, the well was located 4,000 m down-gradient from the center of the AOI. The well was also placed at the level of the water table vertically (zero depth below water table) and along the groundwater plume centerline laterally (zero lateral distance) to provide conservative results as explained below.

The MEPAS aquifer model solves time-varying reactive transport assuming steady, uniform, one-dimensional horizontal flow and advection with three-dimensional dispersion. Thus, the aquifer concentrations at x, y, and z coordinates are computed, but the contaminant plume is assumed to move horizontally along the water table upon entering the aquifer since there is no vertical advection. Contamination can move vertically down in the model only by dispersion. For these reasons, the maximum concentration will always be along the water table surface. The user should enter zero for the vertical depth below the water table of the well intake screen in order to obtain the most conservative results. If the MC enters the aquifer within a recharge zone or at a location that is considerably higher than the down-gradient topography, the plume can actually move downward as it moves down-gradient. This phenomenon can be shown from potential flow theory

or flow nets, resulting in greater down-gradient concentrations below the water table than those at the water table. For such cases, the model may incorrectly indicate much lower concentrations for deep well intakes than actually occurs, whereas model-computed concentrations for well intakes at the water table can be much higher than actually occur. Thus, it is best to place the well intake at zero depth below the water table to ensure conservative results. The theoretical maximum constituent concentrations are always located at the surface of the water table and along the plume centerline.

It is also noted that the MEPAS aquifer model cannot address sinking plumes associated with fluid density differences and cannot address heterogeneities in the porous media and the associated heterogeneous flow and transport fields. Such simulations require rather comprehensive 3D groundwater flow and transport models.

The target well and aquifer information were based upon information in the Phase I ORAP report for Fort A.P. Hill (EA, Inc. 2006). There are several private wells located near the southern boundary of the installation with unknown well depths (EA, Inc. 2006). The target well was assumed to be one of these wells. Furthermore, it was assumed for conservatism that the target well withdraws from the shallow, unconfined, uppermost aquifer, the Yorktown-Eastover aquifer, which has water level elevations between 15 and 25 ft below ground surface (EA, Inc. 2006). Thus, this is the reason the vadose zone thickness was set to 20 ft. The Yorktown-Eastover aquifer is underlain by clayey sediments that act as an impermeable boundary (EA, Inc. 2006). The thickness of the Yorktown-Eastover aquifer is approximately 15.2 m based upon hydrogeologic cross-section information in the Phase I ORAP report for Fort A.P. Hill (EA, Inc. 2006). This aquifer thickness agrees with data from WSS.

The Darcy velocity can be estimated from the product of the saturated hydraulic conductivity and the water table gradient of the groundwater. There is no information pertaining to the gradient of the Yorktown-Eastover aquifer, but because the aquifer is unconfined and flows under the influence of gravity, flow patterns and water levels are expected to generally follow the local topography (EA, Inc. 2006). Thus, the ground surface gradient was used as a rough estimate of the water surface gradient of this aquifer. With a ground slope of 0.06, as determined from a DEM for the site, and a saturated hydraulic conductivity for the site of 62.2 cm/day (see "Soil

Characteristics" above), the Darcy velocity was computed to be 3.73 cm/day. The Darcy velocity value of 3.73 cm/day is less than the value of 16 cm/day, which was used in the Tier 1 POC application.

If there is a target surface water body, then TREECS assumes there is always groundwater discharge to the surface water, but the user must specify how much. To accommodate groundwater discharge, there is a Flux Location tab and screen in the user interface. The user must enter the longitudinal (horizontal) distance from the center of the AOI to the surface water body where it is believed that groundwater flow leaves the aquifer and enters surface water. As with the well location(s), the three dispersivities must be entered, but they can be estimated by the model user interface. It was assumed that groundwater discharge to surface water was very small (1.0E-6 percent of groundwater flow) for the initial Tier 2 POC application. However, a sensitivity test with significant groundwater discharge was run as discussed in Chapter 6.

The half-life in groundwater must be specified for each MC. A very large value of 1.0 E20 years was set for each MC initially to represent no decay/degradation to allow comparison to Tier 1 results. A sensitivity run with decay/degradation is discussed in Chapter 6.

The aquifer $K_d$ value for each MC was set to the same value used for the soil and vadose zone models. The water solubility limit for each MC is also required, but this variable is discussed in the section on Chemical-Specific Properties below.

**Surface water model**

The RECOVERY model was used to represent White Lake, which is consistent with the approach used in Tier 1. The various input parameters required by the RECOVERY model as implemented in Tier 2 are discussed by Dortch et al. (2011). Values used in the Tier 2 POC application are discussed below.

Output from the soil model that is passed to the surface water model includes water and MC mass fluxes due to AOI runoff and erosion. These fluxes can also include any flux due to groundwater discharge to surface water, which is assumed to be zero for this application. The water flux is the product of the runoff depth per year and the AOI area, which is 3,297,427 m³/yr. This flux value is not used by the RECOVERY model;

instead, the water flow-through rate input by the user is applied, which can be different and possibly larger than the AOI surface runoff rate. The value of 47,304,000 m³/yr was used for flow-through rate as discussed in the section titled "Site Dimensions and Physical Characteristics."

Surface water morphometry and hydrology information must be provided, which includes long-term average total suspended solids (TSS) concentration and the weight fraction of organic carbon of the TSS ($f_{oc}$ *water*) in addition to the water surface area, mean depth, and annual average water flow-through rate. The values used for the latter three input variables were discussed in the previous section, "Site Dimensions and Physical Characteristics." The TSS was set to 100 mg/L and $f_{oc}$ *water* was set to 0.01 to be consistent with default values built into the Tier 1 RECOVERY model implementation.

Properties of the sediment layers must be specified. To provide consistency with default values built into the Tier 1 RECOVERY model implementation, the following values were input to the RECOVERY model for the Tier 2 POC application: contaminated sediment depth $L$ was set to 1.0 m; the mixed, surficial sediment layer depth $z$ was set to 0.07 m; the mixed sediment layer surface area $A_m$ was set to 75,000 m² (same as the water surface area); the mixed layer and deep sediment particle specific gravities were set to 2.65; the deep sediment porosity was set to 0.5; and the deep sediment $f_{oc}$ was set to 0.01. The mixed sediment layer porosity and $f_{oc}$ were set to 0.7 and 0.01, respectively, to be consistent with the RECOVERY model inputs for the Tier 1 POC application. The input depth $L$ is needed when there are contaminant concentrations in the bed initially. If there is no initial contamination, this input value has little effect on results.

System properties must be specified. To provide consistency with default values built into the Tier 1 RECOVERY model implementation, the following values were input to the RECOVERY model for the Tier 2 POC application: enhanced diffusion of the mixed layer was set to zero; resuspension rate was set to 1.0 E-20 m/yr (essentially no resuspension); and burial rate was unspecified and left to be calculated. To be consistent with inputs for the Tier 1 POC application, the long-term average wind speed was set to 6 m/sec, and the TSS settling rate was set to 36 m/yr.

Although initial MC concentrations in water, mixed sediment, and deep sediment can be entered, these inputs were set to zero, and zero additional

external loading of MC was entered for this application. All MC decay/degradation rates were set to zero in the Tier 2 POC application to be consistent with the Tier 1 RECOVERY model implementation.

The sediment-water distribution (partition) coefficient, $K_d$ *sediment* (L/kg), is required for deep and upper mixed layer sediments and for the water column TSS. RECOVERY calculates $K_d$ from the octanol-water distribution coefficient $K_{ow}$, where $K_d = .617 f_{oc} K_{ow}$. With $f_{oc}$ of 0.01 and with $K_{ow}$ values of 7.41, 39.8, and 6.6E-8 L/kg for RDX, TNT, and potassium perchlorate, the computed $K_d$ *sediment* values are 0.046, 0.25, and 4.07E-10 L/kg, respectively, which are the same as the values used in the Tier 1 POC application. These values were used for water, mixed sediment layer, and deep sediment layers.

Metal $K_d$ values are not calculated in RECOVERY since $K_{ow}$ should be zero; thus, they must be specified. The $K_d$ *sediment* values for lead and copper were set to 4,000 and 600 L/kg, respectively, which is the same as the values used in the Tier 1 POC application. The $K_d$ *sediment* values for the water column solids and the mixed and deep benthic sediment layers can be different, but all three values were set equal for each MC for this application, the same as the Tier 1 POC application.

Four chemical-specific physical/chemical properties for each MC are also required, but these values are discussed in the section titled "Chemical-Specific Properties." Model control parameters were set to values recommended by Dortch et al. (2011) with the total period of simulation set to 100 years.

## Chemical-specific properties

Six chemical-specific physical/chemical properties are required by the models for fate/transport within TREECS. These properties are shown in Table 2 along with the values used. Definitions for the variables in Table 2 are as follows: molecular weight $MW$ (g-mole); diffusivity in water $D_w$ (cm²/sec); Henry's constant $H_e$ (atm-m³/g-mole), octanol-water partition coefficient $K_{ow}$ (ml/ml), water solubility limit $C_s$ (mg/L); and solid phase particle mass density $\rho_{sm}$ (g/cm³). The Tier 2 soil model requires $MW, H_e,$ $C_s,$ and $\rho_{sm}$. The MEPAS vadose and aquifer models require only $C_s$. The RECOVERY and CMS models require $MW, D_w, H_e,$ and $K_{ow}$.

Table 2. Physical and chemical properties for the five MCs.

| Constituent | MW | $D_w$ | H | $K_{ow}$ | $C_s$ | $\rho_{sm}$ |
|---|---|---|---|---|---|---|
| RDX | 222.12 | 7.1E-6 | 6.31E-8 | 7.41 | 59.8 | 1.82 |
| TNT | 227.13 | 6.36E-6 | 4.57E-7 | 39.8 | 130 | 1.65 |
| Lead | 207.2 | 9.45E-6 | 0 | 0 | 2.24 | 11.35 |
| Copper | 63.55 | 7.33E-6 | 0 | 0 | 0.5 | 8.94 |
| $KClO_4$ | 138.55 | 6.0E-6 | 0 | 6.6E-8 | 20,600 | 1.0[1] |

[1] Assumed value.

The TREECS constituent databases are sources of information for most of the constituent property values as discussed by Dortch et al. (2010). Several property values are different from those used in the Tier 1 POC application as a result of a search for more accurate values. Of particular importance are the values selected for lead and copper solubility. Metal solubility is highly variable and depends on the local geochemistry of the soil. More accurate estimates are needed for metal solubility since solubility affects the dissolution rate, which is not modeled in Tier 1 but is modeled in Tier 2. The solubility values suggested for Tier 2 are based on computations with the equilibrium chemistry model Visual Minteq (http://www.lwr.kth.se/English/OurSoftware/vminteq/). The Visual Minteq (VM) applications and their required inputs are discussed in Appendix A.

From WSS, the pH of the soil at Fort A.P. Hill is indicated to be about 5.5, but the presence of metals such as lead can raise the pH as discussed in Appendix A. Based on the application of VM, the solubility for lead and copper recommended for the Tier 2 POC application is 2.24 and 0.5 mg/L, respectively (see Appendix A). These values are much lower than those used in the Tier 1 POC application. Higher values of solubility were tested for Tier 2 as discussed in Chapter 6. Water solubility could be different in the vadose zone and aquifer, but the same values used for soil were used in those zones.

The solid phase particle mass density was not required for Tier 1, but is required for Tier 2. The values shown in Table 2 were obtained from the literature and property databases. Potassium perchlorate has a high water solubility limit and is considered to be water miscible; therefore, it dissolves in water very rapidly. For this reason, model results are insensitive to inputs for solid phase mass density and initial solid phase particle diameter for perchlorate.

## Summary of model inputs

The input values used for the Tier 2 soil model are summarized in Table 3. The MC residue mass loadings are also an input, and they were discussed in Chapter 3.

Table 3. Summary of Tier 2 soil model input values.

| Parameter | Units | Description | Value |
|-----------|-------|-------------|-------|
| Site Characteristics | | | |
| $L_f$ | m | AOI dimension that is parallel to the groundwater flow | 2,285 |
| $W_f$ | m | AOI dimension that is perpendicular to the groundwater flow | 4,715 |
| A | $m^2$ | AOI surface area ($L_f$ x $W_f$ before rounding off values shown above) | 10,775,905 |
| $Z_b$ | m | Active soil layer thickness | 0.4 |
| $T_{soil}$ | $^oC$ | Average annual temperature of soil-water matrix | 13.4 |
| L | g/yr | MC mass residue loading versus time | See Table 1 |
| $C_S(0)$ | mg/kg | Initial solid phase MC concentration in soil on a soil mass basis at time 0 | 0 for all constituents |
| $C_{ns}(0)$ | mg/kg | Initial total non-solid phase MC concentration in soil on a soil mass basis at time 0 | 0 for all constituents |
| Soil Properties | | | |
| $\theta_w$ | fraction | Volumetric soil moisture content | 0.175 |
| $\rho_b$ | $g/cm^3$ | Soil dry bulk density | 1.48 |
| $\varphi$ | fraction | Soil porosity | 0.442 |
| Hydrology | | | |
| P | m/yr | Average annual precipitation | 0.994 |
| $P_r$ | m/yr | Average annual rainfall | 0.923 |
| E | m/yr | Average annual soil erosion rate | 0.000221 |
| $q_w$ | m/yr | Average annual water infiltration rate (groundwater recharge for no interflow) | 0.201 |
| $q_r$ | m/yr | Average annual surface water runoff rate | 0.306 |
| $F_{if}$ | fraction | Fraction of annual water infiltration flow rate and mass flux that goes to soil interflow | 0 |
| N | $yr^{-1}$ | Average number of rainfall events per year | 99 |

| Parameter | Units | Description | Value |
|---|---|---|---|
| | | Fate/Transport Parameters | |
| $K_d$ | L/kg | Soil-water constituent partition coefficient | RDX: 0.13<br>TNT: 0.31<br>Lead: 597<br>Copper: 92<br>$KClO_4$: 4E-10 |
| $d_e$ | m | Soil exchange layer thickness for rainfall ejection of pore water | 0.005 |
| a | Kg/L | Soil detachability for rainfall ejection of pore water | 0.4 |
| $\lambda_l$ | $yr^{-1}$ | Decay/degradation rate of liquid (water) phase constituent | 0 for all constituents |
| $\lambda_a$ | $yr^{-1}$ | Decay/degradation rate of adsorbed (particulate) phase constituent | 0 for all constituents |
| $d_i$ | μm | Initial mean diameter of solid phase constituent residue particles (assume spherical particles) | RDX: 12,000<br>TNT: 12,000<br>Lead: 500<br>Copper: 5,000<br>$KClO_4$: NA |
| $K_v$ | m/yr | Volatilization rate | RDX: computed, 33.7<br>TNT: computed, 26.8<br>Lead: specified, 0.<br>Copper: specified, 0.<br>$KClO_4$: specified, 0. |
| $J_{ES}$ | Dimension-less | Switch for solid phase erosion (1 is on, and 2 is off) | 2 |
| | | Chemical-specific Properties | |
| $C_s$ | mg/L | Aqueous solubility limit | RDX: 59.8<br>TNT: 130<br>Lead: 2.24<br>Copper: 0.5<br>$KClO_4$: 20,600 |
| $H_e$ | Atm-m$^3$/g-mol | Henry's law constant | RDX: 6.31E-8<br>TNT: 4.57E-7<br>Lead: 0<br>Copper: 0<br>$KClO_4$: 0 |
| MW | g/mol | Molecular weight (molar mass or averaged molecular mass) | RDX: 222.12<br>TNT: 227.13<br>Lead: 207.2<br>Copper: 63.55<br>$KClO_4$: 138.55 |

| Parameter | Units | Description | Value |
|---|---|---|---|
| $\rho_{sm}$ | g/cm³ | Solid phase constituent mass density | RDX: 1.82<br>TNT: 1.65<br>Lead: 11.34<br>Copper: 8.94<br>KClO₄: 1 |
| Model Options | | | |
| T | Years | Time length of simulation | Varies, but typically about 100 years |
| Δt | Years | Time step | 0.01 (does not matter if using adaptive time step) |
| Step type | None | Methods used for equation solution | Adaptive is the default; other alternative is constant time step |

The values of $d_i$ and $\rho_{sm}$ do not matter for $KClO_4$ since it is miscible in water, i.e., it dissolves instantly. Thus, perchlorate was treated as a miscible MC, where the dissolution flux is not solved but set equal to loading flux.

The MEPAS vadose zone and aquifer model inputs are summarized in Tables 4 and 5. In addition to these inputs, the AOI site dimensions and the average annual water infiltration flow rate of 2,165,957 m³/yr were passed to the vadose zone model from the soil model. The infiltration flow rate is the infiltration rate of 0.201 m/yr times the AOI surface area of 10,775,905 m².

The Tier 2 RECOVERY model inputs are summarized in Table 6.

## Time domains

The length of the time domain required to capture the transient features of MC fate and transport through soil, surface water, and groundwater systems can vary considerably. For example, the time response for surface water can be rather quick, on the order of years. Soil and sediments are slower with time responses on the order of decades and longer. The time response for groundwater can be very slow, in many cases on the order of centuries. Thus, it is necessary to carefully set the length of simulation time for each model, as well as the time step for some models.

Table 4. MEPAS vadose model input values.

| Parameter | Units | Description | Value |
|---|---|---|---|
| Inputs Passed from Soil Model | | | |
| $L_f$ | m | AOI dimension that is parallel to the groundwater flow | 2,285 |
| $W_f$ | m | AOI dimension that is perpendicular to the groundwater flow | 4,715 |
| WFF aquifer water flux, $Q_w$ | m³/yr | Water flow rate due to infiltration from soil (rainfall flow rate into vadose zone) | 2,165,957 |
| WFF aquifer mass flux, $F_l$ | g/yr | MC mass flux versus time due to leaching from soil to vadose zone | Time-varying |
| Soil Composition | | | |
| WP-SAND | Percent | Percentage of sand | 63.8 |
| WP-SILT | Percent | Percentage of silt | 25 |
| WP-CLAY | Percent | Percentage of clay | 10 |
| WP-OMC | Percent | Percentage of organic matter | 1.2 |
| WP-IRON | Percent | Percentage of iron and aluminum | Unknown, set to 0 |
| Characteristics | | | |
| pH (WP-PH) | pH units | pH of pore water | 5.5 |
| $\varphi$ (WP-TOTPOR) | Percent | Total porosity | 44.2 |
| $\theta_f$ (WP-FIELDC) | Percent | Field capacity | 17.5 |
| $K_s$ (WP-CONDUC) | cm/day | Saturated hydraulic conductivity | 62.2 |
| $Z_V$ (WP-THICK) | m | Thickness of the vadose zone layer | 6.1 |
| $\alpha_z$ (WP-LDISP) | cm | Longitudinal (vertical direction) dispersivity | 6.1 |
| $\rho_b$ | g/cm³ | Dry bulk density | 1.48 |
| Constituent Properties | | | |
| $K_d$ (WA-SUBKD) | ml/g | Adsorption (partition) coefficient | RDX: 0.13<br>TNT: 0.31<br>Lead: 597<br>Copper: 92<br>$KClO_4$: 4E-10 |
| $C_s$ (WP-(R)SOL) | mg/L | Water solubility of constituent | RDX: 59.8<br>TNT: 130<br>Lead: 2.24<br>Copper: 0.5<br>$KClO_4$: 20,600 |
| $T_{1/2}$ (WP-GHALF) | days | Half-life of constituent in groundwater | 1.0E20 for all constituents |

Table 5. Tier 2 MEPAS aquifer model input values.

| Parameter | Units | Description | Value |
|---|---|---|---|
| Inputs Passed from Vadose Zone Model | | | |
| $L_f$ | m | AOI dimension that is parallel to the groundwater flow | 2,285 |
| $W_f$ | m | AOI dimension that is perpendicular to the groundwater flow | 4,715 |
| WFF aquifer water flux | m³/yr | Water flow rate due to percolation (groundwater recharge) | 2,165,957 |
| WFF aquifer mass flux | g/yr | MC mass flux versus time due to percolation from the vadose zone to the aquifer | Time-varying |
| Composition | | | |
| WZ-SAND | Percent | Percentage of sand | 63.8 |
| WZ-SILT | Percent | Percentage of silt | 25 |
| WZ-CLAY | Percent | Percentage of clay | 10 |
| WZ-OMC | Percent | Percentage of organic matter | 1.2 |
| WZ-IRON | Percent | Percentage of iron and aluminum | Unknown, set to 0 |
| Characteristics | | | |
| WZ-FRAC | Percent | Percentage of constituent flux entering the aquifer | 100 |
| WZ-PH | Dimensionless | pH of the pore water | 5.5 |
| $\phi$, WZ-TOTPOR | Percent | Total porosity | 44.2 |
| $\phi_e$, WZ-EFFPOR | Percent | Effective porosity | 41 |
| $V_d$, WZ-PVELOC | cm/day | Darcy velocity | 3.73 |
| $Z_A$, WZ-THICK | m | Thickness of aquifer | 15.2 |
| $\rho_b$, WZ-BULKD | g/cm³ | Soil dry bulk density | 1.48 |
| Concentration Locations | | | |
| x, WZ-DIST | m | Longitudinal distance to well | 4,000 |
| y, WZ-YDIST | m | Perpendicular distance from plume center-line to well | 0 |
| z, WZ-AQDEPTH | cm | Vertical distance below water table to well intake | 0 |
| $\alpha_x$, WZ-LDISP | m | Longitudinal dispersivity | 400 |
| $\alpha_y$, WZ-TDISP | m | Transverse dispersivity | 132 |
| $\alpha_z$, WZ-VDISP | m | Vertical dispersivity | 1 |

| Parameter | Units | Description | Value |
|---|---|---|---|
| Constituent Properties | | | |
| $K_d$, WA-SUBKD | ml/g | Sorption partitioning coefficient | RDX: 0.13<br>TNT: 0.31<br>Lead: 597<br>Copper: 92<br>$KClO_4$: 4E-10 |
| $C_s$, WZ-RSOL | mg/L | Water solubility | RDX: 59.8<br>TNT: 130<br>Lead: 2.24<br>Copper: 0.5<br>$KClO_4$: 20,800 |
| $T_{1/2}$, WZ-GHALF | days | Half-life of constituent in groundwater | 1.0E20 for all constituents |

Table 6. Tier 2 RECOVERY surface water model input values.

| Parameter | Units | Description | Value |
|---|---|---|---|
| Inputs Passed from Soil Model or Plus-SG Operator | | | |
| WFF (surface water) water flux | m³/yr | Water flow rate from AOI soil runoff and groundwater discharge to surface water, which are combined via the Plus-SG Operator | 3,297,427 (this value is for AOI runoff) |
| WFF (surface water) mass flux | g/yr | Combined mass fluxes exported from AOI soil due to rainfall ejected pore water runoff ($F_r$), soil erosion ($F_e$), and solid phase particle erosion ($F_{es}$) and can also include groundwater mass flux due to groundwater discharge to surface water. Particulate and dissolved fluxes are included in the Surface Water WFF, where the dissolved fluxes include surface runoff (including interflow) and aquifer dissolved fluxes, which are combined by the Plus-SG Operator. The RECOVERY model combines particulate and dissolved fluxes into a total mass loading for model calculations. | Time-varying |
| Surface Water Morphometry and Hydrology | | | |
| $S_w$ | mg/L | Total suspended solids concentration in the water column | 100 |
| $f_{oc}$ water | Fraction | Weight fraction carbon in solids in water column | 0.01 |
| $A_w$ | m² | Long-term average water surface area | 75,000 |
| Water depth, $H_w$ | m | Long-term average of surface water mean depth | 1.0 |
| Q | m³/yr | Average annual water flow through rate | 47,304,000 |

| Parameter | Units | Description | Value |
|---|---|---|---|
| Residence time, $\tau_w$ | Yr | Surface water residence time (computed) | 0.00158 |
| **Mixed Sediment Layer** | | | |
| L | m | Contaminated sediment depth or total sediment bed depth to be modeled | 1.0 |
| z | m | Depth of mixed sediment layer | 0.07 |
| $A_m$ | $m^2$ | Mixed sediment layer surface area | 75,000 |
| $\phi_m$ | Fraction | Mixed sediment layer porosity | 0.7 |
| $\rho_p$ mixed layer | $g/cm^3$ | Mixed sediment particle density or specific gravity | 2.65 |
| $f_{oc}$ mixed layer | Fraction | Mixed sediment layer weight fraction carbon in solids | 0.01 |
| **Deep Sediment Layers** | | | |
| $\phi_s$ | Fraction | Deep sediment porosity | 0.5 |
| $\rho_p$ deep sediment | $g/cm^3$ | Deep sediment particle density or specific gravity | 2.65 |
| $f_{oc}$ deep sediment | Fraction | Deep sediment layer weight fraction carbon in solids | 0.01 |
| **System Properties** | | | |
| $U_w$ | m/sec | Mean wind speed | 6 |
| Diffusion enhanced | $cm^2/sec$ | Enhanced diffusion between mixed sediment layer and deep sediment | 0 |
| Enhanced mixing depth | cm | Enhanced mixing depth between mixed sediment layer and deep sediment | 0 |
| $v_s$ | m/yr | Suspended solids settling velocity | 36 |
| $v_b$ | m/yr | Deep sediment burial velocity (computed) | 4.53E-3 |
| $v_r$ | m/yr | Mixed layer sediment resuspension velocity | 1.0E-20 |
| **Constituent Properties** | | | |
| $c_{w0}$ | µg/L | Initial contaminant concentration of constituent in water | 0 |
| W | kg/yr | Additional constant external loading rate of constituent | 0 |
| $c_{m0}$ | mg/kg | Initial contaminant concentration in mixed sediment | 0 |
| $c_{s0}$ | mg/kg | Initial contaminant concentration in deep sediment | 0 |
| $D_m$ | $cm^2/sec$ | Molecular diffusivity | RDX: 7.1E-6 TNT: 6.36E-6 Lead: 9.45E-6 Copper: 7.33E-6 $KClO_4$: 6.0E-6 |

| Parameter | Units | Description | Value |
|---|---|---|---|
| $H_e$ | atm-m$^3$/g-mole | Henry's Law Constant | RDX: 6.31E-8<br>TNT: 4.57E-7<br>Lead: 0<br>Copper: 0<br>KClO$_4$: 0 |
| MW | g-mole | Molecular weight | RDX: 222.12<br>TNT: 227.13<br>Lead: 207.2<br>Copper: 63.55<br>KClO$_4$: 138.55 |
| $K_{ow}$ | (mg/m$^3$ octanol)/ (mg/m$^3$ water) | Octanol-water partition coefficient | RDX: 7.41<br>TNT: 39.8<br>Lead: NA<br>Copper: NA<br>KClO$_4$: 6.6E-8 |
| $K_{dw}$ | L/kg | Partition coefficient for the water column for inorganic constituents | Lead: 4,000<br>Copper: 600 |
| $K_{dm}$ | L/kg | Partition coefficient for the mixed sediment pore water for inorganic constituents | Lead: 4,000<br>Copper: 600 |
| $K_{ds}$ | L/kg | Partition coefficient for the deep sediment pore water for inorganic constituents | Lead: 4,000<br>Copper: 600 |
| $k_w$ dissolved | 1/yr | Decay coefficient for dissolved contaminant in water | 0 for all constituents |
| $k_m$ dissolved | 1/yr | Decay coefficient for dissolved contaminant in mixed layer | 0 for all constituents |
| $k_s$ dissolved | 1/yr | Decay coefficient for dissolved contaminant in deep sediment | 0 for all constituents |
| $k_w$ particulate | 1/yr | Decay coefficient for particulate contaminant in water | 0 for all constituents |
| $k_m$ particulate | 1/yr | Decay coefficient for particulate contaminant in mixed layer | 0 for all constituents |
| $k_s$ particulate | 1/yr | Decay coefficient for particulate contaminant in deep sediment | 0 for all constituents |
| **Model Control Parameters** | | | |
| T | years | Total period of simulation | 100 |
| N print 1 | Dimensionless | Number of time steps between print intervals for output | 40 |
| N print 2 | Dimensionless | Number of time steps between print intervals for sediment layer output | 20 |
| N layers print | Dimensionless | Number of sediment layers to print in output | 50 |

The simulation times for the soil and surface water models are set within the model user interface (UI) along with other inputs (see Tables 3 and 6). Neither the MEPAS vadose zone nor aquifer models require the time step or the total simulation time as input. The simulation time length is determined within the models to ensure that nearly all of the contamination has moved through the vadose zone and aquifer. The maximum time period allowed for any simulation with the MEPAS vadose and aquifer models is 10,000 years. However, the user can restrict the length of simulation to a user-specified value by clicking 'Options → Advanced' on the menu bar of each model's UI. Both models divide the total simulation time into 40 intervals (or time steps) for computing and saving output variables. These MEPAS models may be modified in the future to increase the number of computation intervals above 40.

For most of the simulations discussed in the next two chapters, the soil and surface water models were run for 100 years, although several simulations were run longer to more fully capture transient features. The groundwater models ran much longer, usually several thousand years or longer, since the groundwater response is very slow for this application, especially for metals. For these reasons, the plots of aquifer concentrations versus time presented in the next two chapters extend over several thousand years.

# 5    Model Results for Baseline Conditions

The Tier 1 soil, aquifer, and surface water/sediment models were re-applied using the input variables and parameters discussed in the previous chapter with one exception. The exception was that the solubility of lead and copper was set to 15 mg/L in all models to avoid exceeding solubility limits. The Tier 1 application was updated to develop a more valid baseline condition for comparing the Tier 2 model results. Various inputs were improved between the time that the Tier 1 POC application was conducted (Dortch et al. 2010) and the Tier 2 POC application presented herein. The results of the updated Tier 1 POC application are presented first, followed by the Tier 2 baseline POC application with inputs consistent with those presented in the previous chapter and the updated Tier 1 POC application.

## Updated Tier 1 POC application

The results of the updated Tier 1 POC application using inputs consistent with those present in Chapter 4 of this report are presented below. The TREECS input file for this application is T1APH_NS.trp, where T1 stands for Tier 1, APH stands for AP Hill, and NS stands for non-spatial. Thus, this Tier 1 application did not use spatially explicit data to estimate input parameters; the *Point* option for HGCT was used. The same is true for the baseline Tier 2 POC application.

### Soil

The soil concentrations and the export fluxes computed by the Tier 1 soil model for the updated Tier 1 POC application are presented in Table 7. Since the Tier 1 soil model is a steady-state model, these concentrations and fluxes do not change in time. For Tier 1, the soil concentrations are assumed to be all in the non-solid, aqueous phase (dissolved and adsorbed to soil) since steady state is assumed without dissolution and system losses (such as degradation and volatilization). It is recognized that the soil concentrations are uncharacteristically high for the aqueous phase, especially for the metals, due to the steady-state assumption that ignores dissolution time (i.e., instantaneous and complete dissolution is assumed).

Table 7. Computed soil concentrations and export fluxes for updated Tier 1 POC application to
Fort A.P. Hill.

| Constituent | Soil concentration, mg/kg | Erosion flux, g/yr | Rainfall ejected runoff flux, g/yr | Combined erosion and runoff, g/yr | Leaching flux, g/yr |
|---|---|---|---|---|---|
| RDX | 1.38E-3 | 4.9 | 3.22E3 | 3.22E3 | 1.20E4 |
| TNT | 8.89E-3 | 31.3 | 1.54E4 | 1.54E4 | 4.53E4 |
| Lead | 5,460 | 1.92E7 | 1.09E7 | 3.01E7 | 1.98E7 |
| Copper | 752 | 2.64E6 | 9.65E6 | 1.23E7 | 1.76E7 |
| $KClO_4$ | 3.44E-6 | 0.01 | 10.8 | 10.81 | 63 |

The fluxes for the updated Tier 1 POC results are fairly similar to those of
the previously reported Tier 1 POC results (Dortch et al. 2010) for RDX,
TNT, and perchlorate since the soil partitioning coefficients are relatively
low for these MCs. However, the results for lead and copper are quite
different due to the much higher soil partitioning of these two MCs com-
pared with the other three MCs. For example, the updated erosion flux for
lead decreased by 58 percent as a portion of total export fluxes while the
combined fluxes for rainfall ejected runoff and leaching increased by the
same amount. The soil concentration for lead increased by a factor of 14.8.
The primary reason for these changes is that the erosion rate decreased by a
factor of 37 for the updated Tier 1 POC modeling compared to the original
Tier 1 POC results (Dortch et al. 2010).

An important aspect of the Tier 1 model is that by assuming steady state,
the model does not consider the time required for weathering and
dissolution. At steady state, or at infinite time with constant loading and
input parameters, all solid phase loading is available in the aqueous phase.
This assumption provides a worst case condition that yields export fluxes
that can be greater than reality, especially for metals that can have slow
weathering and dissolution rates. The steady-state assumption is not as
unreasonable for the HE constituents, since they have much higher
dissolution rates than metals, and their solubility is less dependent on
ambient soil chemistry. The Tier 2 POC results are quite different from the
updated Tier 1 POC results as will be discussed later in this chapter.

**Aquifer**

The MEPAS aquifer model was applied using the leaching export flux
computed from the soil model. The aquifer MC concentrations versus time

at the receptor well are shown in Figures 2 through 6, along with the protective human health benchmarks. The plots of aquifer MC concentrations versus time are more pointedly shaped than the previous Tier 1 POC results due to the lower Darcy velocity used for the updated Tier 1 POC modeling. The computed peak aquifer concentrations are shown in Table 8 along with the benchmarks. The human health protective benchmark is exceeded for all MCs except perchlorate.

**Surface water and sediment**

The RECOVERY surface water and sediment model was applied using the runoff and erosion export fluxes computed from the soil model. The updated Tier 1 POC computed sediment concentrations versus time for the receptor water body (White Lake) are plotted for each of the five MCs in Figures 7 through 11, along with the protective ecological health benchmarks. The peak MC sediment concentrations are shown in Table 9, along with the benchmarks. There is presently no sediment benchmark for perchlorate. The sediment protective health benchmarks for RDX and TNT shown in Table 9 were obtained for a sediment organic carbon of 2%. Lead and copper are the only MCs that exceed the sediment benchmarks.
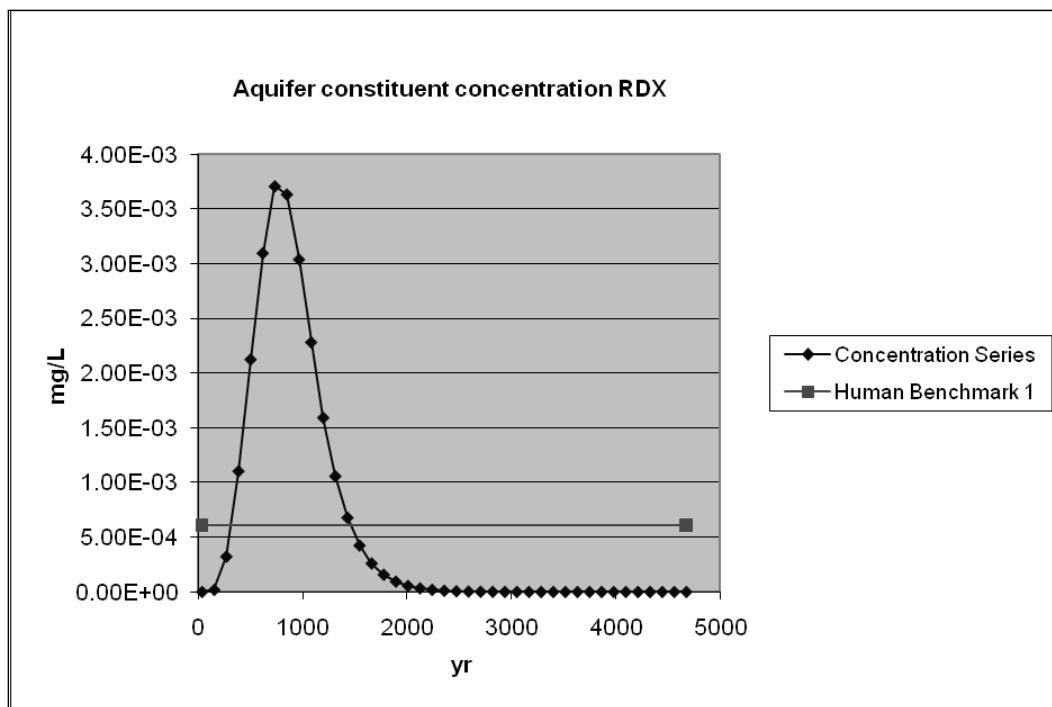


Figure 2. Tier 1 computed RDX concentration versus time in groundwater at the location of the receptor well.
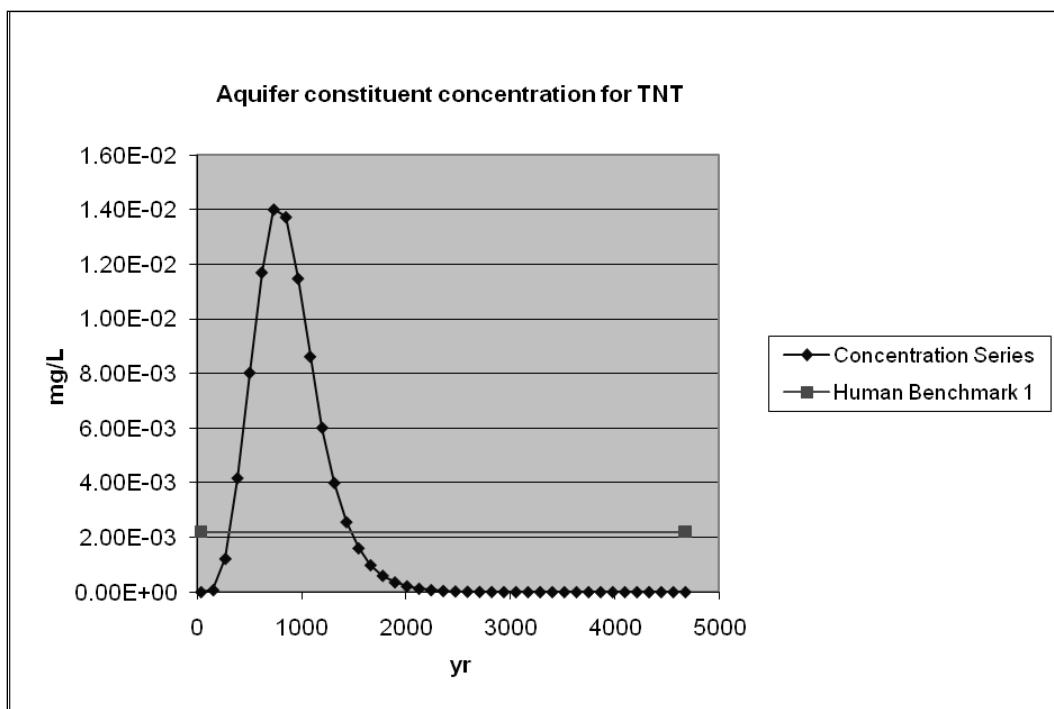
Figure 3. Tier 1 computed TNT concentration versus time in groundwater at the location of the receptor well.
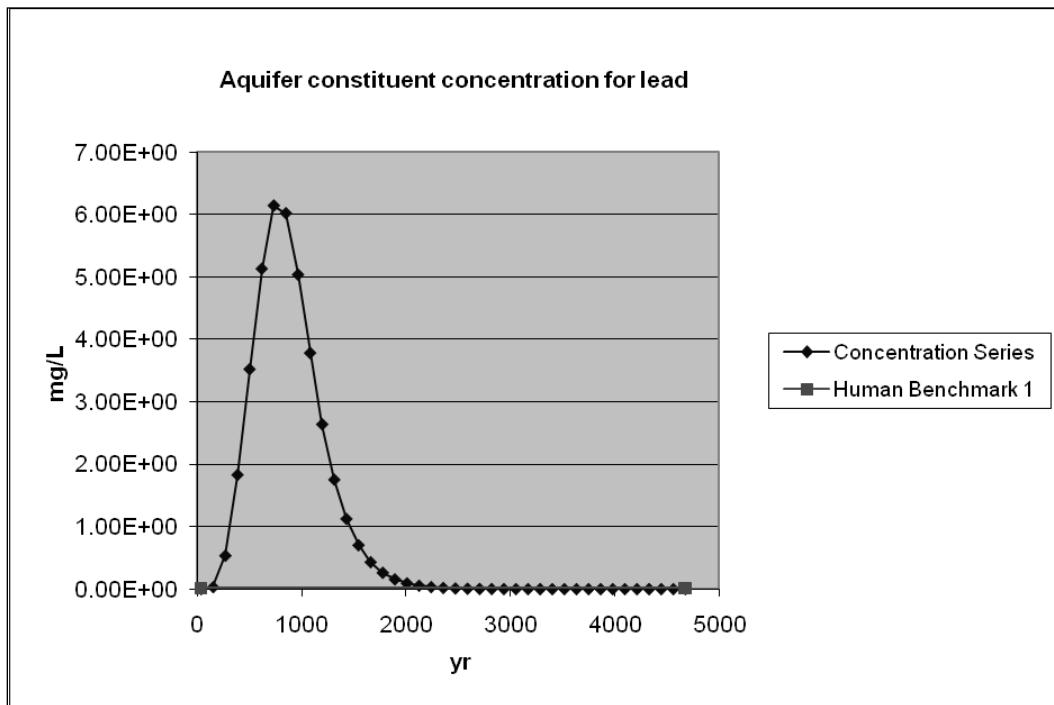


Figure 4. Tier 1 computed lead concentration versus time in groundwater at the location of the receptor well.
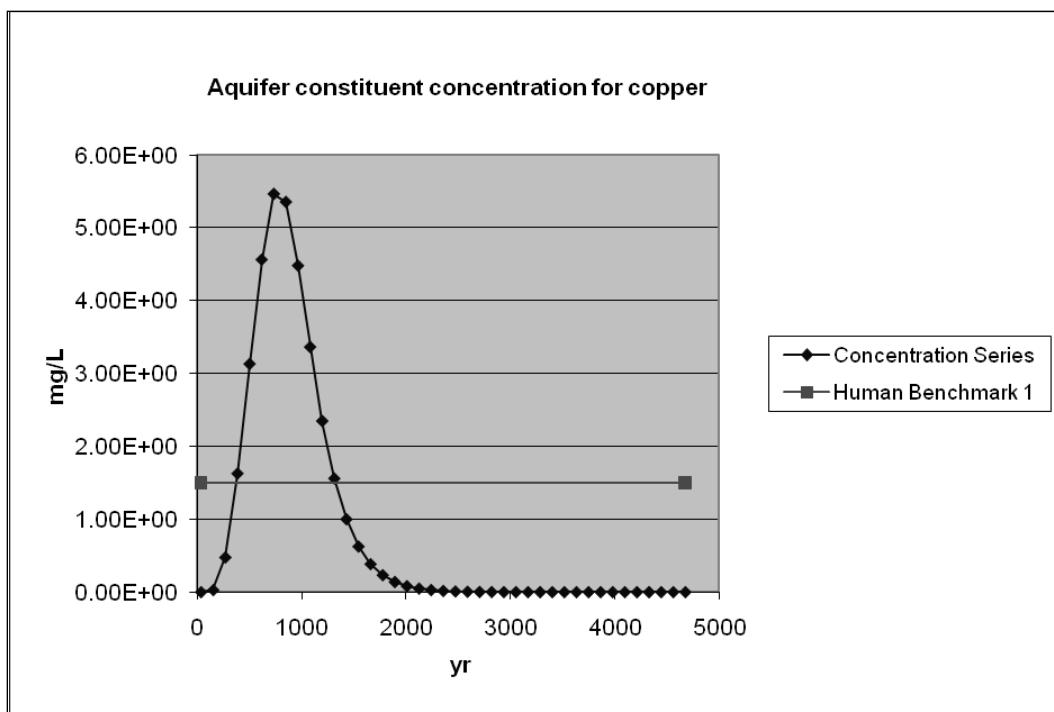
Figure 5. Tier 1 computed copper concentration versus time in groundwater at the location of the receptor well.
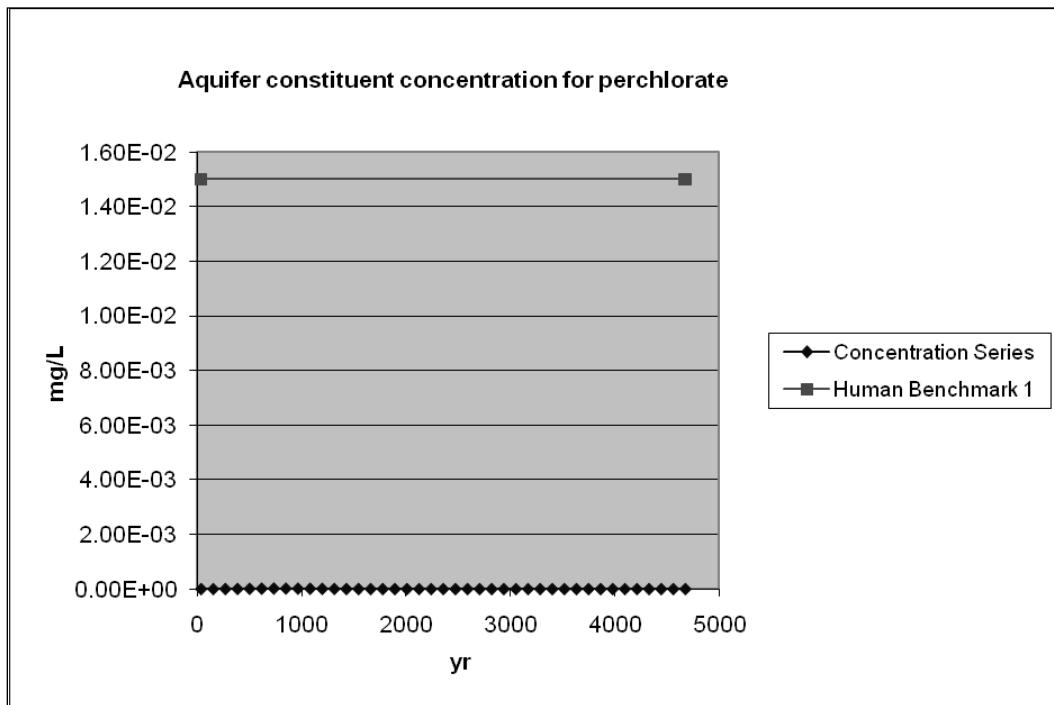


Figure 6. Tier 1 computed $KClO_4$ concentration versus time in groundwater at the location of the receptor well.

Table 8. Tier 1 computed aquifer receptor well peak constituent concentrations and drinking water protective benchmarks.

| Constituent | Aquifer concentration at well, ppb | Protective benchmark, ppb |
|---|---|---|
| RDX | 3.73 | 0.61 |
| TNT | 14.0 | 2.2 |
| Lead | 6,140 | 15 |
| Copper | 5,470 | 1500 |
| $KClO_4$ | 0.019 | 15 |
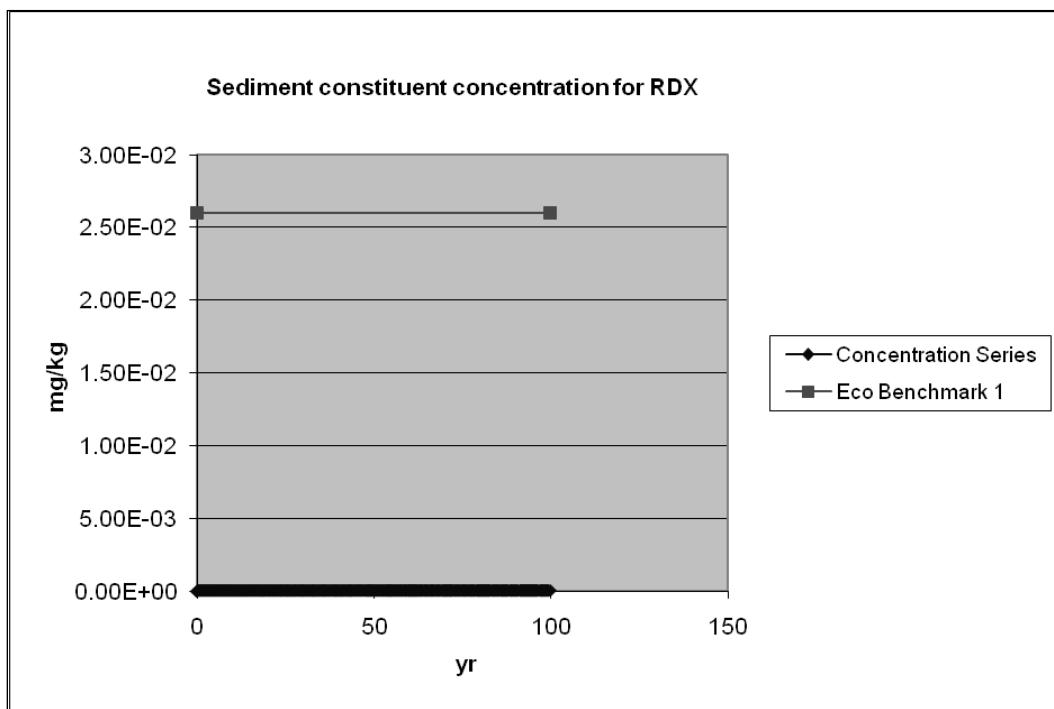


Figure 7. Tier 1 computed sediment total concentration of RDX versus time for White Lake.
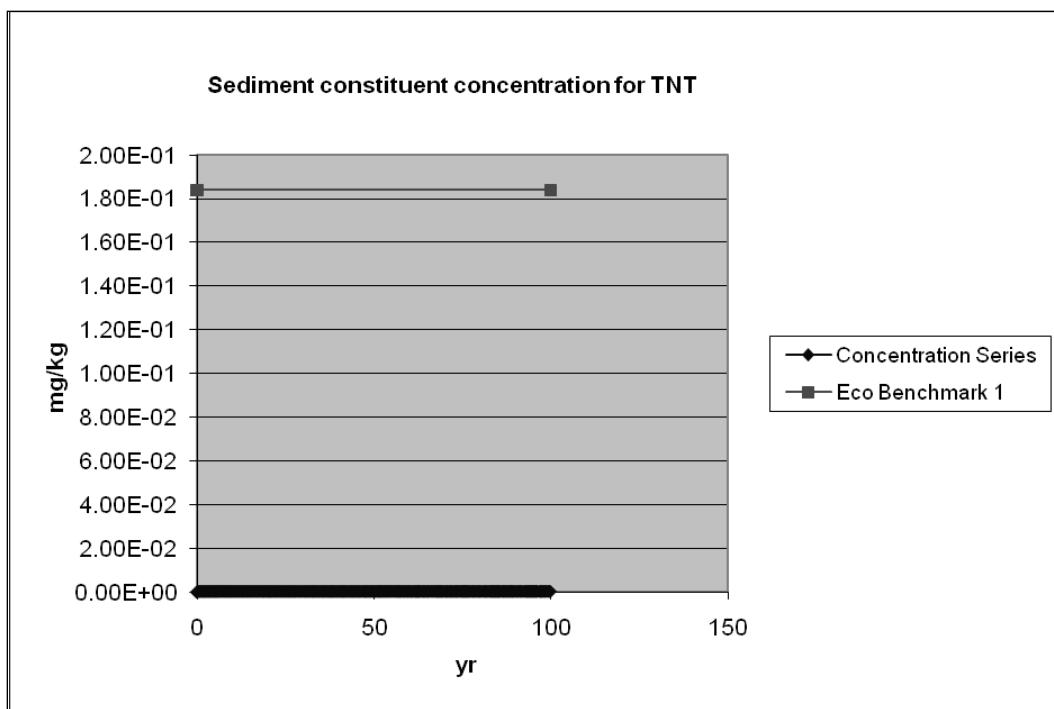
Figure 8. Tier 1 computed sediment total concentration of TNT versus time for White Lake.
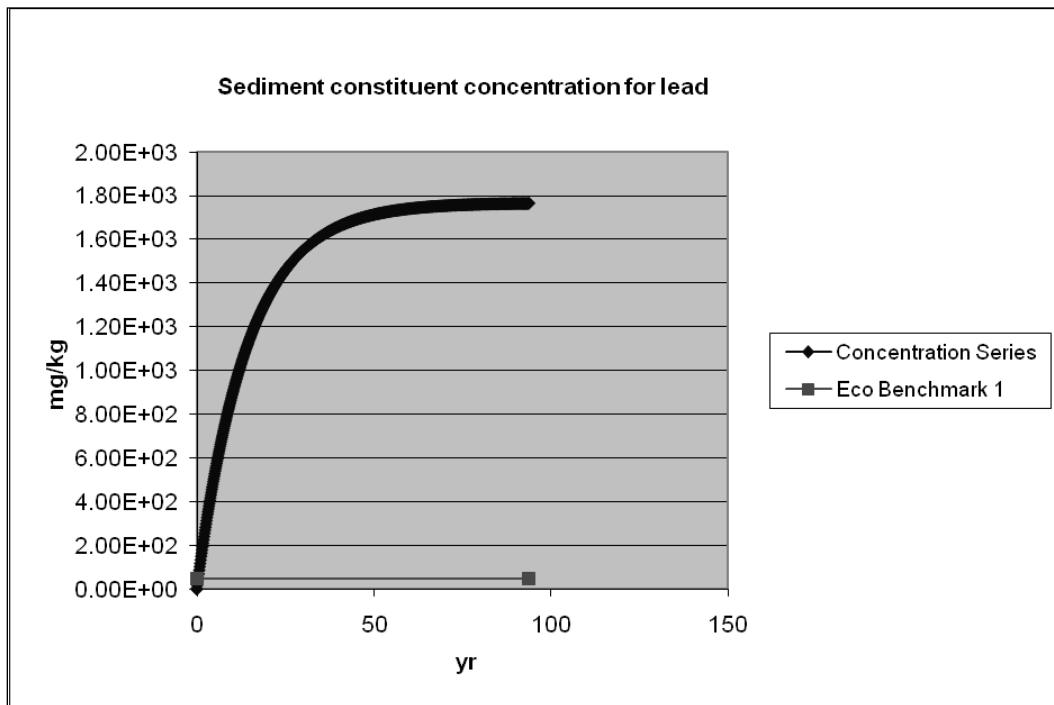


Figure 9. Tier 1 computed sediment total concentration of lead versus time for White Lake.
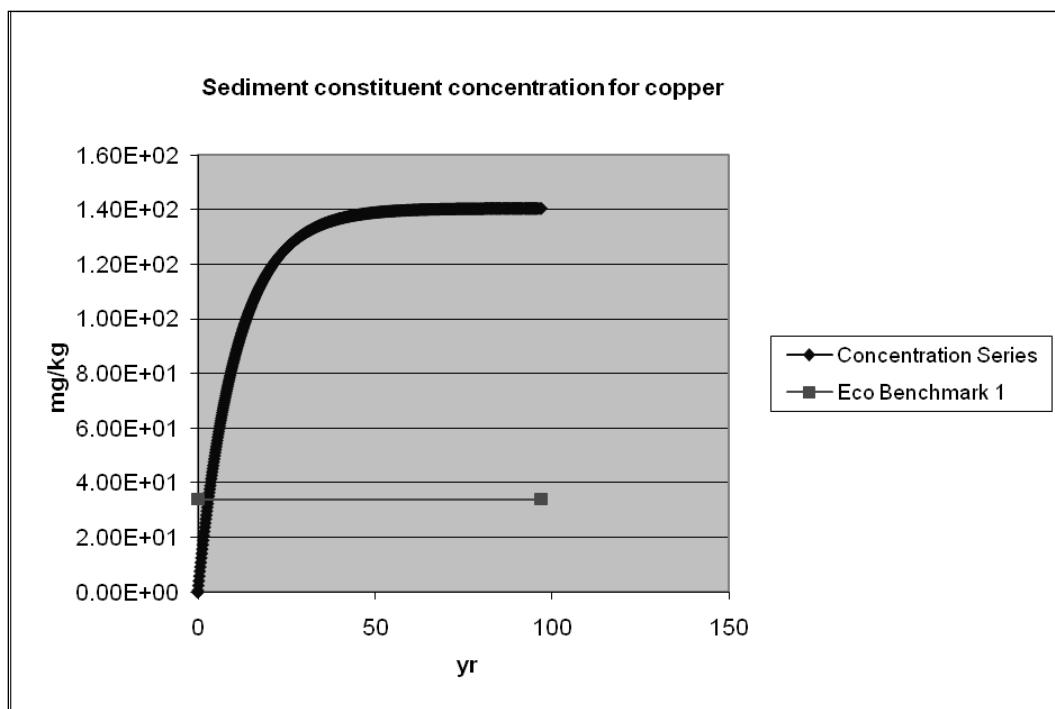
Figure 10. Tier 1 computed sediment total concentration of copper versus time for White Lake.
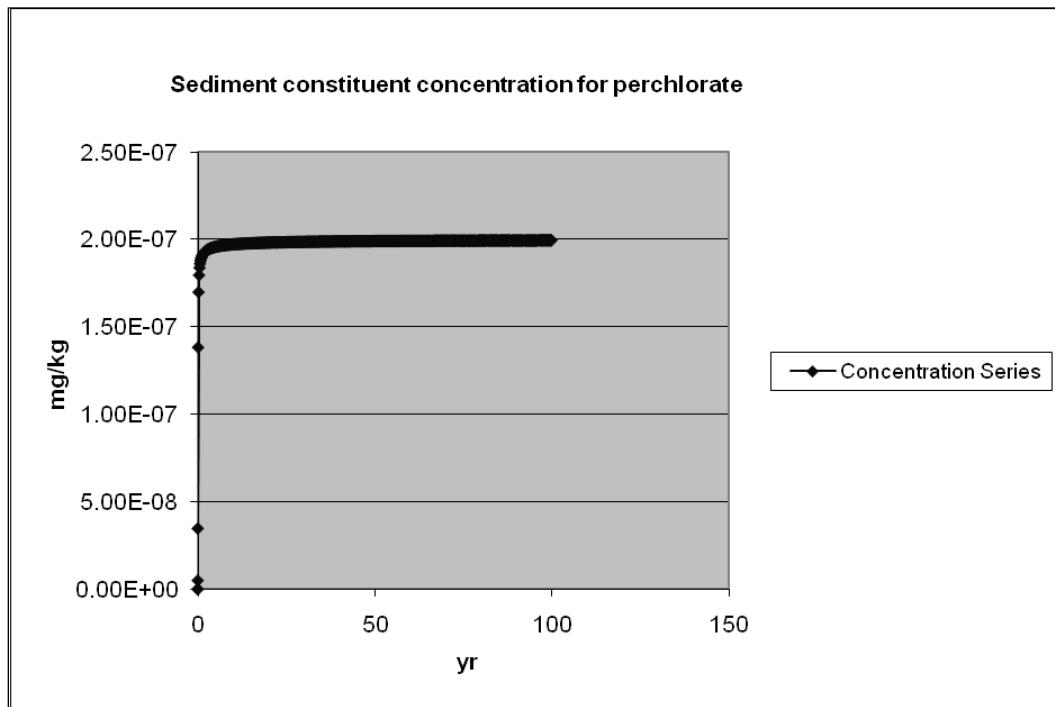


Figure 11. Tier 1 computed sediment total concentration of KClO$_4$ versus time for White Lake.

Table 9. Tier 1 computed White Lake sediment peak MC concentrations and ecologically protective health benchmarks.

| Constituent | Sediment concentration, ppb | Sediment protective benchmark, ppb |
|---|---|---|
| RDX | 0.063 | 26 |
| TNT | 0.36 | 184 |
| Lead | 1,760,000 | 47,000 |
| Copper | 141,000 | 34,000 |
| $KClO_4$ | 2.0E-4 | NA |

The updated Tier 1 POC computed water total concentrations versus time for the receptor water body (White Lake) are plotted for each of the five MC in Figures 12 through 16, along with the protective human health benchmarks. White Lake dissolved water concentrations are plotted in Figures 17 through 21, along with the protective ecological health benchmarks. The peak MC water concentrations are shown in Table 10, along with the benchmarks. Lead is the only MC that exceeds the human health benchmark for surface water. Both lead and copper exceed the surface water ecological benchmarks.
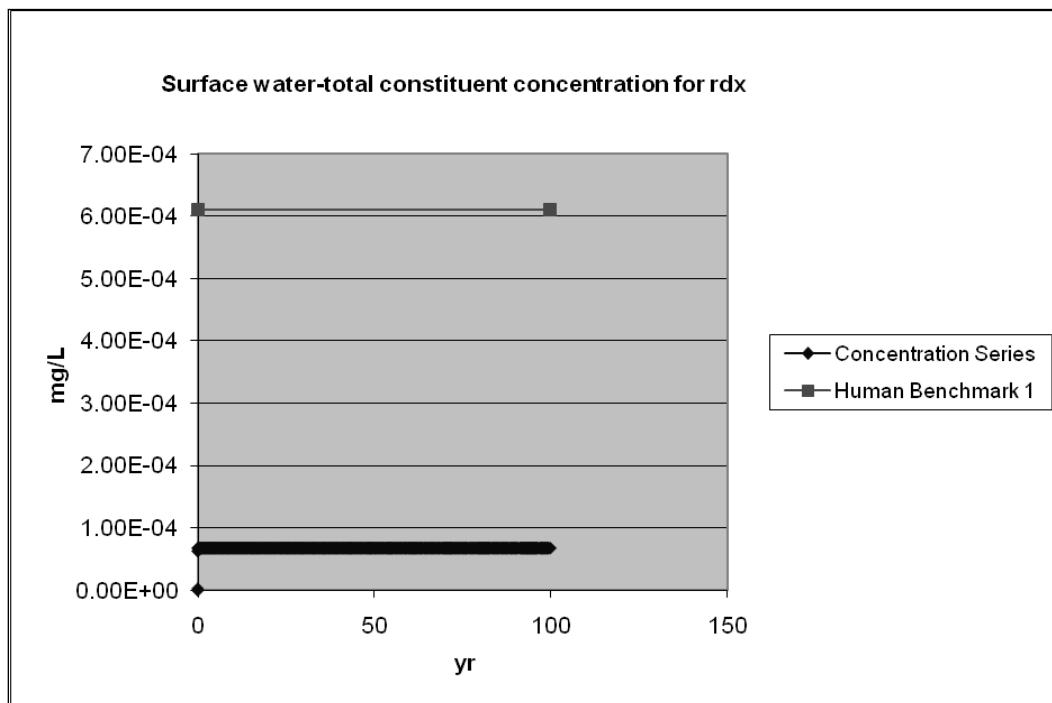


Figure 12. Tier 1 computed water total concentration of RDX versus time for White Lake.
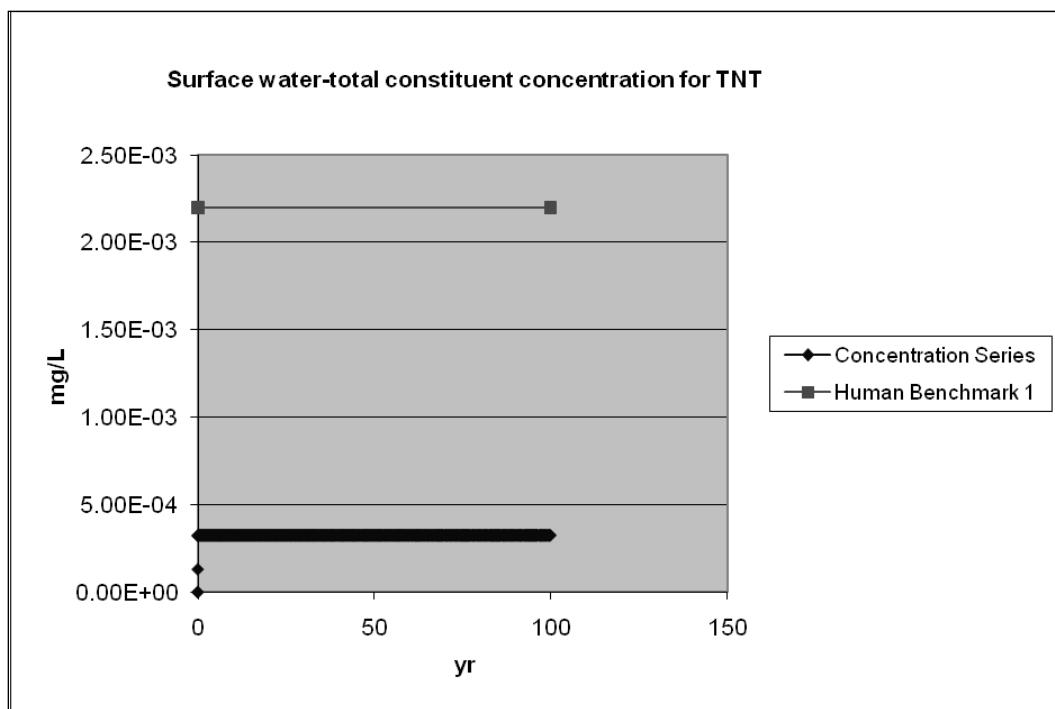
Figure 13. Tier 1 computed water total concentration of TNT versus time for White Lake.
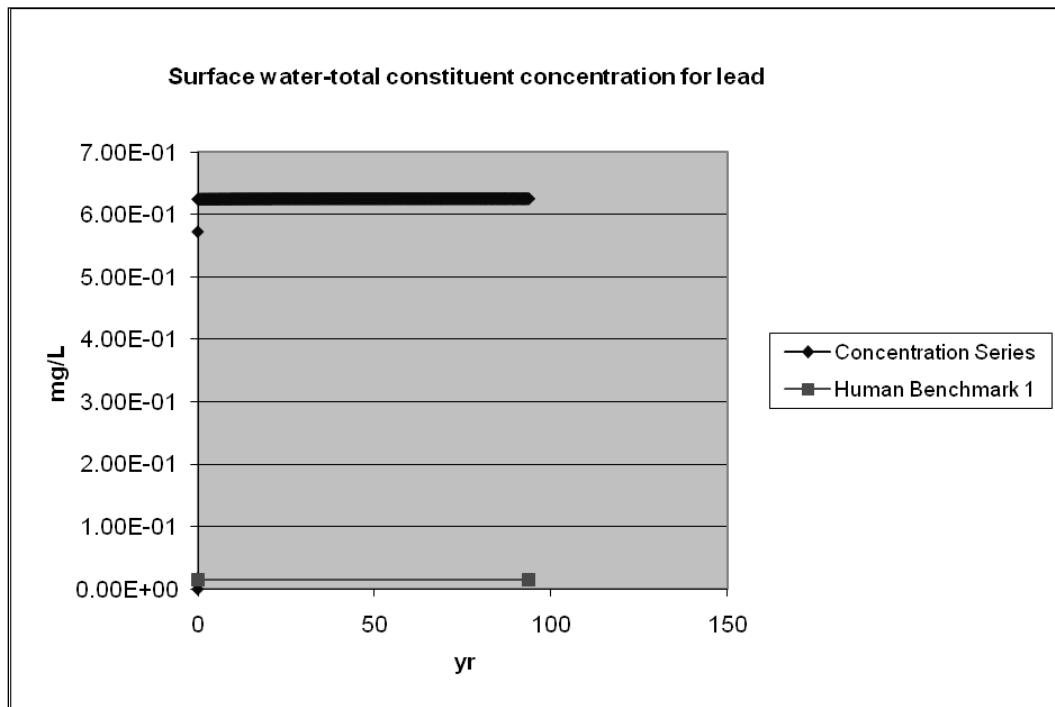


Figure 14. Tier 1 computed water total concentration of lead versus time for White Lake.
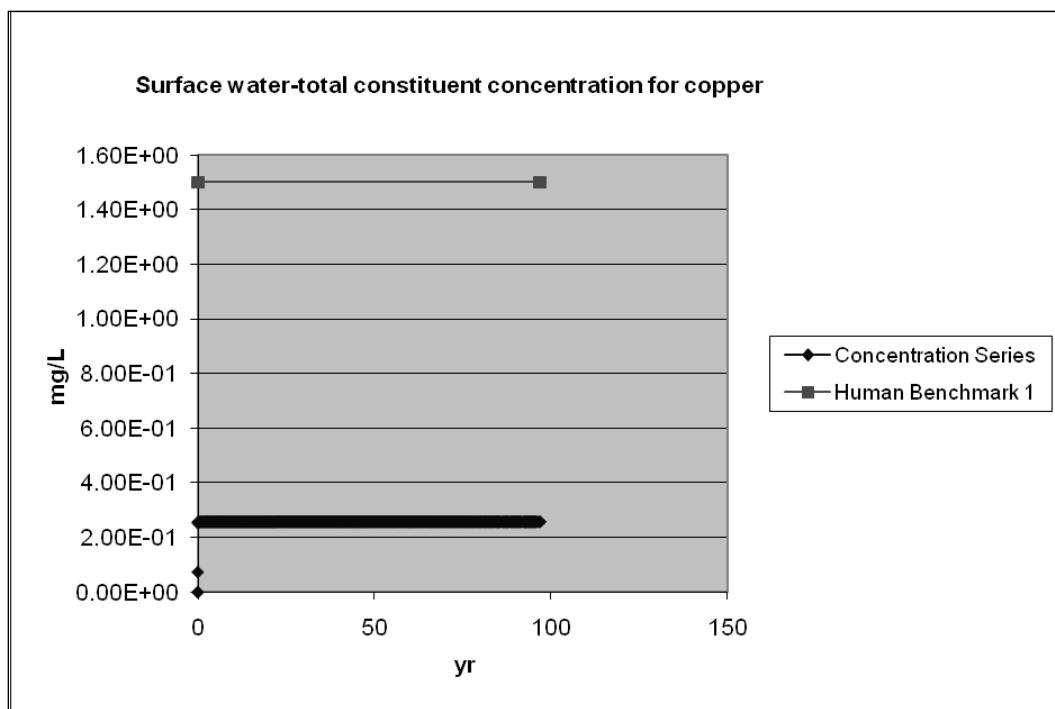
Figure 15. Tier 1 computed water total concentration of copper versus time for White Lake.
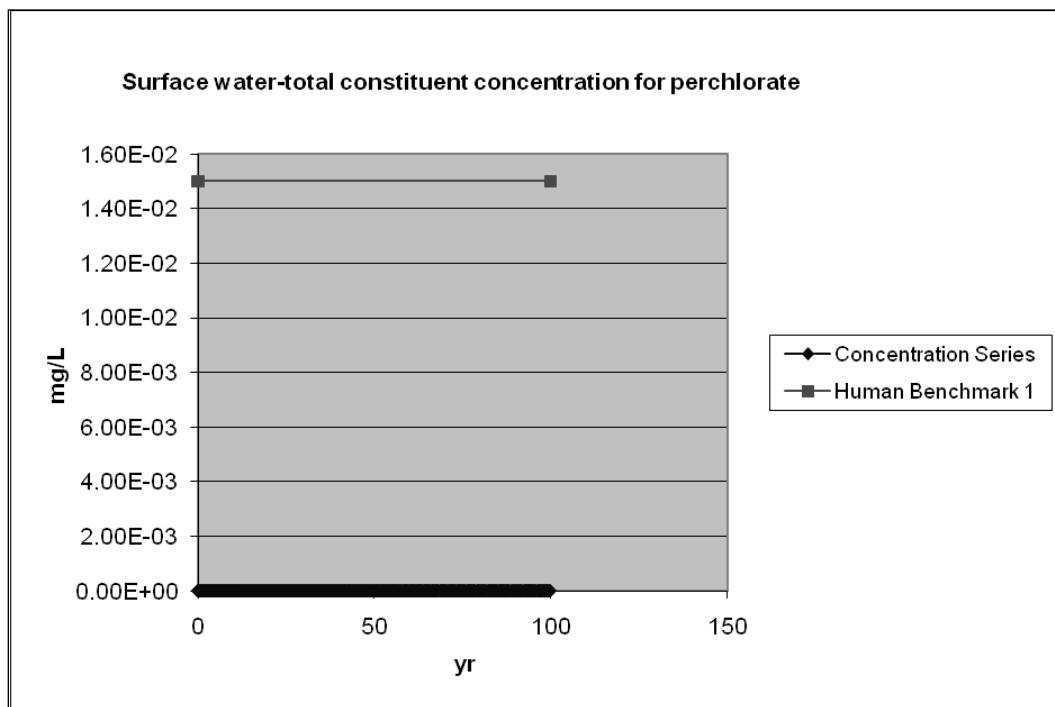


Figure 16. Tier 1 computed water total concentration of KClO₄ versus time for White Lake.

**Surface water-dissolved constituent concentration for RDX**
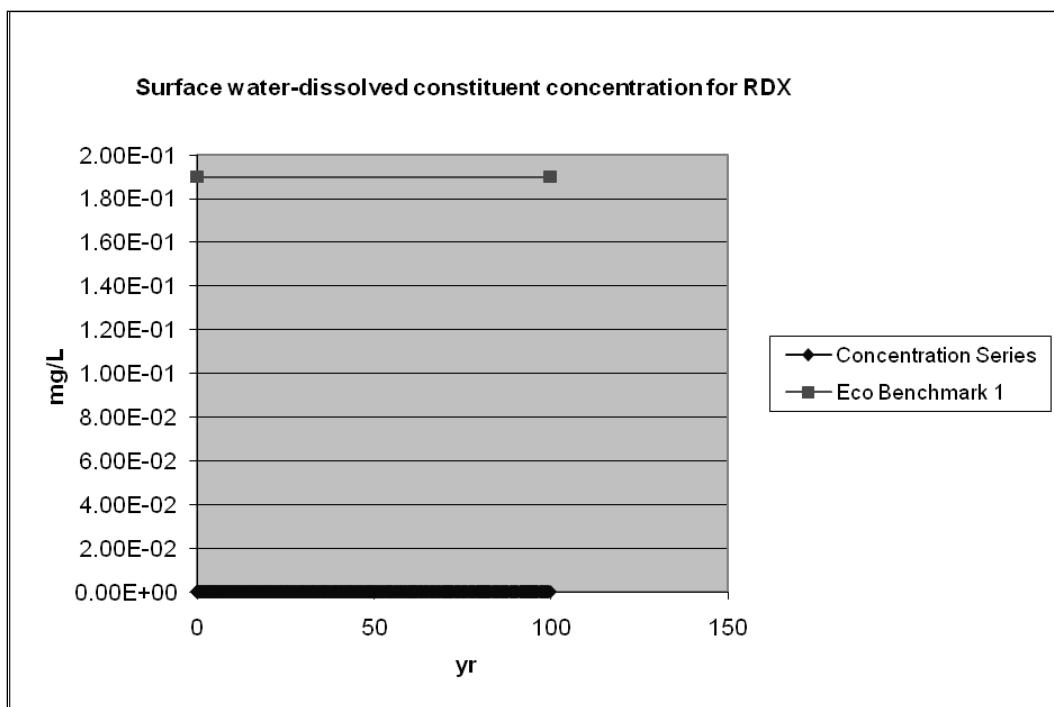
Figure 17. Tier 1 computed water dissolved concentration of RDX versus time for White Lake.

**Surface water-dissolved constituent concentration for TNT**
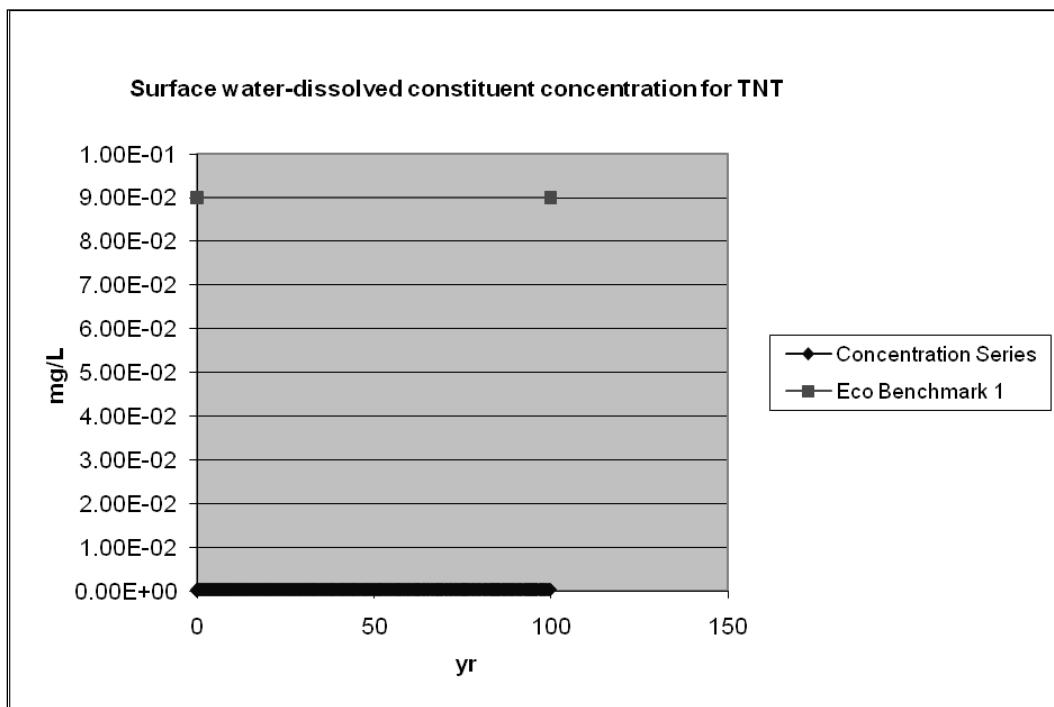
Figure 18. Tier 1 computed water dissolved concentration of TNT versus time for White Lake.
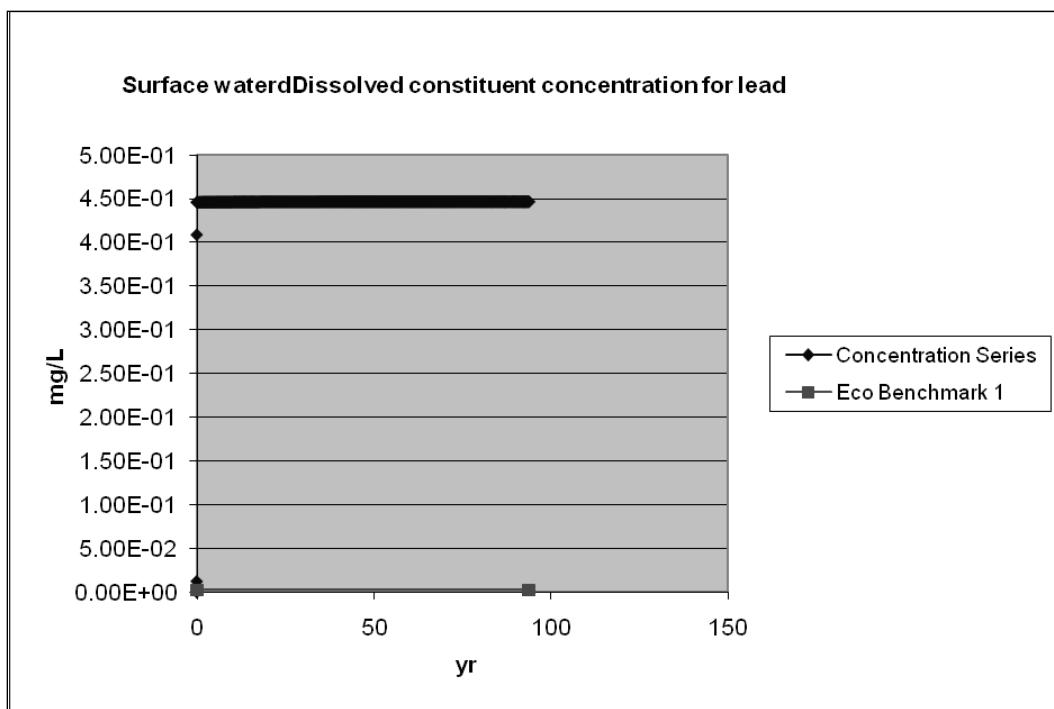
Figure 19. Tier 1 computed water dissolved concentration of lead versus time for White Lake.
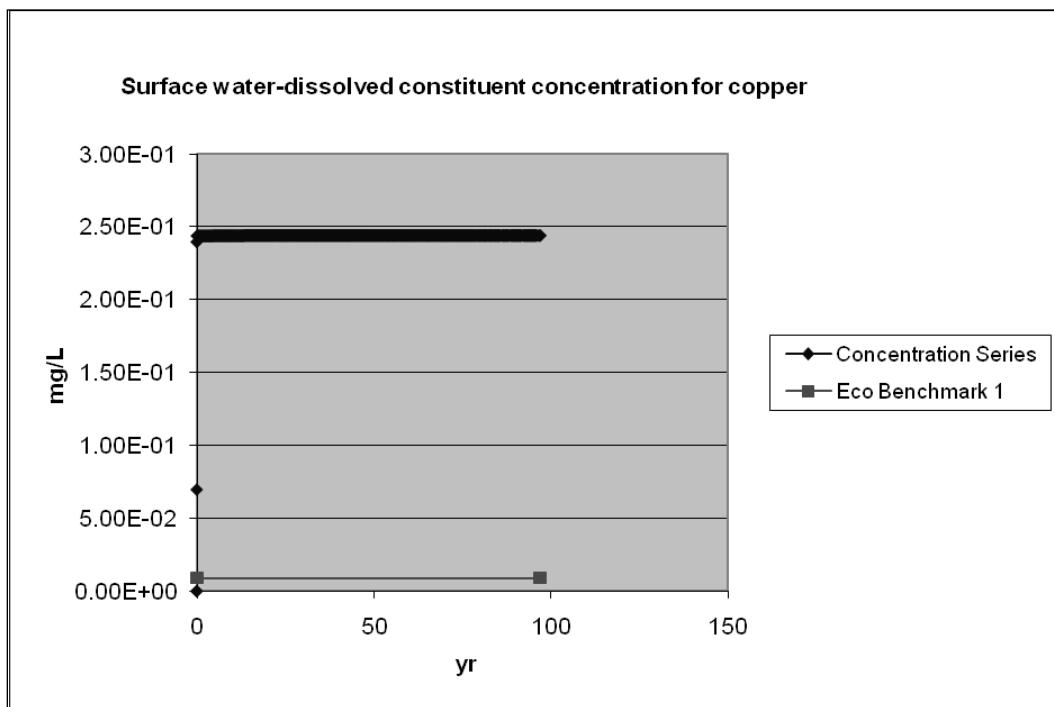


Figure 20. Tier 1 computed water dissolved concentration of copper versus time for White Lake.
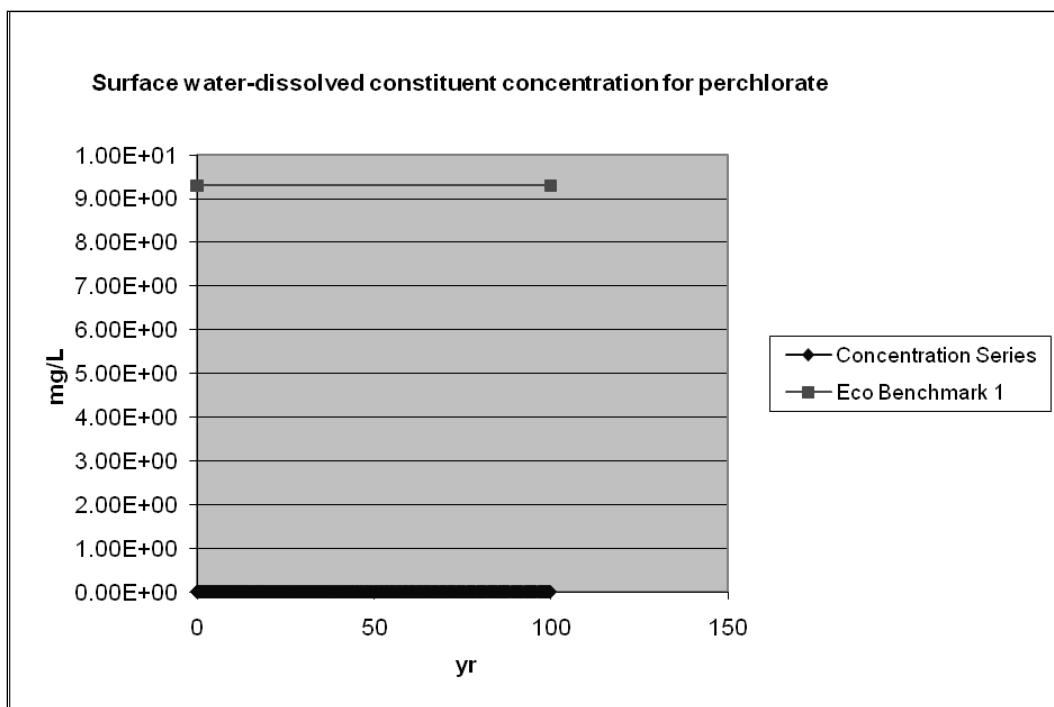
Figure 21. Tier 1 computed water dissolved concentration of $KClO_4$ versus time for White Lake.

Table 10. Tier 1 computed White Lake peak MC concentrations in water and protective human and ecological health benchmarks.

| Constituent | Water peak total concentration, ppb | Water human health protective benchmark, ppb | Water peak dissolved concentration, ppb | Water ecological health protective benchmark, ppb |
|---|---|---|---|---|
| RDX | 0.068 | 0.61 | 0.068 | 190 |
| TNT | 0.32 | 2.2 | 0.32 | 90 |
| Lead | 626 | 15 | 447 | 2.5 |
| Copper | 259 | 1,500 | 244 | 9.0 |
| $KClO_4$ | 2.28E-4 | 15 | 2.28E-4 | 9,300 |

Note: Ecological benchmarks for metals in water are for a hardness of 100 mg/L and were not adjusted for site hardness.

## Tier 2 baseline POC application

The input conditions presented in the previous chapter, which are consistent for the updated Tier 1 POC application, were used to apply the Tier 2 models. The differences between the inputs for the two applications are that more information must be input for Tier 2, and the lower solubility values presented in Chapter 4 were used for lead and copper for the Tier 2

application. The results of this application are referred to as the baseline Tier 2 POC, since they are compared with the updated Tier 1 POC results presented above. Results of this application are presented for soil, aquifer, and surface water/sediments.

**Soil**

The soil MC residue loadings of Table 1 were applied with the Tier 2 soil model for a period of seven years for the baseline conditions. The resulting time-varying soil concentrations for RDX and lead are shown in Figures 22 and 23, respectively. The soil concentrations are total, which includes solid phase mass and particulate, dissolved, and gaseous non-solid phase mass. The time-varying concentrations for TNT and perchlorate look similar to that for RDX except that the peak concentrations are different, and perchlorate reaches a steady peak value much faster, remains at that value longer, and drops off more quickly than do RDX and TNT. The differences in perchlorate response are due to its miscibility and its very low soil partitioning coefficient $K_d$. The plot for copper looks similar to that of lead except for the value of the peak concentration.
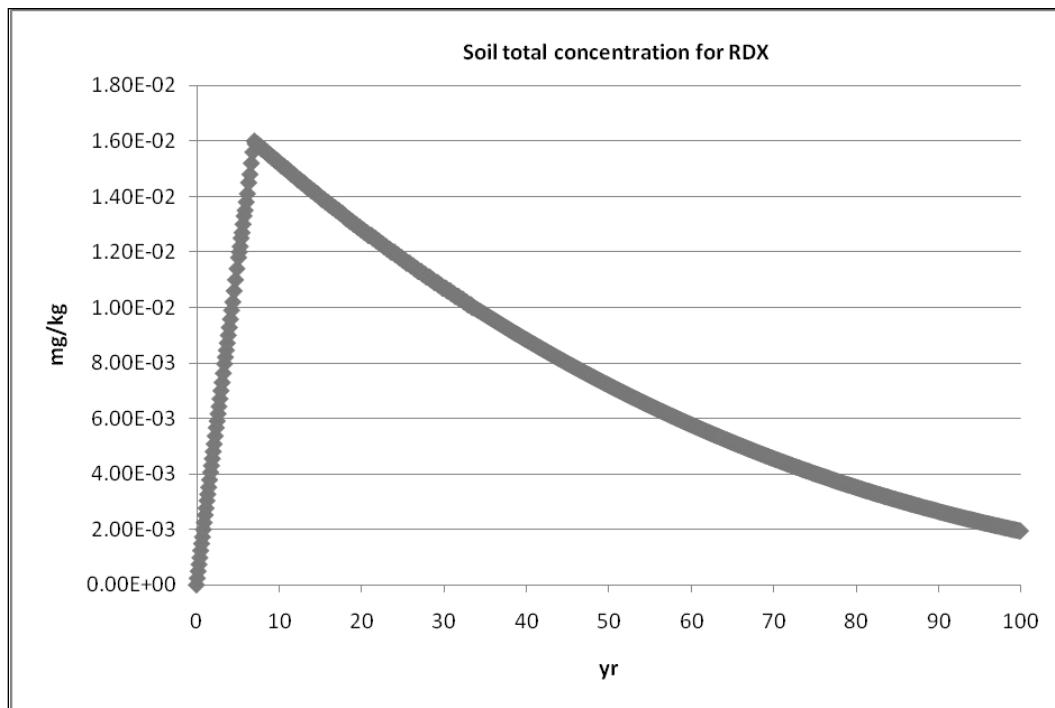


Figure 22. Tier 2 computed soil concentration versus time for RDX using baseline conditions.
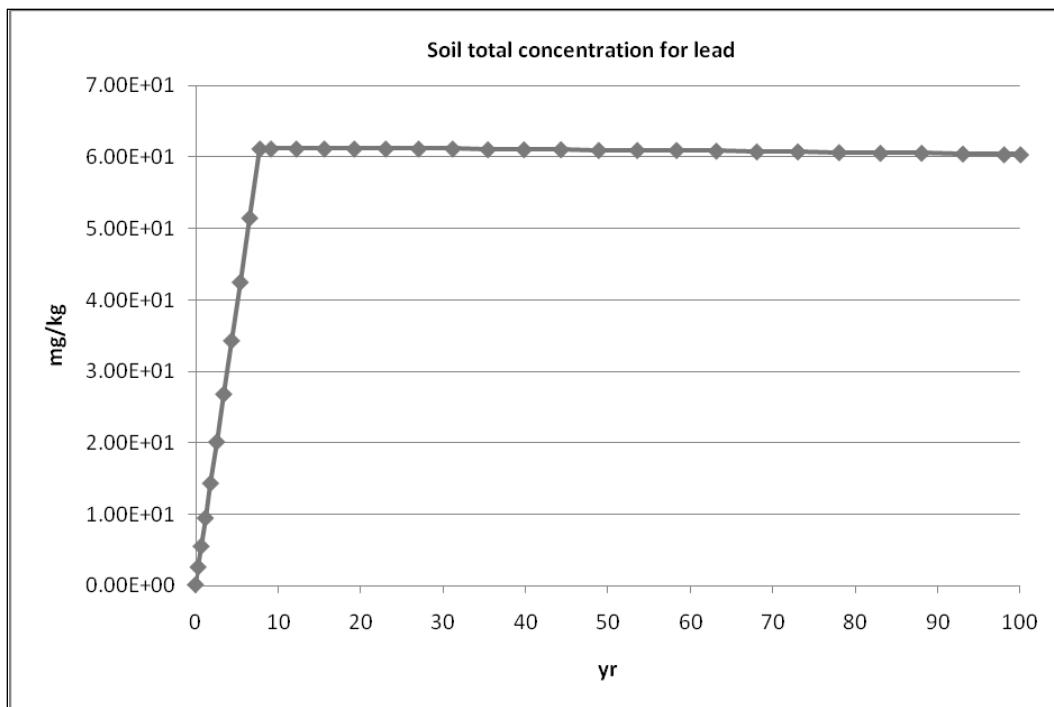
Figure 23. Tier 2 computed soil concentration versus time for lead using baseline conditions.

The plots of time-varying leached mass fluxes exported from soil to the vadose zone for RDX and lead are shown in Figures 24 and 25, respectively. The flux-versus-time plots for the other MCs resemble those for soil concentration, with the exceptions noted previously for perchlorate. Also, the flux plots for the two metals look different than do the soil concentration plots for the metals. The fluxes have not reached a peak and continue to increase at the end of the 100-year simulation. This response is due to the slow dissolution rates and high soil $K_d$ values for the metals.

The time-varying combined runoff and erosion mass fluxes exported from soil to surface water for RDX and lead are shown in Figures 26 and 27, respectively. Like soil concentration and leaching fluxes, the flux versus time plot for TNT and perchlorate resemble that of RDX with the same exceptions previously noted, and the plot for copper resembles the one for lead. The particulate and dissolved mass fluxes from soil to surface water were about the same order of magnitude for the two metals. The dissolved mass flux from soil to surface water was about three orders of magnitude greater than the particulate mass flux for the other three MCs. Erosion of solid phase constituent particle mass was turned off for the baseline conditions.
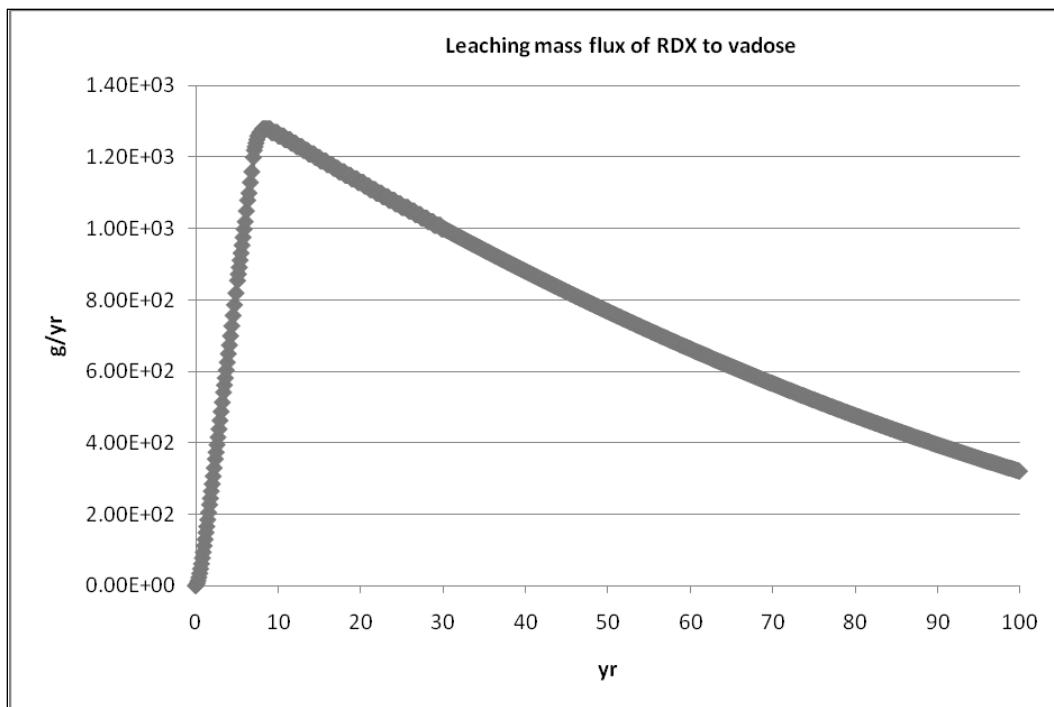
Figure 24. Tier 2 computed soil leaching mass flux of RDX using baseline conditions.
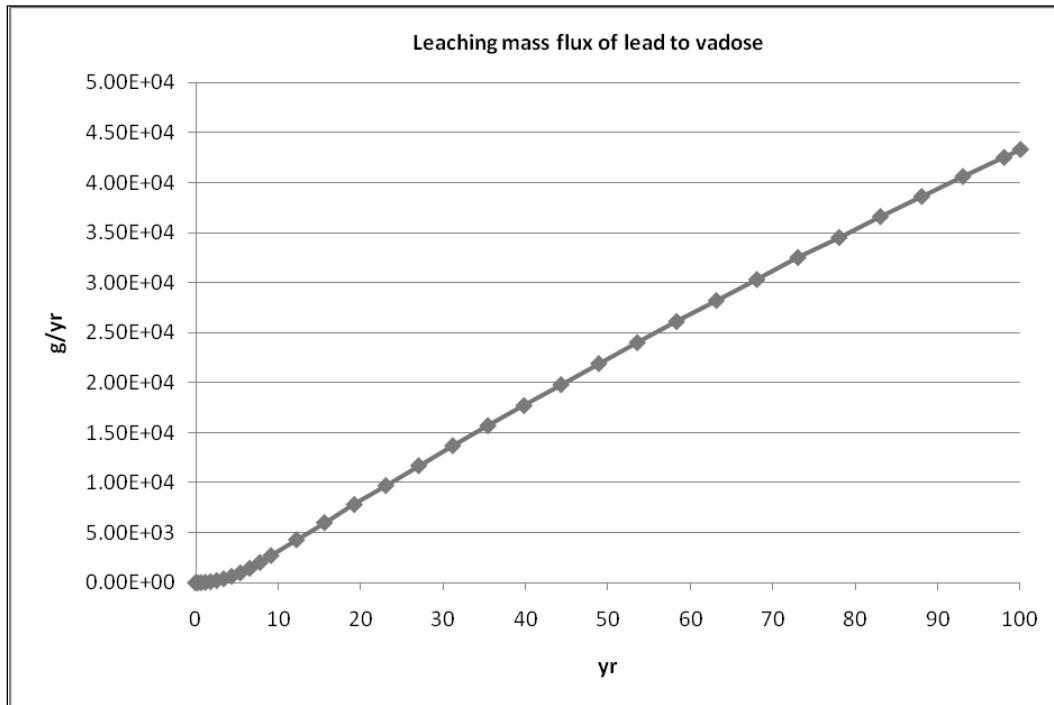


Figure 25. Tier 2 computed soil leaching mass flux of lead using baseline conditions.
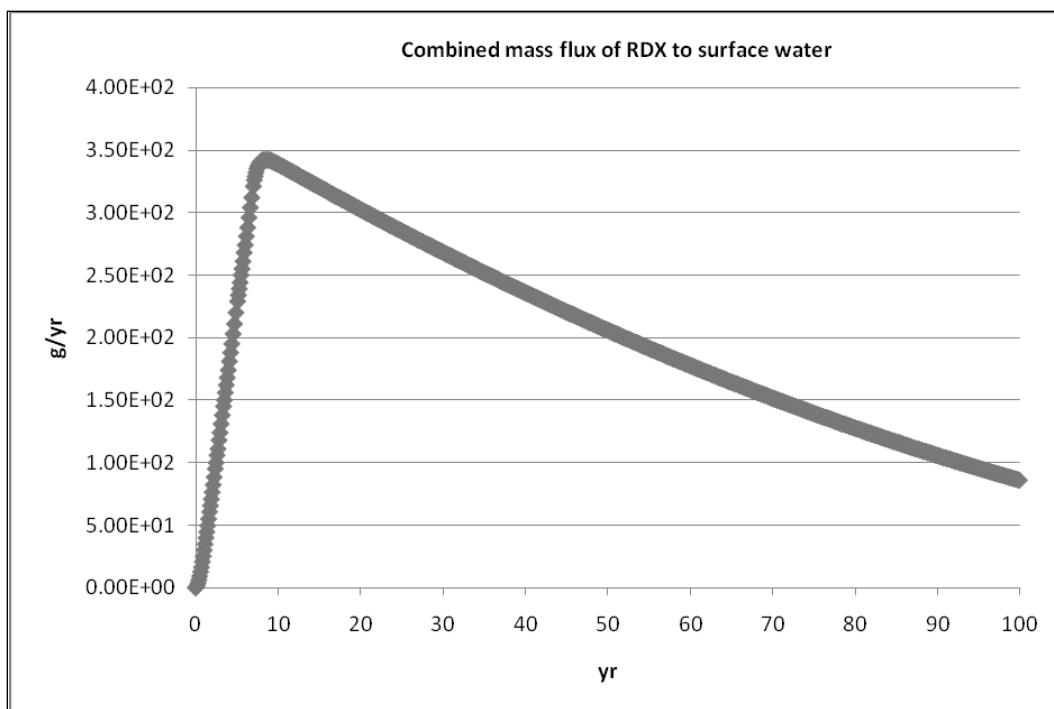
Figure 26. Computed Tier 2 combined runoff and erosion mass flux of RDX from soil to surface water using baseline conditions.
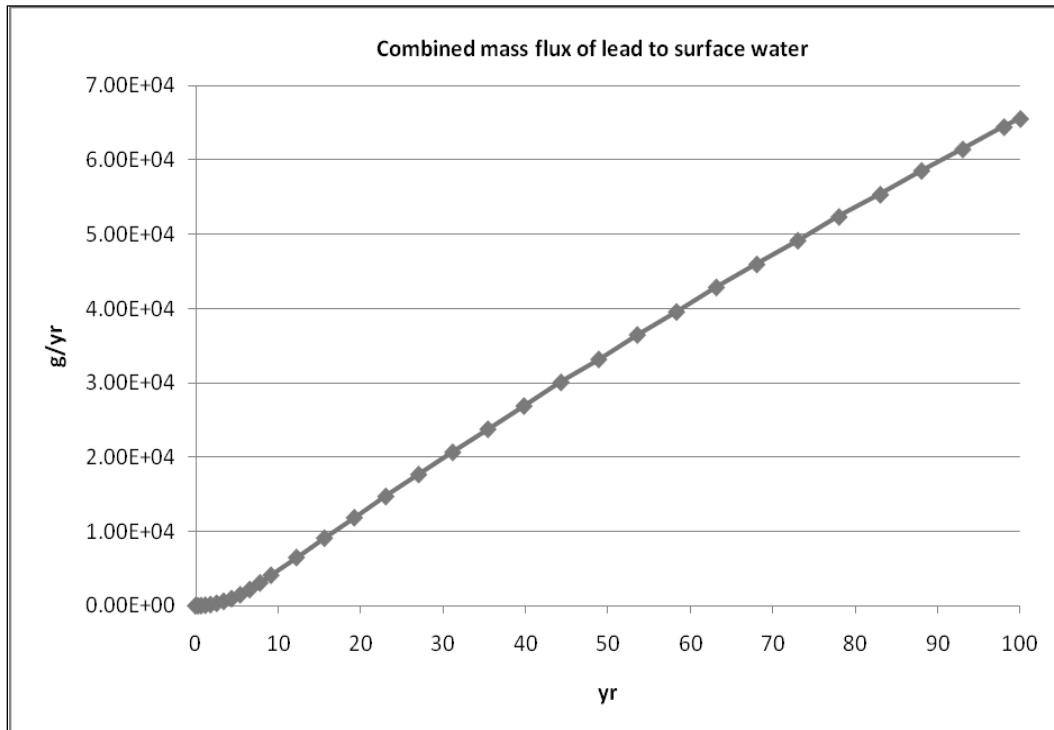


Figure 27. Computed Tier 2 combined runoff and erosion mass flux of lead from soil to surface water using baseline conditions.

The sediment peak concentrations and export peak fluxes computed with Tier 2 for baseline conditions are shown in Table 11 for all five MCs. The values in Table 11 should be compared with the steady-state Tier 1 results shown in Table 7. This comparison reveals that the soil peak concentration and export peak fluxes for perchlorate computed with Tier 2 are nearly identical to those computed with Tier 1. However, the results for the other MCs are considerably different using Tier 2 compared to using Tier 1. Soil peak concentrations are about an order of magnitude greater for the two explosives with Tier 2 compared to Tier 1, while peak fluxes are about an order of magnitude lower. Soil peak concentrations and peak fluxes are orders of magnitude less for the two metals using Tier 2 compared to Tier 1. The primary reason for the differences in Tier 2 responses is the inclusion of the time domain with dissolution. It is noted that the MC loading rates were constant for the seven years of loading.

Table 11. Computed soil peak concentrations and export peak fluxes for Tier 2 using baseline conditions.

| Constituent | Soil total concentration, mg/kg | Combined erosion and runoff, g/yr | Leaching flux, g/yr |
|---|---|---|---|
| RDX | 0.016 | 343 | 1,280 |
| TNT | 0.061 | 3,600 | 10,500 |
| Lead | 61.2 | 65,600 | 43,300 |
| Copper | 36.2 | 2,850 | 4,100 |
| $KClO_4$ | 3.44E-6 | 10.8 | 63.1 |

**Aquifer**

The aquifer concentration versus time plots for RDX and TNT computed with Tier 2 using baseline conditions are shown in Figures 28 and 29, respectively. These plots can be compared with Figures 2 and 3 for Tier 1. The primary difference is that the concentrations are lower using Tier 2, and they do not exceed the protective human health benchmarks as they do using Tier 1. Since Tier 2 considers time-varying conditions with loadings occurring for only seven years, and since groundwater responds slowly to loading, time becomes an important factor affecting groundwater concentrations.
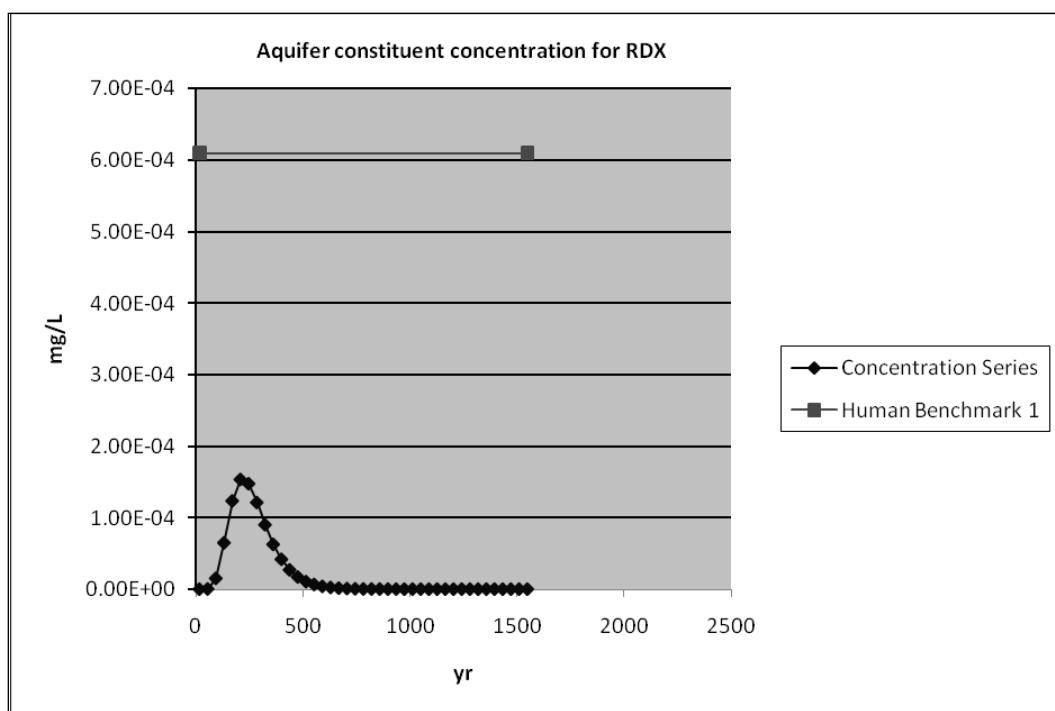
Figure 28. Tier 2 computed RDX concentration versus time in groundwater at the location of the receptor well for baseline conditions.
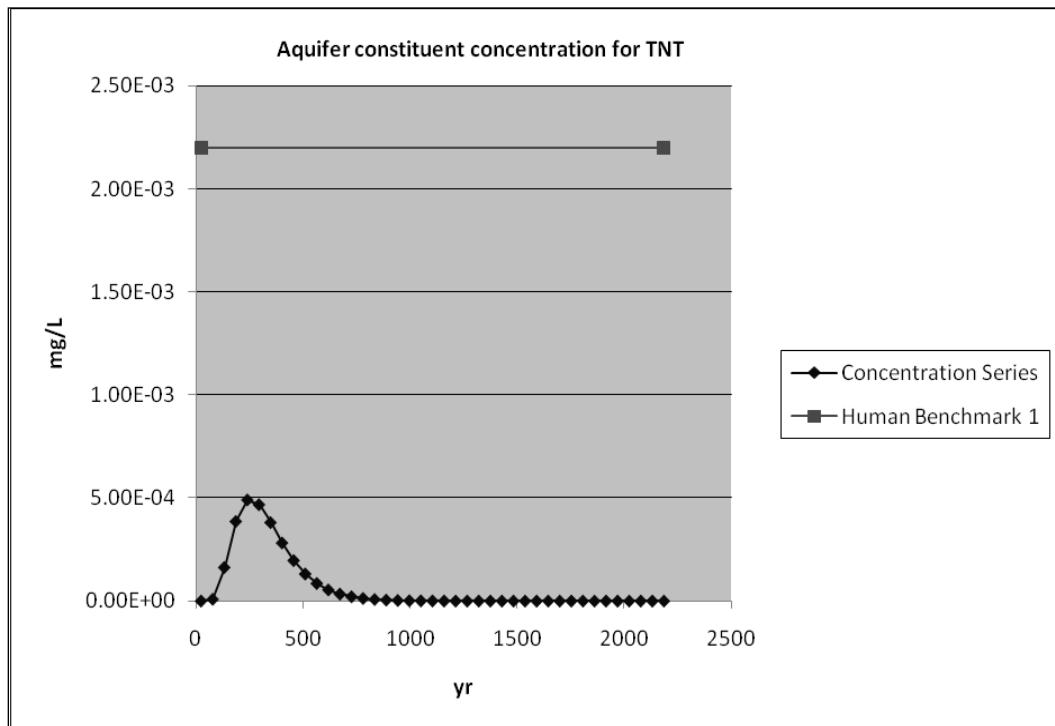


Figure 29. Tier 2 computed TNT concentration versus time in groundwater at the location of the receptor well for baseline conditions.

The aquifer concentration versus time plots for the other three MC are not presented since their concentrations are so small relative to the health benchmark that their values plot close to zero along the horizontal axis. The peak groundwater concentrations at the receptor well for all five MCs are presented in Table 12 along with the protective health benchmarks. This table should be compared with Table 8. None of the MC peak concentrations exceed the benchmarks using Tier 2, whereas RDX, TNT, and lead exceed the benchmarks using Tier 1.

Table 12. Tier 2 computed aquifer receptor well peak concentrations for each MC and for baseline conditions with drinking water protective health benchmarks.

| Constituent | Aquifer concentration at well, ppb | Protective benchmark, ppb |
|---|---|---|
| RDX | 0.15 | 0.61 |
| TNT | 0.49 | 2.2 |
| Lead | 0.0 | 15 |
| Copper | 2.49E-6 | 1500 |
| KClO$_4$ | 1.49E-3 | 15 |

It is noted that it takes hundreds of years for RDX and TNT concentrations to reach their peak values at the receptor well. The metals show zero or nearly zero concentrations even after 10,000 years of simulation. The aquifer results clearly demonstrate the value of using Tier 2 over Tier 1 to refine predictions for groundwater. It is emphasized that Tier 1 assumes constant, steady-state (never ending) loadings with instantaneous dissolution, which is appropriate for a steady-state analysis. Thus, Tier 1 should and does produce highly conservative results, especially for metals in groundwater.

## Surface water and sediments

The sediment concentration versus time plot for lead computed for White Lake with Tier 2 using baseline conditions is shown in Figure 30. This plot can be compared with Figure 9 for Tier 1. The primary difference is that the concentrations are lower using Tier 2, and they do not exceed the protective ecological health benchmarks as they do using Tier 1.
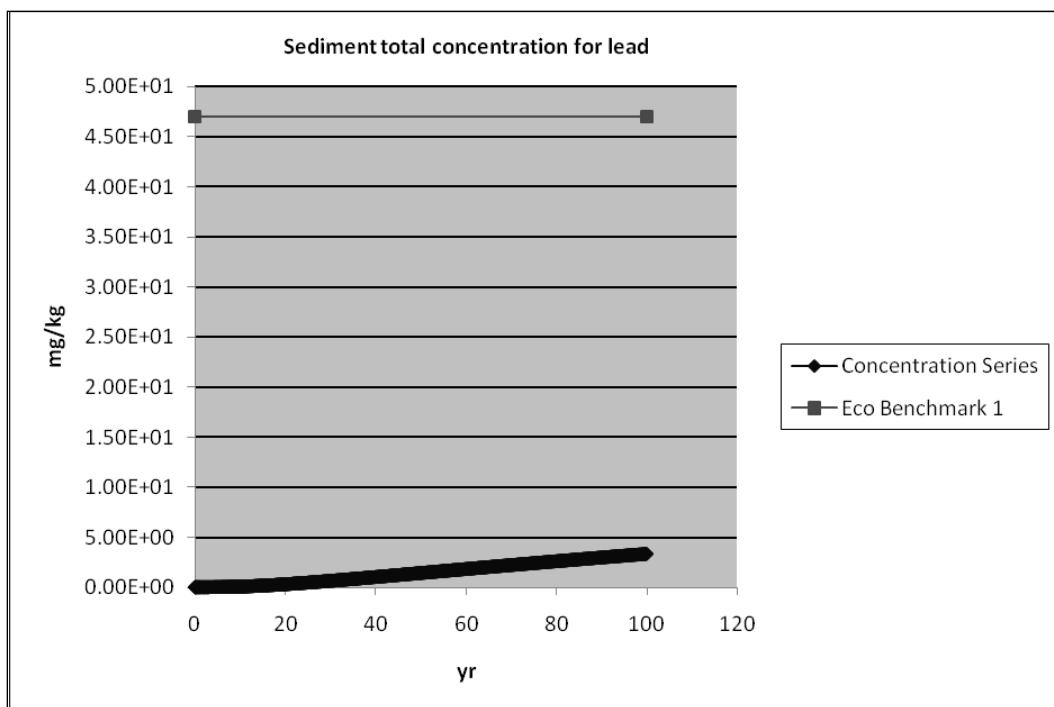
Figure 30. Tier 2 computed sediment total concentration of lead versus time for White Lake using baseline conditions.

The sediment concentration-versus-time plots for the other four MCs are not presented since their concentrations are small relative to the protective benchmarks that their values plot close to zero along the horizontal axis. The sediment peak concentrations in White Lake for all five MCs are presented in Table 13 along with the protective health benchmarks. This table should be compared with Table 9. None of the MC peak concentrations exceed the benchmarks using Tier 2, whereas lead and copper exceed the benchmarks using Tier 1. Sediment peak concentrations for RDX, TNT, lead, and copper are considerably less for Tier 2 compared to Tier 1.

Table 13. Tier 2 computed White Lake sediment peak concentrations for each MC and for baseline conditions with ecologically protective health benchmarks.

| Constituent | Sediment concentration, ppb | Sediment protective benchmark, ppb |
|---|---|---|
| RDX | 6.53E-3 | 26 |
| TNT | 0.082 | 184 |
| Lead | 3,340 | 47,000 |
| Copper | 29.7 | 34,000 |
| $KClO_4$ | 2.0E-4 | NA |

ERDC/EL TR-11-10 54

The White Lake total (particulate and dissolved) water concentration versus time plots for TNT and lead computed with Tier 2 using baseline conditions are shown in Figures 31 and 32, respectively. These plots can be compared with Figures 13 and 14 for Tier 1. The primary difference is that the concentrations are lower using Tier 2, and they do not exceed the protective human health benchmarks for lead as they do using Tier 1. The water total concentrations-versus-time plots for the other three MCs are not presented since the concentrations are so small relative to the benchmarks that their values plot close to zero along the horizontal axis.

The water peak total concentrations in White Lake for all five MCs are presented in Table 14 along with the protective human health benchmarks. This table should be compared with Table 10. None of the MC total concentration values exceeds the benchmark using Tier 2, whereas lead exceeds its benchmark using Tier 1. Water peak total concentrations for RDX, TNT, lead, and copper are considerably less for Tier 2 compared to Tier 1.
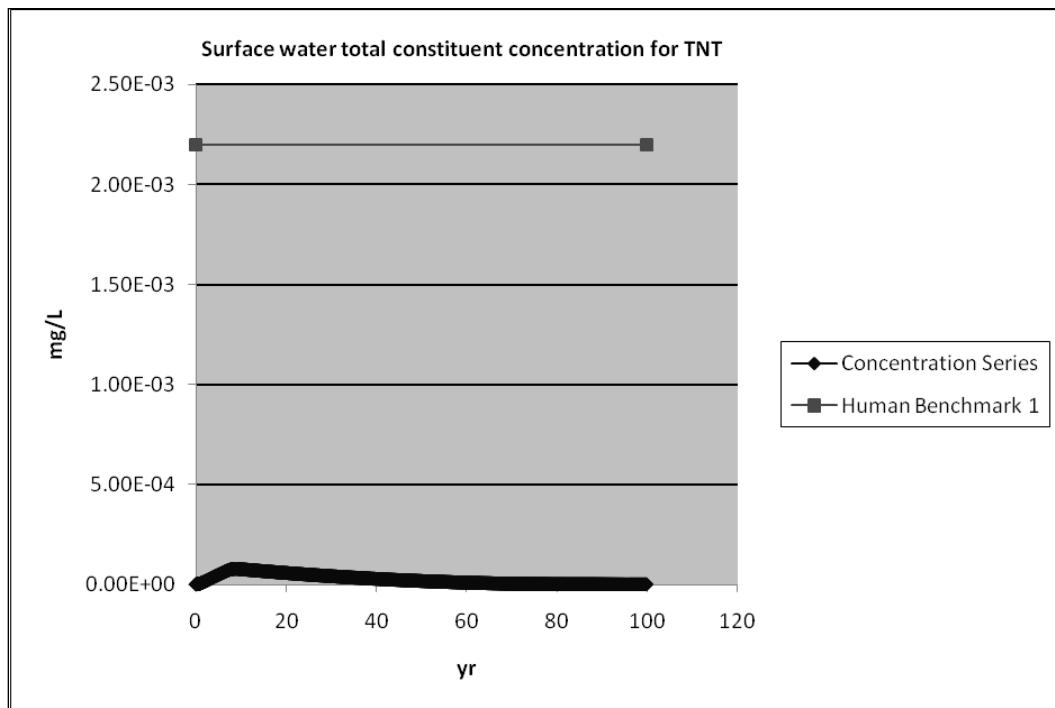


Figure 31. Tier 2 computed water total concentration of TNT versus time for White Lake using baseline conditions.
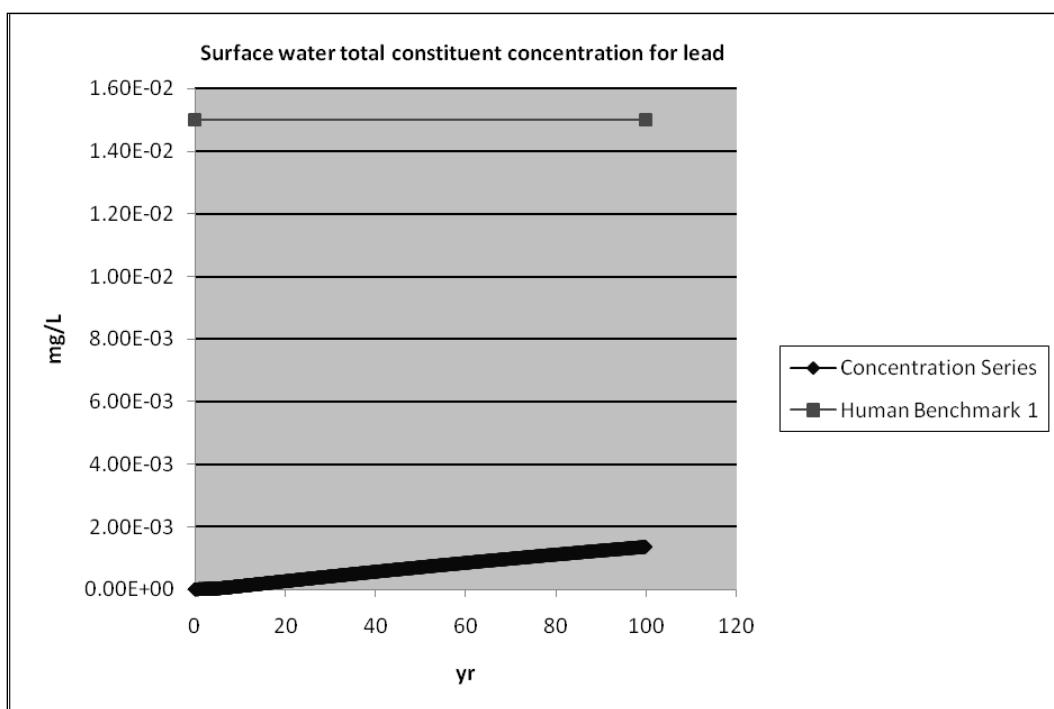
Figure 32. Tier 2 computed water total concentration of lead versus time for White Lake using baseline conditions.

Table 14. Tier 2 computed water peak concentrations for each MC in White Lake for baseline conditions with protective human and ecological health benchmarks.

| Constituent | Water total concentration, ppb | Water human health protective benchmark, ppb | Water dissolved concentration, ppb | Water ecological health protective benchmark, ppb |
|---|---|---|---|---|
| RDX | 0.007 | 0.61 | 0.007 | 190 |
| TNT | 0.076 | 2.2 | 0.076 | 90 |
| Lead | 1.36 | 15 | 0.97 | 2.5 |
| Copper | 0.06 | 1,500 | 0.057 | 9.0 |
| KClO$_4$ | 2.29E-4 | 15 | 2.29E-4 | 9,300 |

The White Lake dissolved water concentration versus time plot for lead computed with Tier 2 using baseline conditions is shown in Figure 33. This plot can be compared with Figure 19 for Tier 1. The primary difference is that the concentrations are lower using Tier 2, and they do not exceed the protective ecological health benchmark as they do using Tier 1. The water dissolved concentration versus time plots for the other four MCs are not presented since the concentrations are so small relative to the benchmarks that their values plot near zero along the horizontal axis.
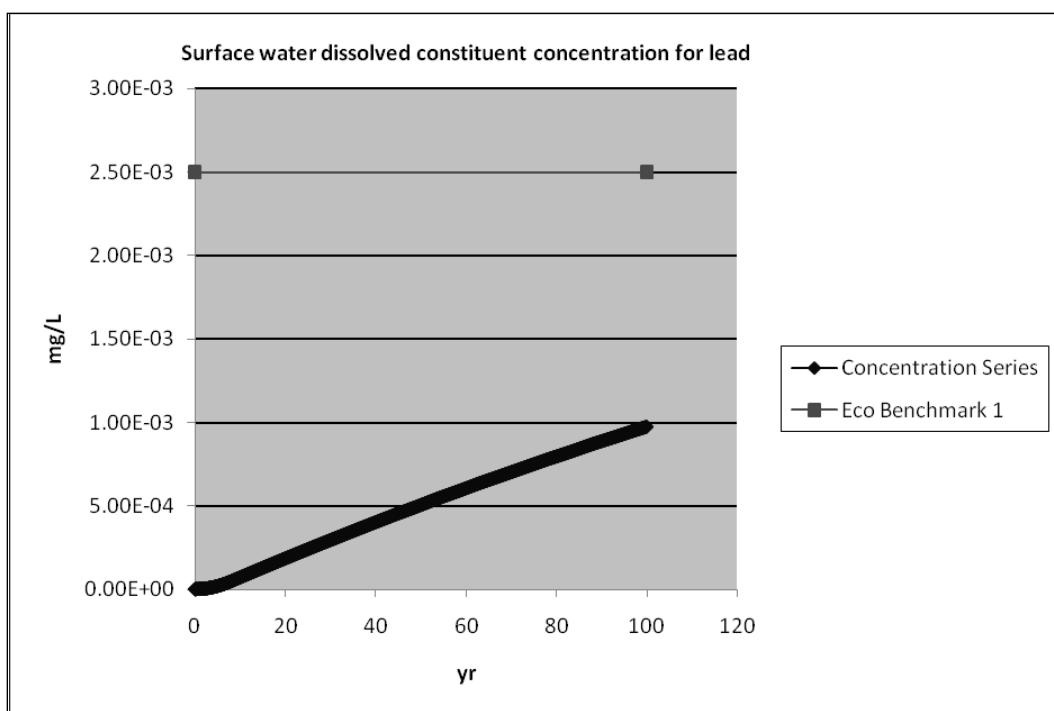
Figure 33. Tier 2 computed water dissolved concentration of lead versus time for White Lake using baseline conditions.

The peak dissolved concentrations in White Lake water for all five MCs are presented in Table 14 along with the protective ecological health benchmarks. This table should be compared with Table 10. None of the five MC values exceeds its protective benchmark using Tier 2, whereas lead and copper exceed their benchmarks using Tier 1. Similar to soil, sediment, and water total concentrations, the peak water-dissolved concentrations for RDX, TNT, lead, and copper are considerably less using Tier 2 than the concentrations computed with Tier 1.

The baseline conditions were rerun with a longer simulation time of 700 years to determine if the metal concentrations in surface water and sediment would exceed any protective benchmarks at some later point in time. The only protective benchmark that is exceeded is the ecological water benchmark for lead. The peak water dissolved concentration of lead, which occurs at about 600 years, is 2.63 µg/L compared to 2.5 µg/L for the benchmark. These simulations demonstrate the long response times for MCs with slow dissolution rates and high adsorption characteristics, such as lead and copper.

## Summary

Since perchlorate is miscible and highly mobile in water, it responds nearly identically for Tier 2 and Tier 1. Perchlorate soil concentrations, soil export fluxes, sediment concentrations, and water total and dissolved concentrations are nearly the same for Tier 1 and Tier 2. All receiving media concentrations are considerably less with Tier 2 compared to Tier 1 for the other four MC due to the inclusion of the time domain in Tier 2 with attenuation effects associated with a finite MC loading period, dissolution, and adsorption. None of the five MCs exceeds protective health benchmarks for any media for the 100-year simulation. Only lead slightly exceeds the surface water ecological benchmark after 600 years of simulation.

Lead and copper respond much differently under Tier 2 compared with Tier 1, especially for groundwater. Essentially zero concentrations were computed at the receptor well for thousands of years. The computed surface water and sediment concentrations for the two metals are two to four orders of magnitude less for Tier 2 compared to Tier 1. The explosives concentrations in sediment and surface water were about an order of magnitude lower for Tier 2 compared with Tier 1.

Although RDX and TNT concentrations did not exceed protective benchmarks for groundwater, their concentrations were within the same order of magnitude as the benchmarks. Thus, for different conditions, such as longer loading periods, these two MCs could potentially be a concern for groundwater at this site as demonstrated in Test 2 in the next chapter.

Overall, the two metals are not expected to ever be a concern in the groundwater of this site, whereas explosives, particularly RDX, could potentially be a concern in groundwater. TNT is less likely to be a concern due to the fact that it usually degrades much faster than RDX. Zero degradation was used in all media for the baseline simulations. Lead is a potential concern for surface water at this site, but such concerns should not occur for many years (centuries). Explosives are not expected to be a concern in surface water and sediments. It is noted that very high loading rates for the metals were used. Lower loading rates for metals are discussed in the next chapter. Perchlorate is of no concern at this site for surface water or groundwater, since its loadings were estimated to be quite small.

# 6 Additional Testing

## Sensitivity testing

Sensitivity tests were conducted to evaluate the effects of various inputs for the Tier 2 modeling and to assess that these effects are logical, thus helping to ensure correct implementation. Sensitivity tests that were conducted during the Tier 1 POC application (Dortch et al. 2010) were not repeated for Tier 2 since roughly the same effects are expected. The Tier 2 sensitivity tests were focused on new features of the models not encountered for Tier 1. Thus, most of the Tier 2 sensitivity tests dealt with features of the Tier 2 soil model.

The following tests were run for sensitivity using the baseline conditions described in Chapter 4 except for changes associated with the sensitivity test:

1. Lead and copper loading per year were reduced to 1/7 of the values used for baseline conditions.
2. Same conditions as sensitivity Test 1 above but with loadings for all MC extending for 60 years rather than 7 years.
3. Same conditions as sensitivity Test 2 above but with soil interflow, which occurs when infiltration exceeds percolation.
4. Same conditions as sensitivity Test 2 above but with groundwater discharge to surface water of 50 percent of aquifer total water flux.
5. Same conditions as sensitivity Test 2 above but with an active soil layer thickness of 0.2 m rather than 0.4 m.
6. Same conditions as sensitivity Test 2 above but with an active soil layer thickness of 0.8 m rather than 0.4 m.
7. Same conditions as sensitivity Test 2 above but with AOI surface area doubled.
8. Same conditions as sensitivity Test 2 above but with AOI surface area halved.
9. Same conditions as sensitivity Test 2 above but allowing solid phase particle erosion.
10. Same conditions as sensitivity Test 2 above but with each MC initial solid phase particle diameter reduced ten-fold.
11. Same conditions as sensitivity Test 2 above but with each MC initial solid phase particle diameter increased ten-fold.

12. Same conditions as sensitivity Test 2 above but with non-zero degradation rates in soil.
13. Same conditions as sensitivity Test 2 above but with metal water solubility in the soil layer increased by a factor of 10.
14. Same conditions as sensitivity Test 2 above but with cylindrical solid phase particles.
15. Same conditions as sensitivity Test 2 above but with variations in the vadose zone thickness and its saturated hydraulic conductivity.

Sensitivity Test 2 above essentially becomes the new standard or baseline for comparing other sensitivity tests. The reason for this is that the loading conditions for Test 2 are believed to be more representative of what has actually occurred at Fort A.P. Hill.

**Test 1**

The conditions for Test 1 were identical to those of the baseline Tier 2 simulations with the exception that the number of rounds fired per year for small arms was reduced by 1/7th from 22E6 rounds per year to 3,142,857 rounds per year to be more consistent with what is believed to be the correct firing rate. This reduction reduced the mass loading for lead and copper from 50E6 and 30E6 g/yr to 7.13E6 and 4.28E6 g/yr, respectively.

The results for lead and copper are the only ones that differed from the baseline results discussed in Chapter 5, and only the results for surface water and sediment merit discussion since the aquifer results for metals are near zero as before. The sediment concentration for lead and copper in Test 1 are 485 and 4.24 ppb, respectively, at 100 years compared with 3,342 and 29.7 ppb for baseline Tier 2 loadings. Thus, the sediment concentrations were reduced by 1/7th as expected. The media concentrations computed with Tier 2 vary linearly with soil loading rates, the same as for Tier 1. The sediment concentrations for lead and copper computed for Test 1 are respectively 3 and 4 orders of magnitude lower than the protective ecological health benchmarks.

Results similar to those for sediment were computed for surface water in Test 1. Thus, media concentrations are reduced by 1/7th, and neither lead nor copper exceed the protective ecological health benchmarks for surface water.

**Test 2**

Test 2 had the same conditions as Test 1 except that loadings for all MC were extended from 7 years to 60 years, which is believed to be a more accurate estimate of the length of time that the Fort A.P. Hill ranges have been used. However, it is possible that the loading rates may have varied substantially over the past 60 years, and the average rates for that period could be different from the rates used in this analysis, which represent the average rates over the years 2000 through 2006. Regardless, the averages of the rates for 2000–2006 were used for 60 years. This test demonstrates the importance of the duration of range use on media concentrations, especially for groundwater. The results of Test 2 are used as a standard for comparing the rest of the sensitivity tests, since the remaining tests are based on Test 2 plus an additional change for each test.

The plots of aquifer concentration versus time at the receptor well are shown in Figures 34 and 35 for RDX and TNT, respectively. Both MCs exceed the protective human health benchmarks by almost a factor of two as shown by the two figures. RDX exceeds the benchmark after about 170 years, and TNT exceeds its benchmark after about 200 years due to its higher soil-water partitioning coefficient $K_d$. The other three MCs were computed to have near zero concentrations, so their concentrations are well below the benchmarks. RDX and TNT were below the protective benchmarks for the baseline conditions and Test 1. Thus, extending the loading duration has the effect of increasing peak groundwater concentrations. It is emphasized that these results are with zero degradation rates. The effect of degradation will be examined in Test 12.

The computed sediment peak concentrations for lead and copper for Test 2 are 2,560 ppb and 24.4 ppb, respectively, which are fairly close to the values computed with the baseline conditions, but much higher than the results for Test 1. Although the annual loadings of lead and copper are 1/7th of the baseline conditions, the duration of loadings is more than eight times longer. Since the metals take a relatively long time to reach equilibrium conditions for a constant loading, the 60-year duration of loading has the effect of magnifying the soil concentrations, soil export, and resulting surface water and sediment concentrations. MCs with faster response times, like the explosives and perchlorate, tend to reach equilibrium much faster, and the loading duration is not as important and has less effect on peak surface water and sediment concentrations. The plot of sediment concentration versus time for lead is not presented, but it looks similar to that of
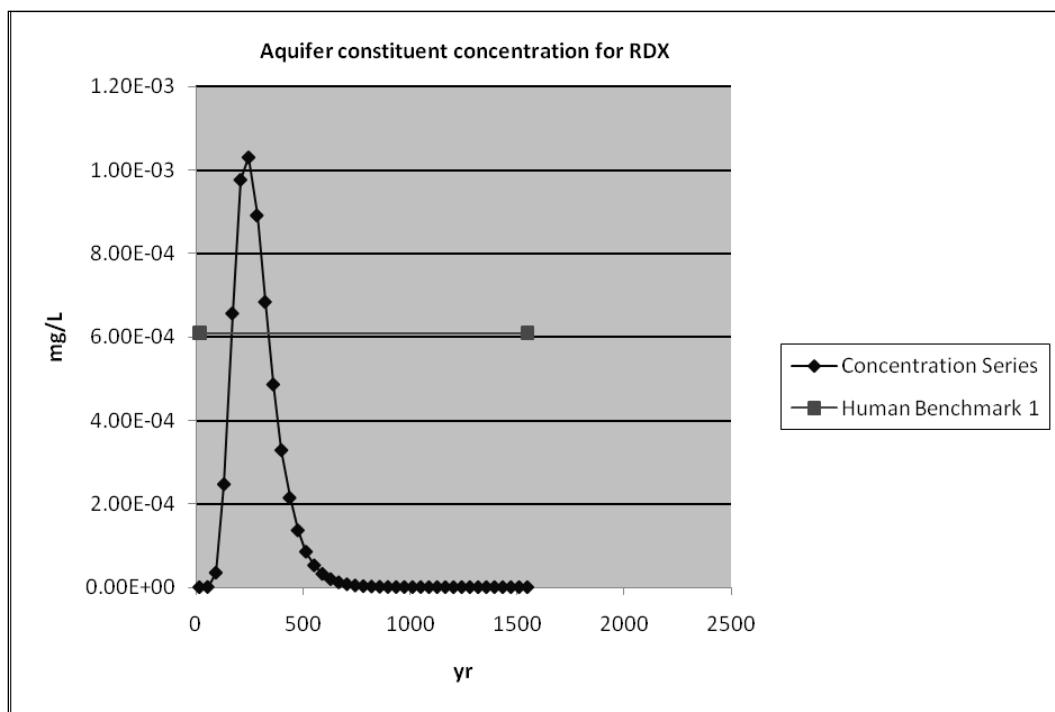
Figure 34. Tier 2 computed RDX concentration versus time in groundwater at the location of the receptor well for Test 2 conditions.
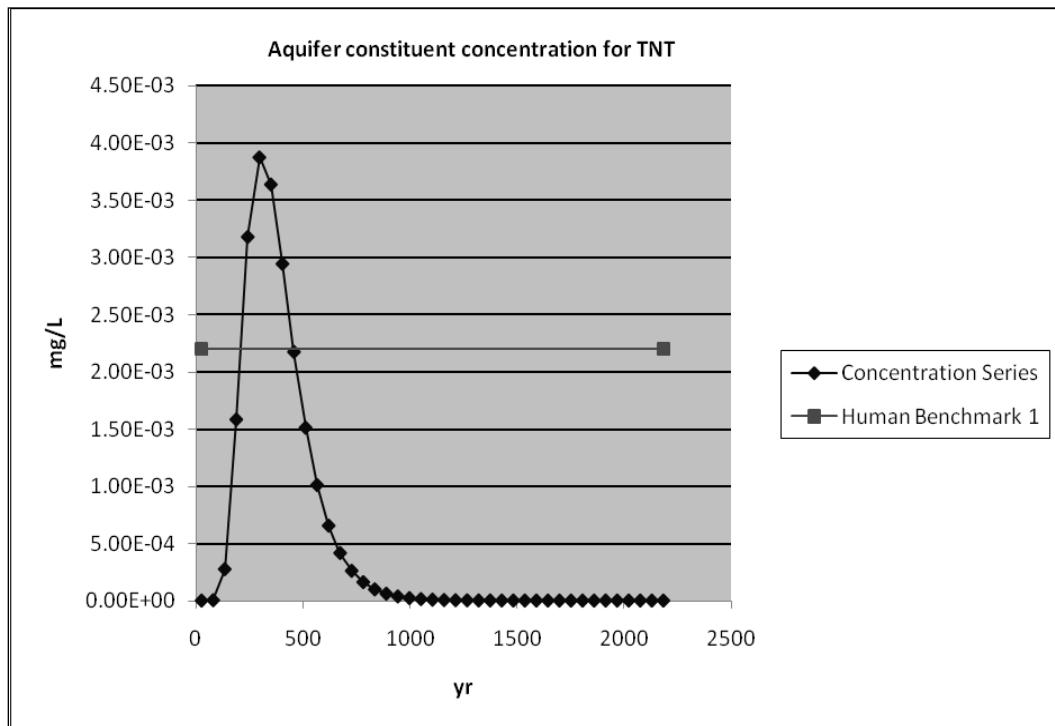


Figure 35. Tier 2 computed TNT concentration versus time in groundwater at the location of the receptor well for Test 2 conditions.

Figure 30. The sediment concentrations of the other four MCs plot along the time axis near zero since the concentrations are low relative to the protective benchmarks. The sediment peak concentration of perchlorate is the same as for the baseline conditions except that the duration of the peak is about 60 years instead of 7 years.

The plots of surface water total concentration versus time for TNT and lead with Test 2 conditions are shown in Figures 36 and 37, respectively, along with the human health benchmarks. The plot for RDX is similar to the one for TNT, and the plot for copper is similar to the one for lead except that the copper concentrations are much less than the copper benchmark. The concentration of perchlorate is essentially zero compared to its benchmark.

The plot of surface water dissolved concentration versus time for lead with Test 2 conditions is shown in Figure 38. Although the concentration is below the benchmark, it is approaching the benchmark with increasing time. The peak water-dissolved concentrations for the other MCs are well below the protective ecological benchmarks.
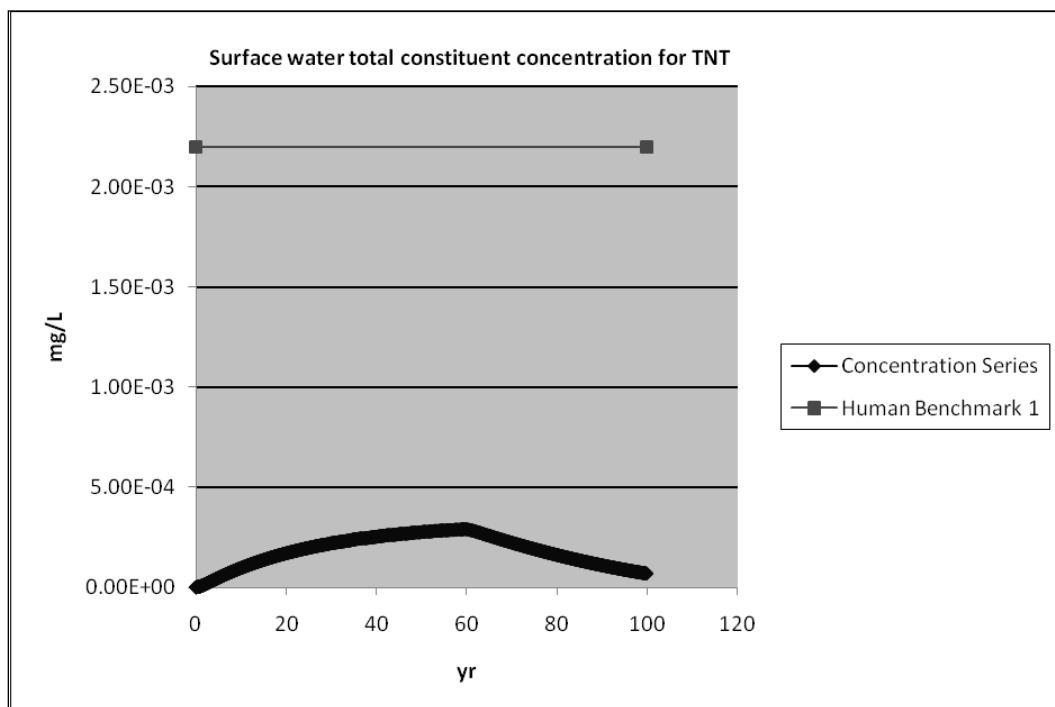


Figure 36. Tier 2 computed water total concentration of TNT versus time for White Lake using Test 2 conditions.
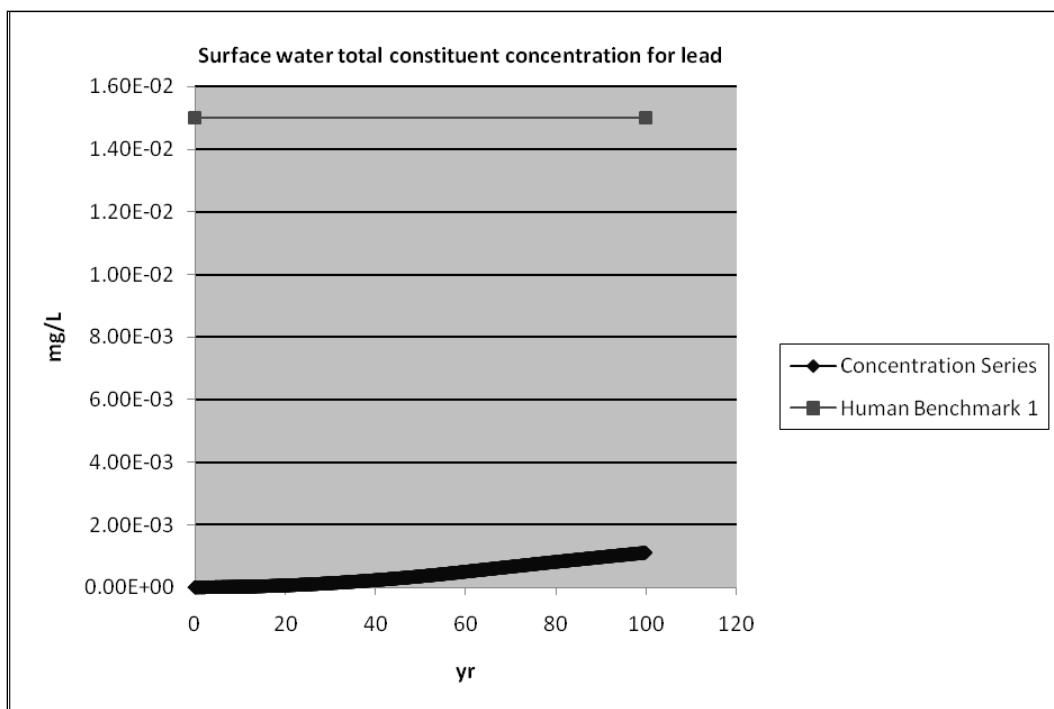
Figure 37. Tier 2 computed water total concentration of lead versus time for White Lake using Test 2 conditions.
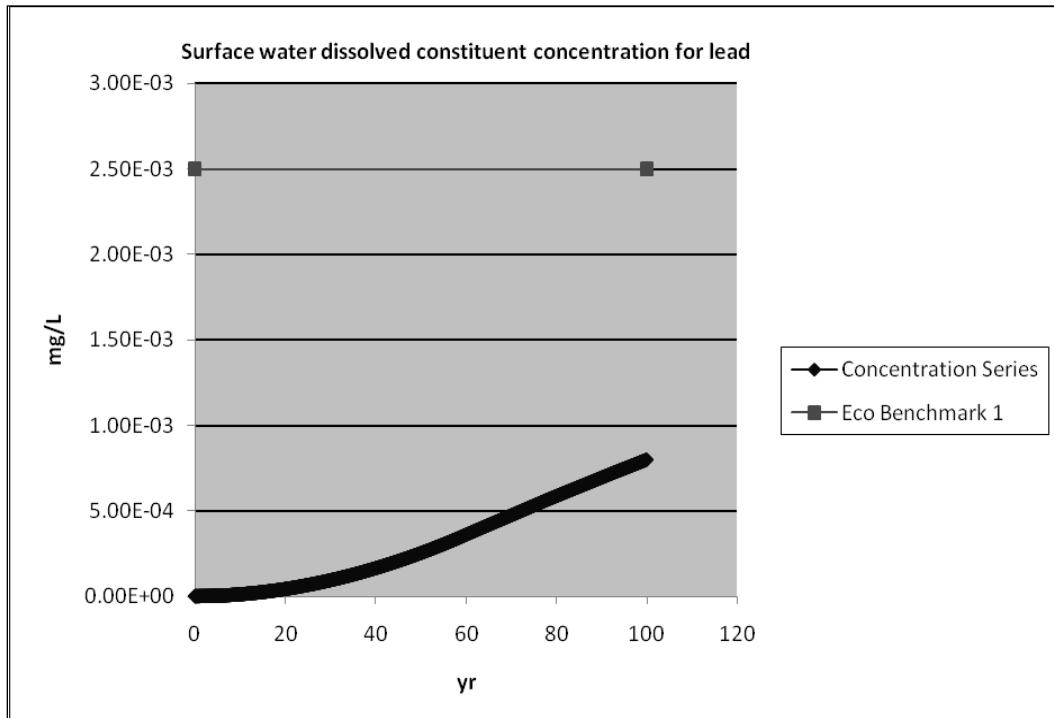


Figure 38. Tier 2 computed water dissolved concentration of lead versus time for White Lake using Test 2 conditions.

Test 2 conditions were re-run with the total simulation time increased from 100 to 700 years to examine the peak. Upon comparing peak concentrations for the aquifer receptor well, it was discovered that the peak RDX concentration for this run is higher than that shown in Figure 34. The peak RDX concentration is about 1.3 ppb for the 700-year run versus about 1.0 ppb for the Test 2 run of 100 years. The reason for the increase is that the soil concentrations for RDX have not been depleted for the 100-year run, whereas its soil concentration has been depleted for the 700-year run. The aquifer peak concentration for TNT is about the same for the 700-year run as the 100-year run, since most of the TNT soil concentration has been depleted after 100 years due to its greater solubility and dissolution rate. The soil concentrations of lead and copper are not depleted even after 700 years, but their aquifer concentrations are so small that it does not make a noticeable difference in results relative to the benchmarks. Of course, the soil concentrations of perchlorate are depleted almost as soon as loadings to soil cease at year 60. Although the vadose zone and aquifer models run for as long as 10,000 years, the loadings to the vadose zone are assumed to be zero at the end of the soil model simulation time. Thus, the longer 700-year run results in greater loadings from soil to the vadose zone and aquifer and consequently higher aquifer concentrations, especially for RDX.

The surface water peak total concentration for lead is about 4 ppb, which is below the protective human health benchmark of 15 ppb, and occurs after about 600 years. However, the surface water peak dissolved concentration for lead is 2.91 ppb after 600 years, which is above the protective ecological health benchmark of 2.5 ppb. These results for lead are similar to the long-term run conducted for the baseline conditions. This 700-year simulation indicates the importance of running the models long enough to ensure that peak receiving media concentrations have been reached.

The peak media concentrations for Test 2 (run to 100 years) and the respective protective health benchmarks are summarized in Table 15 for all five MCs. This table should be compared with the baseline results summarized in Tables 12, 13, and 14 for aquifer, sediment, and water, respectively. The comparison reveals that RDX and TNT exceed the protective benchmarks for Test 2 whereas they did not exceed the benchmarks for baseline conditions. Otherwise, the results of Test 2 are quite similar to those of the baseline conditions.

Table 15. Tier 2 computed peak media concentrations for Test 2 with protective health benchmarks.

| MC | Aquifer conc. at well, ppb | Aquifer bench, ppb | Sed. conc., ppb | Sed. bench, ppb | Water total conc., ppb | Water human bench, ppb | Water diss. conc., ppb | Water eco bench, ppb |
|---|---|---|---|---|---|---|---|---|
| RDX | 1.03 | 0.61 | 0.038 | 26 | 0.042 | 0.61 | 0.042 | 190 |
| TNT | 3.88 | 2.2 | 0.33 | 184 | 0.29 | 2.2 | 0.29 | 90 |
| Lead | 0.0 | 15 | 2,560 | 47,000 | 1.12 | 15 | 0.80 | 2.5 |
| Copper | 1.6E-6 | 1500 | 24.4 | 34,000 | 0.052 | 1,500 | 0.049 | 9.0 |
| KClO$_4$ | 0.012 | 15 | 2.0E-4 | NA | 2.29E-4 | 15 | 2.29E-4 | 9,300 |

Test 2 is used to compare the results of the remaining tests and clearly demonstrates the importance of the loading duration, i.e., the duration of range use.

**Test 3**

Test 3 had the same conditions as Test 2, with interflow from soil to surface water occurring. This test was run to assure proper functioning of the interflow feature. Interflow can be activated in two different ways on the Hydrology tab within the soil model user interface:

1. Specify the percent of soil infiltration rate that is interflow.
2. Specify a vadose zone saturated hydraulic conductivity that is less than the soil infiltration rate, and using that value, have the interface calculate the percentage of infiltration being diverted to interflow.

The latter approach was used with the conductivity set to 0.15 m/yr. This resulted in 25 percent of the infiltration being diverted to interflow.

The diversion of infiltration to interflow causes a decrease in loading to aquifer and lower aquifer concentrations and an increase in loading to surface water and higher surface water and sediment concentrations. The mass export flux from soil to the vadose zone decreases by 25 percent. This decrease in flux is diverted to surface water via interflow as designed. The increase in mass flux from soil to surface water is more than 25 percent in most cases because the diverted mass flux is relatively large in comparison to the flux to surface water in Test 2. There is less change in the mass flux from soil to surface water for lead since very little lead mass leaches from the soil. As a result, the increase in surface water fluxes ranges from about

140 to 250 percent, with the percentage of increase inversely proportional to the MC $K_d$. Thus, perchlorate experiences the greatest increase of mass flux from soil to surface water.

The aquifer results for Test 3 are very similar to those of Test 2, with RDX and TNT peaking at about the same concentrations as in Test 2. The sediment and water concentrations are substantially higher in Test 3 than in Test 2 due to the rather large increase in loadings from soil to surface water associated with the interflow. The MCs with low $K_d$ values for soil experience water and sediment concentration increases of about the same magnitude as their loading increase, whereas the media concentrations for the two metals increase less. Overall, this test demonstrated that the soil interflow feature is working properly and causes a diversion in loading fluxes from vadose zone to surface water, resulting in higher surface water and sediment concentrations.

**Test 4**

Test 4 had the same conditions as Test 2 above but with groundwater discharge to surface water of 50 percent of total water flux in the aquifer. This condition was imposed by opening the aquifer model UI and resaving all previously entered inputs. This action launches another UI for setting the groundwater flow rate to surface water where the user can either specify the groundwater discharge rate or the percent of groundwater flow that discharges to surface water. The latter option was used to specify 50 percent of groundwater flow discharged to surface water.

The longitudinal distance from the AOI to the location of the groundwater discharge to surface must also be specified on the Flux Location tab of the aquifer UI. This distance was set to 3,000 m for the Fort A.P. Hill POC application.

This test is similar to Test 3 as it diverts mass flux from aquifer to surface water. However, in this case, it takes a much longer time for the diversion water to reach surface water due to the long transit time through the aquifer. The aquifer receptor well concentrations do not change since a decrease in aquifer mass flux within the aquifer due to groundwater discharge does not affect the aquifer concentrations.

The computed sediment and surface water peak concentrations for Test 4 are very close to the values computed for Test 2 since the models were only

run for 100 years. If the models are run longer, then sediment and water concentrations are affected by groundwater discharge but long after soil loadings have started decreasing due to the 60-year soil loading duration. The larger the $K_d$ value in the aquifer, the longer it takes for sediment and surface water to exhibit groundwater discharge loading effects.

To further examine the effects of delayed groundwater discharge, the models were run for 300 years. The effects of groundwater discharge in surface water show up for RDX, TNT, and perchlorate. However, there are no effects of groundwater discharge for lead and copper since their groundwater concentrations are so low and it takes so long for these constituents to reach groundwater at this site. The sediment concentration versus time for RDX is shown in Figure 39 to illustrate the effect of groundwater discharge. Although the sediment and water concentrations peak a second time due to groundwater discharge, the 50-percent flux was not quite high enough to cause concentrations as high as the first peak, which is due to soil erosion and runoff fluxes. Overall, groundwater discharge to surface water causes later surface water and sediment peak concentrations associated with the slower groundwater movement.
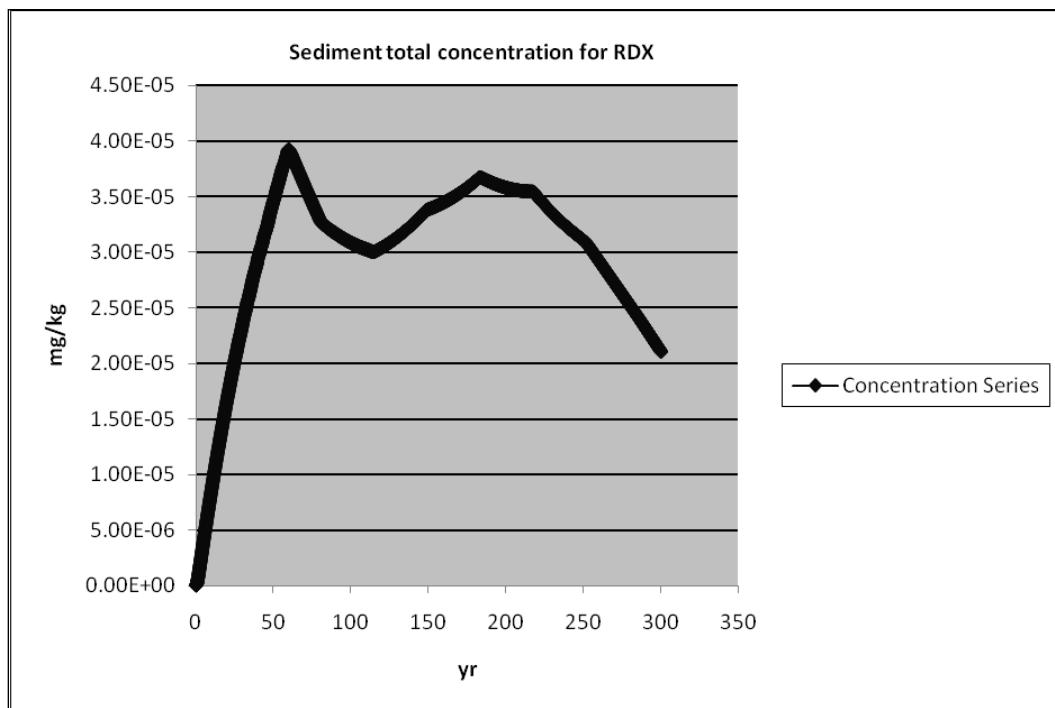


Figure 39. Tier 2 computed sediment concentration of RDX versus time for White Lake using Test 4 conditions.

**Test 5**

Test 5 had the same conditions as Test 2 above but with the active soil layer thickness set to 0.2 m rather than 0.4 m. The active soil layer thickness is the zone of surficial soil where MCs are believed to reside and to be subjected to fate and export processes. This input variable is required to provide the vertical dimension and soil compartment volume for the soil model, which is based on a single, fully mixed or homogeneous soil compartment as described by Dortch et al. (2011). This input is specified on the Site Characteristics tab of the soil model UI.

Halving the active soil layer thickness doubles the soil MC concentrations for all MCs except perchlorate. The perchlorate soil concentrations do not change, since perchlorate is treated as water miscible. All of the perchlorate soil concentration resides in the soil pore water; thus, its concentration is independent of the soil thickness. The pore-water concentration is relatively small relative to the soil total concentration for the other four MCs.

The sediment peak concentrations for RDX and TNT for Test 5 are about the same as for Test 2. The sediment peak concentration for perchlorate for Test 5 is identical to that of Test 2. The sediment peak concentrations at year 100 for lead and copper are 4,830 and 40.4 ppb, respectively, for Test 5 compared with 2,560 and 24.4 ppb for Test 2. Water concentrations for Test 5 parallel those for sediment, with higher concentrations for the metals for Test 5 compared with Test 2. There are no perceivable differences in aquifer concentrations when comparing results of Test 5 with those of Test 2.

The surface water and sediment peak concentrations for MCs with relatively low soil $K_d$ values are about the same for Tests 5 and 2, whereas the peak concentrations in these media for Test 5 are almost double those for Test 2 for the metals, which have high soil $K_d$ values. Therefore, it is concluded that the effect of the active soil layer thickness on receiving media concentrations is negligible for MCs with relatively low soil $K_d$ values. However, for MCs with relatively high soil $K_d$ values, the effect of halving the soil active layer thickness tends to nearly double the receiving surface water and sediment concentrations. Munitions constituents that are relatively mobile in water are insensitive to specification of the active soil layer thickness, whereas relatively immobile constituents respond almost linearly to the input thickness. Clearly the active soil layer thickness should be treated as an uncertain variable for the more immobile MCs, such as metals.

**Test 6**

Test 6 conditions were identical to Test 5 except the active soil layer thickness was set to 0.8 m or double the thickness used for Test 2. The results are similar to those of Test 5 except in the opposite direction for the metals. Thus, doubling the active soil layer thickness has the effect of nearly halving the computed surface water and sediment concentrations for the metals while having little to no effect on the other MCs.

**Test 7**

Test 7 had the same conditions as sensitivity Test 2 above but with the AOI surface area doubled. This was accomplished by increasing the width and length of the AOI by a factor of 1.414. Thus, the length was increased to 3,231.5 m, and the width was increased to 6,668 m, resulting in an AOI surface area of 21,547,642 m² or about double the baseline area. The AOI dimensions are specified on the Site Characteristics tab of the soil model UI.

Doubling the AOI surface area has the effect of halving the computed soil concentrations for all MCs. This result was expected since the same effect was found for the Tier 1 models. Also, like Tier 1, doubling the AOI surface area has no effect on the computed export mass fluxes from soil to surface water and groundwater for each MC. However, increasing the AOI site dimensions does affect aquifer concentrations because the infiltrating (and percolating) water flow rate for Test 7 is double the rate for Test 2 due to twice the site area for the same infiltration rate, but the leaching mass flux for Test 2 and Test 7 are the same. This has the effect of halving the influx concentration of MCs entering the aquifer. Thus, the computed aquifer peak concentrations for Test 7 are about half of those computed for Test 2. The AOI length and width also slightly affect the aquifer concentrations due to the proximity of the well to the AOI relative to the AOI dimensions. The computed MC concentrations for surface water and sediment are identical when comparing Tests 7 and 2. No protective health benchmarks are exceeded for Test 7.

**Test 8**

Test 8 was like Test 7 except the AOI surface area was halved. This was accomplished by reducing the length and width of the AOI by a factor of 1.414. Thus, the length was reduced to 1,615.7 m, and the width was

reduced to 3,334 m, resulting in an AOI surface area of 5,386,744 m² or about half the baseline area.

The results of Test 8 are inversely analogous to those of Test 7. Thus, aquifer concentrations approximately doubled rather than halved for Test 8.

In summary, the AOI site surface area is important only for the effect on aquifer concentrations of MCs. Aquifer concentrations are inversely affected by AOI surface area that is input. As previously stated, the mass flux to groundwater does not change as AOI surface area is changed (assuming the loading of MCs to soil is the same). Thus, halving the surface area also halves the site groundwater percolation flow rate. The decrease in percolation flow rate increases the MC flux concentration entering the aquifer beneath the site, thus resulting in an increase in well concentrations. Further testing revealed that the effect of AOI surface area on aquifer concentrations is highly nonlinear such that the increase in aquifer concentrations greatly diminishes and asymptotically approaches a limit as surface area is greatly reduced. For some applications, it may be important to consider small individual range areas as an AOI to more fully assess the impacts on groundwater.

**Test 9**

Test 9 had the same conditions as Test 2 above but allowed solid phase particle erosion for all MCs. Solid phase particle erosion cannot be turned on for perchlorate since it was declared a miscible MC on the Site Characteristics tab of the soil model UI. Solid phase particle erosion for the other four MCs was turned on (or checked) on the Fate/Transport Parameters tab of the soil model UI.

There are only very slight differences in computed soil concentrations between Tests 9 and 2. For example, the peak total concentration of lead in soil is 68 mg/kg for Test 2 compared to 66.4 mg/kg for Test 9. Lead exhibits the most change in soil total concentration when comparing Test 9 to Test 2 probably due to its high soil $K_d$. It is reasonable that soil concentrations would be slightly lower for Test 9 due to the additional export of solid phase particles by erosion. The metals exhibit the greatest solid phase particle export with maximums of 2.2E5 and 1.4E5 g/yr for lead and copper, respectively. This result is due to the high $K_d$ values and low solubility and dissolution rates of the metals, as well as the high residue loading rates for the metals. The soil metal export associated with solid phase particle

erosion is one to two orders of magnitude greater than the other mass export rates for the two metals. The opposite is the case for the explosives, which are much more mobile in water.

There are essentially no differences between Tests 9 and 2 in computed aquifer concentrations for all five MCs. The sediment peak concentrations for the two explosives are slightly greater for Test 9 compared with Test 2. For example, the sediment peak concentration for RDX is 0.044 ppb for Test 9 compared with 0.038 for Test 2. However, the sediment peak concentrations at year 100 for the metals are substantially higher for Test 9 compared with Test 2. For example, the sediment peak concentration for lead is 14,200 ppb for Test 9 compared with 2,560 for Test 2. The effect on copper is even more pronounced. The sediment peak concentration for copper at year 100 is 1,590 ppb for Test 9 compared with 24.4 ppb for Test 2, or about a factor of 65 greater.

It is interesting that the peak sediment and water concentrations for the metals occur at about year 100 for Test 9, whereas it takes about 600 years for them to peak with Test 2. This change from Test 2 to Test 9 is due to the solid phase particle erosion, which has a profound effect on increasing the metals export rate from soil.

The rather high sediment concentrations for the metals coincide with much higher surface water concentrations as well. The peak dissolved lead concentration in surface water for Test 9 is 3.6 ppb, which is greater than the protective ecological benchmark of 2.5 ppb. The peak dissolved copper concentration in surface water for Test 9 is 3 ppb, which is a third of the protective benchmark of 9 ppb. In conclusion, turning on the solid phase particle erosion is quite important for metals but has little significance for explosives and other relatively water-mobile MCs.

**Test 10**

Test 10 had the same conditions as Test 2 above but with each MC's initial, solid-phase, particle diameter reduced ten-fold. This diameter is actually the initial mean particle diameter of MC residue loaded onto the AOI and is set for each MC on the Fate/Transport Parameters screen of the soil model UI. The diameters were changed from 12,000 to 1,200 μm for RDX and TNT, from 500 to 50 μm for lead, and from 5,000 to 500 μm for copper. Particle diameter is not required for perchlorate since it is miscible and dissolves into water instantly.

Decreasing the initial particle diameter has the effect of increasing the dissolution rate, and making MCs more mobile in water. Thus, the soil peak concentrations are less when comparing Test 10 results with those of Test 2 for all MC except perchlorate, which is the same since it is miscible. There is essentially no difference in Test 10 and Test 2 soil concentrations for copper and little difference for lead because of their low solubility and high $K_d$ values. Although the soil total (solid and non-solid phase mass) concentration for the metals are about the same for Tests 10 and 2, the non-solid phase mass is about an order of magnitude greater for Test 10 compared with Test 2, while the solid phase mass was about an order of magnitude lower. The soil total concentrations of the two explosives are more sensitive to changes in particle diameter. Their soil peak concentrations were reduced by about a factor of 6.

Decreasing soil concentration and solid phase mass coincide with increasing soil export fluxes, which should increase receiving media concentrations. Aquifer peak concentrations at the receptor well are increased for the two explosives when comparing Test 10 to Test 2. The increase for RDX is about a factor of 1.5, while that for TNT is about a factor of 1.1.

The increases in surface water and sediment concentrations are more substantial. The sediment peak concentration for RDX in Test 10 is about double that in Test 2, or 0.062 ppb, but the amount of increase for TNT is less (0.36 versus 0.33 ppb). The increase in sediment concentrations for the metals is very pronounced. For example, the sediment peak concentration at year 100 for lead is 14,600 ppb for Test 10 compared with 2,560 ppb for Test 2, or nearly a sixfold increase. The increase for copper is almost ten-fold. Similar increases are exhibited for the surface water concentrations. For example, the dissolved concentration of lead in surface water increases from a peak of 0.8 ppb in Test 2 to 4.23 ppb in Test 10, thus exceeding the protective ecological health benchmark of 2.5 ppb, which was not exceeded for Test 2.

The overall effect of decreasing solid phase particle diameter is to increase MC dissolution rates and mobility in water. These changes result in lower soil concentrations and greater aquifer concentrations for relatively mobile MCs and greater surface water and sediment concentrations for all MCs. The less mobile MCs, such as metals, exhibit a greater increase in surface water and sediment concentrations, as particle diameter is reduced.

**Test 11**

Test 11 was identical to Test 10 except that the solid phase particle diameters were increased tenfold. Thus, the diameters were changed to 120,000 μm for RDX and TNT, to 5,000 μm for lead, and to 50,000 μm for copper.

Increasing the particle diameter has the inverse effect of decreasing it, but the changes are nonlinear for the different MCs and media. For example, the aquifer peak concentration of RDX for Test 10 is about double that of Test 2, but the result for Test 11 is about sixfold less than that of Test 2. Aquifer peak concentration for TNT is about fourfold less for Test 11 compared with Test 2. The explosives do not exceed protective health benchmarks for Test 11, whereas they do for Test 2. The surface water and sediment peak concentrations decrease about the same amount as the aquifer concentrations when comparing Test 11 against Test 2. The surface water and sediment peak concentrations for the metals are about tenfold lower for Test 11 compared with Test 2.

It is concluded that receiving media concentrations are sensitive to the solid phase particle diameter of MC residue that is input for the Tier 2 soil model. Tenfold changes in the diameter can result in tenfold changes in media concentrations.

**Test 12**

Test 12 had the same conditions as Test 2 above but with non-zero degradation rates for RDX and TNT. The degradation half-life in soil for the aqueous dissolved phase for RDX and TNT was set to 90 days or 0.25 year. The half-life in soil of the aqueous adsorbed phase for each explosive was set to 1.0E20, which is essentially no degradation, the same as for the Test 2 and baseline conditions. The soil model presently does not allow for degradation of the solid phase MCs. There was no degradation in the other media (vadose, aquifer, surface water and surface water sediments), the same as for the Test 2 and baseline conditions.

Soil total concentrations for the two explosives are almost identical for Test 12 compared with Test 2. This is because the solid phase mass, which did not degrade, is about two orders of magnitude greater than the non-solid phase mass (of which the dissolved portion did degrade).

The aquifer peak concentrations at the receptor well are about a factor of 1.7 lower for Test 12 compared with Test 2. As a result, the peak concentration for RDX is slightly less than its health benchmark, and TNT is slightly greater than its benchmark for Test 12. Similar decreases (i.e., a factor of about 1.7 lower) occur for surface water and sediments. Degradation decreases media concentrations as expected. Allowing degradation in other media, such as groundwater, also contributes to reducing exposure concentrations.

**Test 13**

Test 13 had the same conditions as Test 2 above but with water solubility in the soil layer of the two metals increased by a factor of 10. Thus, the solubility values of lead and copper were set to 22.4 and 5.0 mg/L, respectively. Solubility is set on the Chemical-Specific Properties tab of the soil model UI.

Increasing solubility should increase the dissolution rate resulting in more mobility in water. This change caused slightly lower soil total concentration for lead but resulted in little to no change for copper. A much greater change can be observed for lead concentration in sediment. The computed peak concentration for lead in sediment increases from 2,560 ppb for Test 2 to 14,600 ppb (or almost sixfold) for Test 13 due to the tenfold increase in lead solubility. An almost tenfold increase occurs for copper. Similar increases occur for surface water when comparing results of Test 13 with Test 2. Peak dissolved lead concentration in water at year 100 of 4.23 ppb for Test 13 exceeds the protective ecological health benchmark of 2.5 ppb, whereas this benchmark is not exceeded for Test 2. As expected, increasing MC solubility increases receiving media concentrations.

**Test 14**

Test 14 had the same conditions as Test 2 above but with cylindrical solid phase particles assumed for lead and copper, which could be a reasonable choice for bullets. Spherical and cylindrical particle shapes can be selected on the Fate/Transport Parameters tab of the soil model UI. Making this selection also requires inputting the cylinder length (μm). The same diameter was kept for lead and copper as in Test 2 (i.e., 500 and 5,000 μm, respectively). A cylinder length of 5 mm (5,000 μm) was input for both metals; thus, the cylinder length was 10 times the particle diameter for lead and equal to the particle diameter for copper.

The soil concentrations for the two metals are the same for Test 14 as for Test 2. The sediment peak concentration at year 100 is about a factor of 2.4 lower for lead in Test 14 compared with Test 2. However, the sediment concentrations are the same for copper in Test 14 compared with Test 2. Dissolution rates are lower for lead when comparing Test 14 (where the cylinder length is 10 times greater than the diameter) with Test 2. Dissolution rates for copper are the same for Test 14 (where the cylinder length is the same as the diameter) compared with Test 2.

Although more sensitivity testing of cylinder length is warranted, it appears that the model results are insensitive to whether particles are declared as spheres or cylinders as long as the cylinder length is about the same as the diameter. If the length is much larger than the diameter, then dissolution rates are decreased as well as receiving media concentrations.

**Test 15**

Test 15 had the same conditions as Test 2 above but with changes in the vadose zone thickness and its saturated hydraulic conductivity. The thickness of the vadose zone layer was reduced by half to 3 m, and the saturated hydraulic conductivity was doubled to 1.24 m/day. These two changes were made to cause a more rapid transmission of MCs from soil to aquifer. These inputs are specified on the Characteristics tab of the vadose model UI. It is noted that the vadose zone is not included in Tier 1 of TREECS, since Tier 1 assumes steady state.

As anticipated, the conditions for Test 15 do not alter any of the results for soil, surface water, or sediment compared with Test 2 results. It was expected that only aquifer results might be affected. Only very subtle effects are exhibited for aquifer concentrations at the receptor well for RDX and TNT. For example, the aquifer peak TNT concentration occurs 7 years sooner for Test 15 compared with Test 2 and has a peak value of 3.91 ppb for Test 15 compared with a peak of 3.88 ppb for Test 2. In conclusion, the results for the Fort A.P. Hill application are relatively insensitive to the vadose zone model input values for vadose zone thickness and saturated hydraulic conductivity.

**Summary of sensitivity tests**

As with Tier 1, the MC residue loading rates are critically important regarding the resulting concentrations in receiving media since receiving

media concentrations vary linearly with residue loading rate. Additionally, the duration of residue loading is very important for Tier 2, which is not a factor in Tier 1 due to the steady-state assumptions of Tier 1. With the inclusion of the time domain in Tier 2, the timing and duration of loadings becomes an important factor that can be used to manage ranges to avoid exceedence of protective health benchmarks.

Soil interflow causes a diversion in loading fluxes from vadose zone to surface water, causing higher surface water and sediment concentrations. Likewise, groundwater discharge to surface water increases surface water and sediment concentrations, but these increases occur much later, resulting in a second peak in surface water and sediment concentrations associated with the slower groundwater movement. These effects are manifested primarily for the more water-mobile MCs (RDX, TNT, and perchlorate), and effects of groundwater discharge of metals are undetectable. The MC concentrations in the aquifer at the receptor well do not change with groundwater discharge since a diversion of aquifer mass flux does not affect aquifer concentrations. It is important to run the models long enough to determine the effects of groundwater discharge, which can require runs of hundreds of years or longer.

Munitions constituents that are relatively mobile in water (i.e., low soil $K_d$ values) are insensitive to specification of the active soil layer thickness, whereas relatively immobile constituents (i.e., high soil $K_d$ values) respond almost linearly and inversely to the input thickness. Thus, halving or doubling the active soil layer thickness tends to nearly double or halve the receiving surface water and sediment concentrations for metals. The active soil layer thickness should be treated as an uncertain variable for more immobile MCs, such as metals.

The AOI surface area linearly and inversely affects computed soil concentrations of MCs and water infiltration and percolation flow rate from soil, but it does not affect the soil mass flux exports to surface water and groundwater, nor does it affect receiving surface water and sediment concentrations of MCs. Aquifer concentrations are inversely affected by AOI surface area input; thus, a decrease in the input surface area will increase the computed well concentration for the same infiltration/percolation rate and MC mass flux to groundwater. The effect of surface area is highly nonlinear such that the increase in aquifer concentrations greatly diminishes and asymptotically

approaches a limit as surface area is greatly reduced. AOI surface area is an important input parameter for MCs that easily migrate to groundwater.

Turning on solid phase particle erosion has little to no effect on computed soil and aquifer concentrations for all five MCs. However, activating this feature is quite important for the effect on metal concentrations in surface water/sediment, while it has little significance for explosives and other relatively water-mobile MCs. Turning on this feature increased receiving surface water and sediment concentrations by one to two orders of magnitude for lead and copper.

Receiving media concentrations are sensitive to the solid phase particle diameter of MC residue that is input for the Tier 2 soil model. MC dissolution rates and mobility in water increase as the average initial solid phase particle diameter decreases. These changes result in lower soil concentrations and higher aquifer concentrations for relatively mobile MCs and greater surface water and sediment concentrations for all MCs. The less mobile MCs, such as metals, exhibit a greater increase in surface water and sediment concentrations as particle diameter is reduced. Similarly, increasing particle diameter has the inverse effect on mobility and receiving media concentrations. Tenfold changes in diameter can result in about tenfold changes in media concentrations.

Allowing MC degradation in soil for the two explosives reduces receiving media concentrations about equally for each medium. A soil half-life of 90 days reduced media peak concentrations by about a factor of 1.7. Degradation can also occur in the receiving media and will reduce the media concentrations even further, but this feature was not examined during sensitivity testing.

A tenfold increase in the solubility of the two metals causes nearly a tenfold increase in surface water and sediment concentrations. Thus, as expected, MC solubility is an important input.

Model results are insensitive to whether particles are declared as spheres or cylinders, as long as the cylinder length is about the same as the diameter. If the length is much larger than the diameter, then dissolution rates are decreased as well as receiving media concentrations. The conservative approach is to treat MC residue particles as spheres.

The results for the Fort A.P. Hill POC application are relatively insensitive to the vadose zone model input values for vadose zone thickness and saturated hydraulic conductivity.

Based on the above 15 tests, it is recommended that extra consideration be given to the following inputs and conditions when conducting an application:

- MC residue loading rate and duration.
- Occurrence of soil interflow and groundwater discharge.
- Variations in the input for active soil layer thickness if modeling metals or highly adsorbing MCs and their fate in surface water/sediment.
- Variations in the input for surface area of the AOI if modeling aquifer concentrations of MCs.
- Activating (or not) solid phase particle erosion if modeling metals or other more immobile MCs and their fate in surface water/sediment.
- Variations in the input for average, initial solid phase particle diameter of MC residue.
- Allowing degradation in soil (and perhaps other media) for MCs that can degrade, such as explosives, although zero degradation (very long half-life) is more conservative.
- Variations in the input for MC solubility if it is less certain, such as for metals.

Other input parameters that were not tested as discussed above can affect media concentrations. For example, other testing revealed that a tenfold change in Darcy velocity can result in a tenfold change in aquifer concentration. A 10-percent change in aquifer porosity can result in about a 10-percent change in aquifer concentration. Other inputs not discussed in the sensitivity results above that are highly sensitive, such as Darcy velocity, should be carefully considered during a site application and possibly treated as uncertain within the uncertainty analyses.

## Testing of the CMS

All of the tests discussed in this report thus far were conducted using the RECOVERY model for surface water and sediment. TREECS also offers the option of using the Contaminant Model for Streams (CMS) for surface water and sediment. A test was conducted to ensure that this option functions properly or as planned.

The conditions of Test 2 were repeated except with CMS used for White Lake rather than RECOVERY. The inputs for CMS were specified to conform as much as possible to the White Lake conditions used for RECOVERY and discussed in Chapter 4 of this report and in the Tier 1 POC application report (Dortch et al. 2010). Most of the inputs were the same as the RECOVERY inputs except where additional information was required for the more detailed geometrical inputs for this model, such as reach length and width. The White Lake length of 1,500 m was represented with 15 nodes, with each node being 100 m long. A lake width of 50 m and depth of 1 m were input to the model. The selection of a time step of 0.1 yr was somewhat arbitrary since CMS is unconditionally stable, but a small enough time step was chosen to help ensure adequate temporal resolution in the results. The dispersion coefficient of 2 m²/sec is fairly representative of small stream conditions.

The background flow at the point of entry (headwater of the modeled reach) was set to 44,006,573 m³/yr to account for the fact that the total flow, which includes the background flow plus the AOI runoff flow, needed to equal the total flow used with RECOVERY. The flow used with RECOVERY was 47,304,000 m³/yr, and the AOI runoff flow is 3,297,427 m³/yr. Thus, the difference is the background flow of 44,006,573 m³/yr.

The sediment-water partitioning coefficients for the explosives and perchlorate and the volatilization rates for the explosives were computed by the CMS model UI. These computed values were very close to the values computed by the RECOVERY UI. The mass transfer rates across the sediment-water interface computed by the CMS UI were the same order of magnitude as those computed by the RECOVERY UI, but the values were different. For example, the values computed for RDX by CMS and RECOVERY were 3.63E-3 and 2.11E-3 m/day, respectively. The sediment burial rate computed by the CMS UI was identical to that computed by the RECOVERY UI. All CMS input values are summarized in Table 16.

The results computed by CMS for Test 2 conditions are very similar to those computed by RECOVERY for Test 2. The sediment and water concentrations for RDX, TNT, and perchlorate are practically identical when comparing the two sets of results. There are slight differences in the two model results for the metals. Both metals have slightly higher concentrations at the end of the 100-year simulation for CMS compared with results from RECOVERY. For example, the sediment peak concentration at year 100 for

Table 16. Values of input parameters for CMS used in the Tier 2 POC application for Test 2 conditions.

| Parameter Name | Units | Description | Value |
|---|---|---|---|
| System Parameters | | | |
| Number of segments | NA | Number of computational segments in the modeled stream reach | 15 |
| Segment length | m | Length of each computational segment | 100 |
| $\Delta t$ | yr | Model time step | 0.1 |
| $T_p$ | yr | Total period of time for the simulation | 100 |
| $D_x$ | m²/sec | Longitudinal dispersion coefficient | 2 |
| TSS | mg/L | Total suspended solids concentration in the water column | 100 |
| h | m | Depth of the active benthic sediment layer | 0.07 |
| $\rho_s$ | g/L | Dry sediment particle density | 2,650 |
| $\phi$ | fraction | Sediment porosity | 0.7 |
| $f_{oc}$ water | fraction | Fraction organic carbon in solids (water column) | 0.01 |
| $f_{oc}$ sediment | fraction | Fraction organic carbon in solids (sediment) | 0.01 |
| T | deg C | Water and sediment mean temperature | 20 |
| W | m/sec | Mean wind speed at 10 m above surface | 6 |
| Hydraulic Parameters | | | |
| X | km | Usage location, i.e., distance downstream from the upstream boundary to the location of interest | 1,500 |
| Geometric option | NA | Select option of either entering stream width and depth or entering cross-sectional area | Used width and depth |
| B | m | Stream constant top width for option of entering stream width and hydraulic depth | 50 |
| H | m | Stream constant hydraulic depth for option of entering stream width and hydraulic depth | 1 |
| Cross-sectional area option | NA | For option of entering cross-sectional area, includes option of either entering a constant value for cross-sectional area or entering a function related to flow rate | NA |
| A | m² | Constant cross-sectional area of the flow for option of entering cross-sectional area | NA |
| a | NA | Parameter in the function $A = aQ^b$ for option of entering a function for cross-sectional area as related to flow | NA |
| b | NA | Parameter in the function $A = aQ^b$ for option of entering a function for cross-sectional area as related to flow | NA |

| Parameter Name | Units | Description | Value |
|---|---|---|---|
| c | NA | Parameter in the function $H = cA^d$ for option of entering a function for hydraulic depth as related to flow cross-sectional area | NA |
| d | NA | Parameter in the function $H = cA^d$ for option of entering a function for hydraulic depth as related to flow cross-sectional area | NA |
| Q | m³/yr | Constant background stream flow rate (e.g., annual mean flow) at the head of the reach (without any flow from the AOI) | 44,006,573 |
| Constituent Parameters | | | |
| $C_i$ | mg/L | Constant constituent background concentration in stream at the head of the reach | 0. |
| $C_{bi}$ | mg/kg | Initial constituent concentration in the sediment bed | 0. |
| $k_{dw}$ | day$^{-1}$ | Decay rate of dissolved phase in water column | 0. |
| $k_{pw}$ | day$^{-1}$ | Decay rate of particulate phase in water column | 0. |
| $k_{db}$ | day$^{-1}$ | Decay rate of dissolved phase in sediment bed | 0. |
| $k_{pb}$ | day$^{-1}$ | Decay rate of particulate phase in sediment bed | 0. |
| $K_{ow}$ | ml/ml | Constituent octanol-water partition coefficient | RDX: 7.41 <br> TNT: 39.8 <br> Lead: NA <br> Copper: NA <br> KClO$_4$: 6.6E-8 |
| $K_{dw}$ | L/kg | Constituent sediment-water partition coefficient in water column | RDX: 0.046 computed <br> TNT: 0.246 computed <br> Lead: 4,000 input <br> Copper: 600 input <br> KClO$_4$: 4.07E-10 computed |
| $K_{db}$ | L/kg | Constituent sediment-water partition coefficient in sediment bed | RDX: 0.046 computed <br> TNT: 0.246 computed <br> Lead: 4,000 input <br> Copper: 600 input <br> KClO$_4$: 4.07E-10 computed |

| Parameter Name | Units | Description | Value |
|---|---|---|---|
| $k_v$ | m/day | Constituent volatilization rate | RDX: 1.41E-3 computed<br>TNT: 1.0E-2 computed<br>Lead: 0.0 input<br>Copper: 0.0 input<br>$KClO_4$: 0.0 input |
| $V_d$ | m/day | Constituent mass transfer rate across the sediment-water interface resulting from diffusion of dissolved constituent (computed by the model user interface) | RDX: 3.63E-3<br>TNT: 3.57E-3<br>Lead: 3.80E-3<br>Copper: 8.35E-3<br>$KClO_4$: 4.97E-3 |
| MW | g/g-mol | Constituent molecular weight | RDX: 222.1<br>TNT: 227.1<br>Lead: 207.0<br>Copper: 63.55<br>$KClO_4$: 138.5 |
| $D_m$ | $cm^2$/sec | Constituent molecular diffusivity in water | RDX: 7.10E-6<br>TNT: 6.36E-6<br>Lead: 9.45E-6<br>Copper: 7.33E-6<br>$KClO_4$: 6.00E-6 |
| $H_e$ | atm-$m^3$/g-mol | Constituent Henry's law constant | RDX: 6.31E-8<br>TNT: 4.57E-7<br>Lead: 0<br>Copper: 0<br>$KClO_4$: 0 |
| Sedimentation Parameters | | | |
| $V_s$ | m/yr | Suspended sediment settling rate | 36 |
| $V_b$ | m/day | Bed sediment burial rate | 1.24E-5 computed |
| $V_r$ | m/yr | Bed sediment resuspension rate | 1.0E-20 |

lead using CMS is 28.3 ppb compared with 24.4 ppb with RECOVERY. The surface water concentrations are practically identical for all five MCs between the two tests. The differences in the sediment metal concentrations between the two model results are probably due to the differences in the sediment-water column mass transfer rates used by the models. The location of the CMS concentration results discussed above is the end of the White Lake reach.

It is not surprising that the results from CMS are very close to those for RECOVERY since White Lake is a rather small lake of relatively short length. The two models should give comparable results when the water body

is of short reach, and the water residence time is small. The residence time or reach travel time for the White Lake conditions is 0.57 day. The results of CMS are more prone to differ from those of RECOVERY for long, narrow water bodies, such as rivers. CMS results do exhibit a slight gradient of decreasing sediment and water concentrations along the length of the lake in the downstream direction. An example of this slight concentration gradient is shown in Figure 40 for lead.
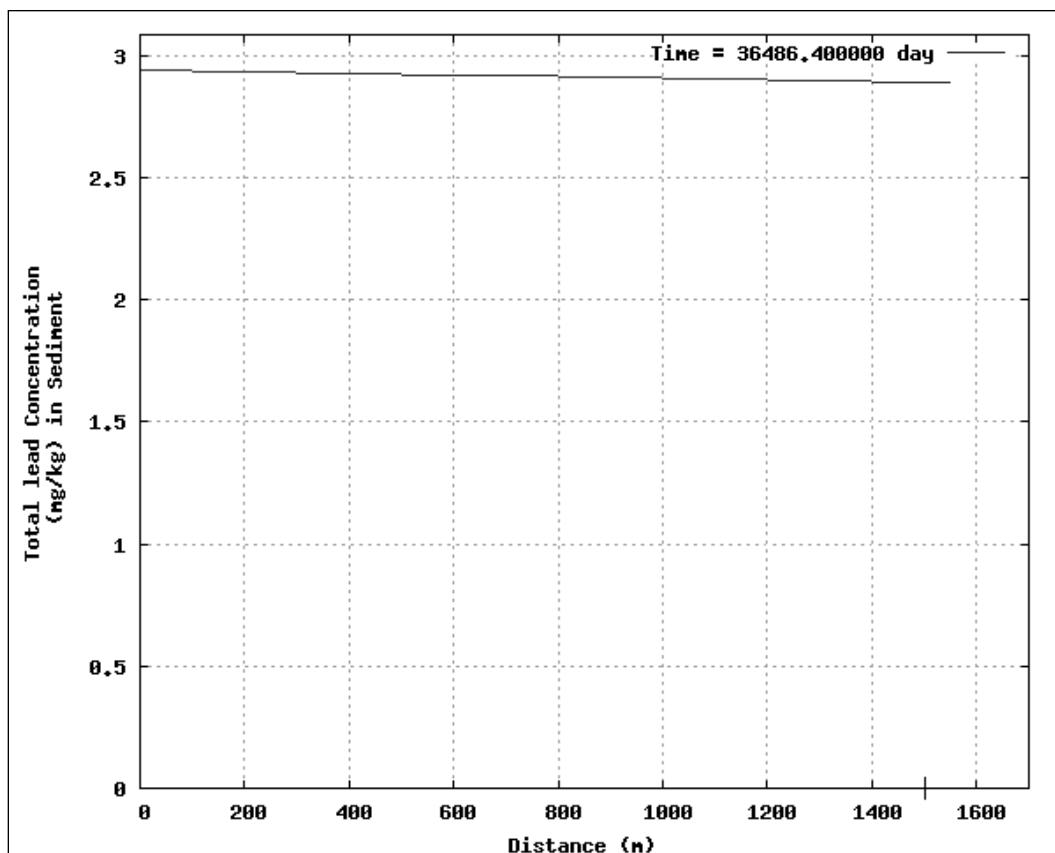


Figure 40. Lead total concentration in sediment versus distance along White Lake from headwater to outlet computed by CMS for Test 2 conditions.

## Testing Tier 2 soil model against laboratory data

A study of leachability and surface runoff of heavy metals from six soils was conducted by Larson et al. (2005) using laboratory rainfall lysimeter test cells. The results for lead obtained from the control test cell (i.e., the test without phosphate amendment) for the silty sand B soil was used for testing the Tier 2 soil model. This model test was conducted to see how well the model would perform for predicting the leached dissolved lead mass and runoff total lead mass. The description and results of this testing are presented in Appendix B.

The summary of results is as follows. The computed dissolved lead leachate was less than observed by a factor of 2 to 3, but this could be a result of using an assumed lead solubility that is lower than actually occurs for the chemistry of the test soil. It is also suspected that very small solid phase lead particles may have been passed with the leachate, which is a pathway the model does not simulate. Only dissolved phase MCs can move with leachate in the model.

The computed and observed total lead values in the runoff are of the same order of magnitude. The runoff lead is mostly solid phase lead particles according to the model. This seems reasonable since the 16-week test period was probably not long enough to generate much lead corrosion and dissolution, which are required to feed the other soil export processes.

It is possible for very small solid phase metal particles, or colloidal metal, to exist in SAFR soils, and such colloidal material can move as if it is dissolved. To handle such conditions, the Tier 2 soil model should be modified to include an additional term to account for solid phase mass that is small enough to function as dissolved mass. The greatest difficulty in applying such a revised model will be estimating the fraction of solid phase mass that is colloidal size.

## Testing the sensitivity and uncertainty feature

TREECS includes a module for conducting a formal and quantitative sensitivity and uncertainty analysis using Monte Carlo simulation with Latin hypercube sampling. The sensitivity and uncertainty (S/U) feature of TREECS was tested using the conditions of Test 2. The more sensitive input parameters discussed in the previous section titled "Sensitivity Testing" were treated as uncertain for this testing. However, the modeling was restricted to two MCs, RDX and lead. These two MCs were selected because they span the types of MCs that can occur (low and high $K_d$, organic and inorganic, relatively fast and slow dissolution, etc.). Additionally, potential health concerns are associated with each of these two MCs for this POC application (computed RDX concentrations exceed human health protective benchmarks in groundwater and lead exceeds ecological health protective benchmarks for dissolved concentration in surface water). Limiting the number of MCs in the analysis also greatly reduces the length of time required to run the Monte Carlo simulations. TNT also exceeds its health benchmark for groundwater, but TNT is expected to degrade much more rapidly than RDX.

The uncertain inputs selected were:

- AOI surface area (which affects RDX concentration in groundwater).
- AOI soil active layer thickness (which affects lead concentration in surface water).
- Initial particle diameters of the two MCs residue.
- Half-life of aqueous dissolved phase RDX in soil.
- Half-life of RDX in groundwater.
- Solubility of lead.

The half-life of RDX in groundwater was included in the S/U analysis since this is a highly uncertain parameter, and it is known from past experience to have a profound impact on computed aquifer concentrations.

The next task was to develop the statistical distributions for the uncertain input parameters. The type of assumed distribution and the distribution statistics for each uncertainty input parameter are shown in Table 17. The basis of each distribution is explained below.

Table 17. Uncertain parameters, their assumed distribution and statistics.

| Uncertain input parameter | Type of distribution | Lower bound | Mean | Mean of logs | Upper bound | Stand. Dev. | Stand. Dev. of logs |
|---|---|---|---|---|---|---|---|
| AOI surface area, $m^2$ | Normal | 5,387,953 | 10,775,905 | NA | 21,551,810 | 2,693,976 | NA |
| Soil active layer thickness, m | Normal | 0.2 | 0.4 | NA | 0.8 | 0.1 | NA |
| RDX residue initial particle diameter, µm | Log normal | 1,200 | 12,000 | 4.08 | 100,000 | 16,467 | 0.32 |
| Lead residue initial particle diameter, µm | Log normal | 63 | 500 | 2.70 | 6700 | 1,106 | 0.34 |
| RDX aqueous dissolved phase half life in soil, yrs | Log normal | 0.25 | 10 | 1 | 100 | 16.63 | 0.43 |
| RDX half life in groundwater, yrs | Log normal | 10 | 100 | 2 | 500 | 81.7 | 0.28 |
| Lead solubility, mg/L | Log normal | 0.224 | 2.24 | .35 | 22.4 | 3.7 | 0.33 |

The AOI surface area and soil active layer thickness were assumed to vary from half to double their input values for Test 2. The MC residue initial particle diameters were assumed to vary from their approximate minimum to maximum values based on studies by Larson et al. (2005) and Pennington et al. (2005), which resulted in an order of magnitude variation from the means. The half-lives of RDX were varied based upon past modeling experiences with this MC (Dortch et al. 2007) with conservative bounds (i.e., tilted towards lower degradation rates or long half-lives); these bounds also varied almost an order of magnitude from the means. Lead solubility was assumed to vary one order of magnitude from the mean. However, lead solubility was only assumed to vary in soil since this input is not important for groundwater and surface water due to the low concentrations, and the surface water model does not handle precipitation due to concentration saturation.

Five of the six distributions were assumed to be log normal based upon their upper and lower bounds. Since sample populations were not analyzed, it was necessary to estimate the standard deviations using the upper and lower bounds. For the normal distributions the standard deviation was estimated to be the difference in the upper and lower bounds divided by 6. The mean and the standard deviation of the log values of the sample distribution are required as input for the log normal distributions in the S/U module. The mean of the logs was estimated by simply taking the log of the linear mean values shown in Table 17. The standard deviation of the logs was estimated by dividing the difference in the logs of the upper and lower bounds by 6.

The S/U module requires decay rate for soil rather than half-life since the soil model uses decay rate, which is stored in the soil model section of the global input data (GID) file. The Tier 2 soil model UI converts the half-life input into decay rates. Thus, the soil half-lives in Table 17 were converted to the following decay rates ($yr^{-1}$): mean = 0.069, lower bound = 0.0069, and upper bound = 2.77. These decay rates were then converted to the mean of the logs and standard deviation of the logs (-1.159 and 0.43, respectively), as required by the S/U module for a log normal distribution.

Test 2 was originally run with no degradation in soil or groundwater, whereas degradation was active for both media for the S/U analysis. In order to provide a base condition with which to examine the upper and lower confidence limits, it was necessary to rerun Test 2 with the mean

degradation rates (decay rates and half-lives) that were used for the S/U analysis. Thus, half-lives of 10 years and 100 years were used for soil and groundwater, respectively, for the base conditions of Test 2, which will be plotted with the S/U confidence limits. With degradation included, the computed aquifer peak concentration for RDX at the receptor well is 0.37 ppb, which is almost half of the protective health benchmark of 0.61 ppb. The original results for Text 2 (with no degradation) were 0.4 ppb above the RDX benchmark. Almost all of the decrease in aquifer concentration of RDX is due to degradation in groundwater associated with the 100-year half-life rather than the 10-year half-life in soil. Degradation in the vadose zone can be important too, but it usually does not decrease well concentrations as much as degradation in the aquifer.

During the testing of the S/U module, it was found that it is beneficial to have the soil and surface water models run longer than the last time point for determining confidence limits. The last confidence limit time point was set to 100 years; thus, the two models were run for 101 years. This ensured that there was output to compute the confidence limits for the last time point.

The number of Monte Carlo iterations for S/U was set to 500. This S/U simulation required almost 2 hr of CPU time. The computed aquifer concentration of RDX at the receptor well versus time is shown in Figure 41 for Test 2 conditions with degradation of RDX. The 5% and 95% exceedence (the upper and lower 5% confidence limits) associated with the above S/U analysis and the protective health benchmark are also included on the plot. The results show that there is at least a 5% probability that the protective health benchmark for RDX will be exceeded. At the 10% confidence level, the protective health benchmark is still slightly exceeded by the upper band, but at the 15% level, the benchmark is not exceeded. Thus, the benchmark is exceeded between the 10% and 15% uncertainty levels. Inclusion of the confidence bands places bounds on the expected output of the models for reasonable but uncertain inputs. The plots for aquifer concentrations of lead are not shown since the computed concentrations are zero at the receptor well.

The computed surface water dissolved concentration of lead versus time for White Lake is shown in Figure 42 for Test 2 conditions. The 5% and 95% exceedence (the upper and lower 5% confidence limits) associated with the above S/U analysis and the protective health benchmark are also
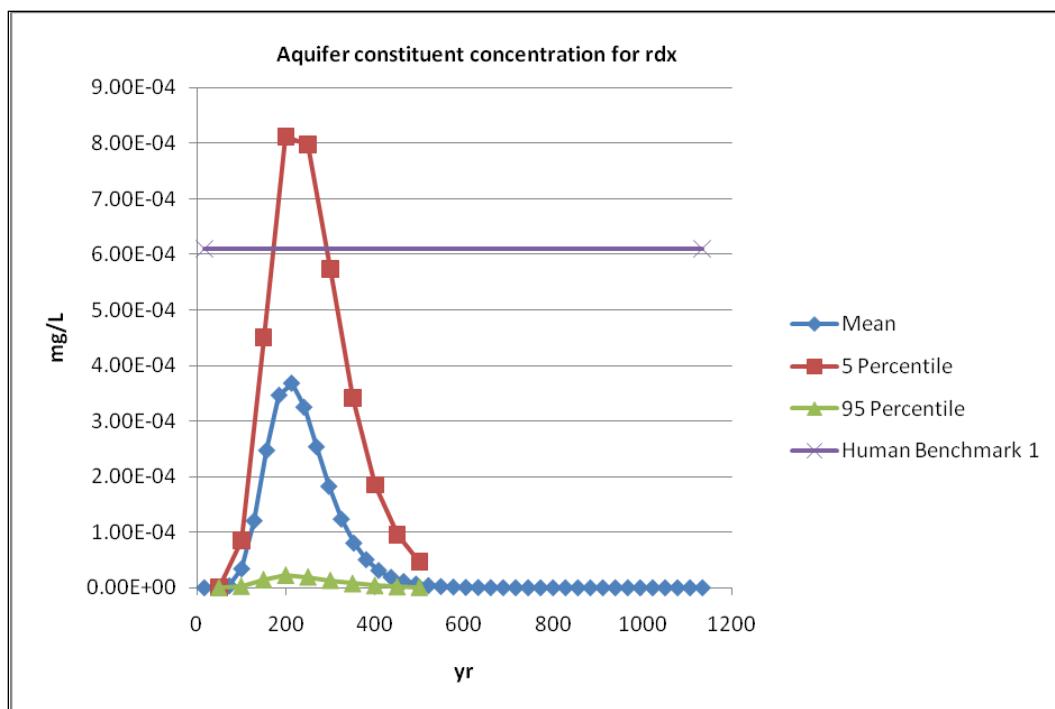
Figure 41. Tier 2 computed RDX mean concentration and uncertainty confidence bands versus time in groundwater at the location of the receptor well for Test 2 conditions with degradation.
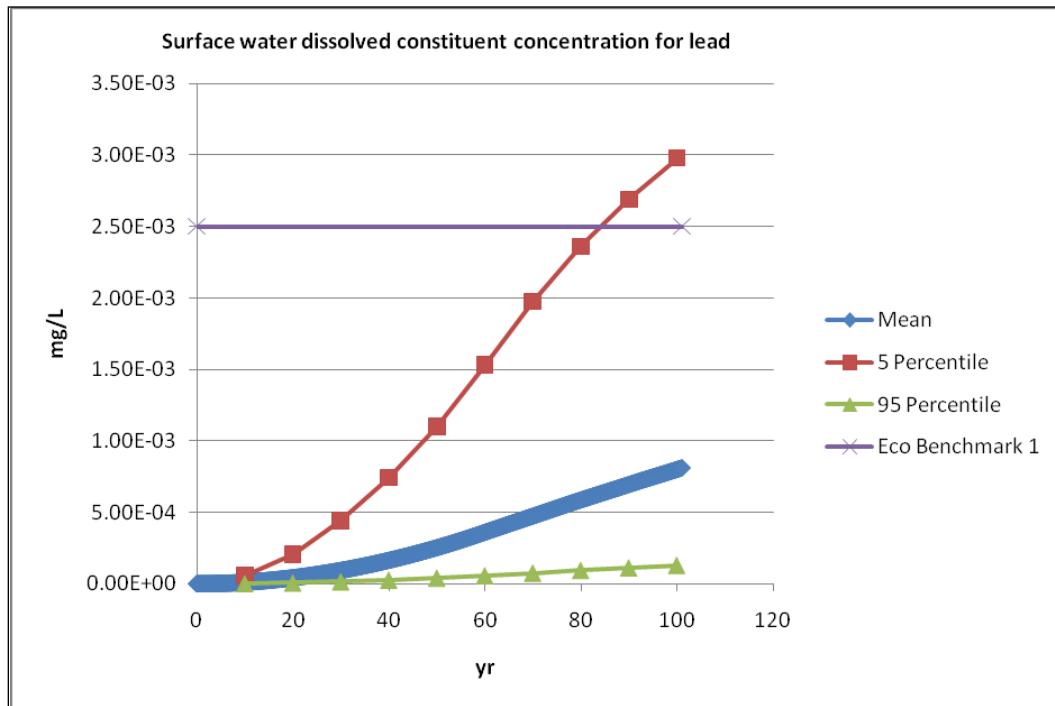


Figure 42. Tier 2 computed water-dissolved mean concentration and uncertainty confidence bands of lead versus time for White Lake using Test 2 conditions and with degradation.

included on the plot. The results show that the protective health bench-mark for lead is slightly exceeded for the upper confidence band after about 80 years. The upper confidence band does not exceed the bench-mark at the 10% confidence level. It is noted that lead concentration in surface water and sediment continues to increase with time as discussed in Chapter 5, eventually peaking after about 600 years. It is assumed for the S/U analysis that only the first 100 years are of interest. The surface water concentrations of RDX are not shown, since they are so much less than the protective health benchmark that their values plot close to zero along the horizontal axis. The plot for lead demonstrates the relatively broad range of expected results when uncertainty is considered.

As stated previously, the above S/U results were conducted with 500 Monte Carlo iterations. The analysis was repeated with only 10 iterations to examine the difference compared with the 500-iteration results. The results of the 10-iteration simulation are shown in Figures 43 and 44 for RDX in aquifer and lead in surface water, respectively. Surprisingly, the results are remarkably similar to those in Figures 41 and 42. This comparison demon-strates that it does not require a large number of iterations to obtain reasonable S/U results, which may be due to the efficiency of the Latin hypercube sampling method that is used with the Monte Carlo simulations. However, when the random seed of the 10-iteration simulation was changed from 5 to 1, the results were noticeably different from those shown in Figures 43 and 44. For example, the upper bound for peak RDX concentra-tion in the aquifer was at about 0.9 ppb rather than 0.64 ppb. Random seeds of 5 and 1 were also tested with the 500-iteration simulation, and they had very little effect on the confidence band results for those two runs. The value for the random seed is important for the 10-iteration simulation but not for the 500-iteration simulation.

The S/U module of TREECS includes the capability to evaluate sensitivity of each uncertain input variable. The sensitivity analysis uses the freeware statistical software package R-Project (http://www.r-project.org). R-Project provides a wide variety of statistical (linear and nonlinear modeling, classical statistical tests, time-series analysis, classification, clustering, etc.) and graphical techniques and is highly extensible. R-Project is linked to output from the Monte Carlo simulations (Castleton et al. 2006). For each selected output variable, a regression analysis is performed that shows the contribution of each sampled input to the multiple R-squared value, thus capturing the degree that each sampled input has on influencing the variability of each selected output.
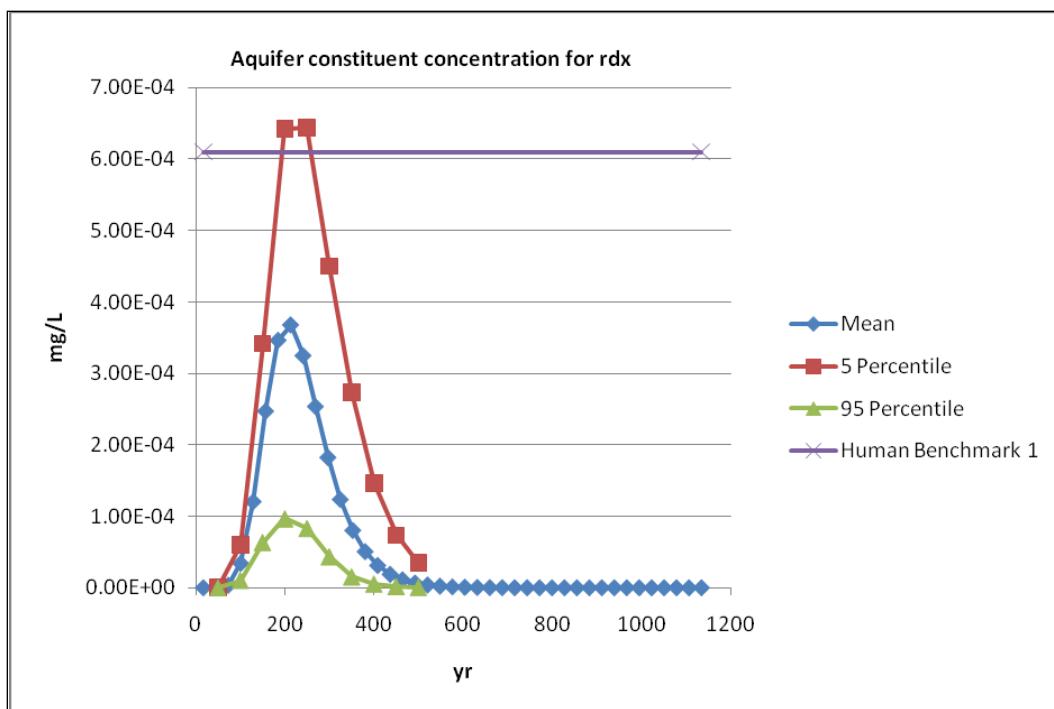
Figure 43. Tier 2 computed RDX mean concentration and confidence bands versus time in groundwater at the location of the receptor well for Test 2 S/U analysis but with 10 Monte Carlo iterations instead of 500.
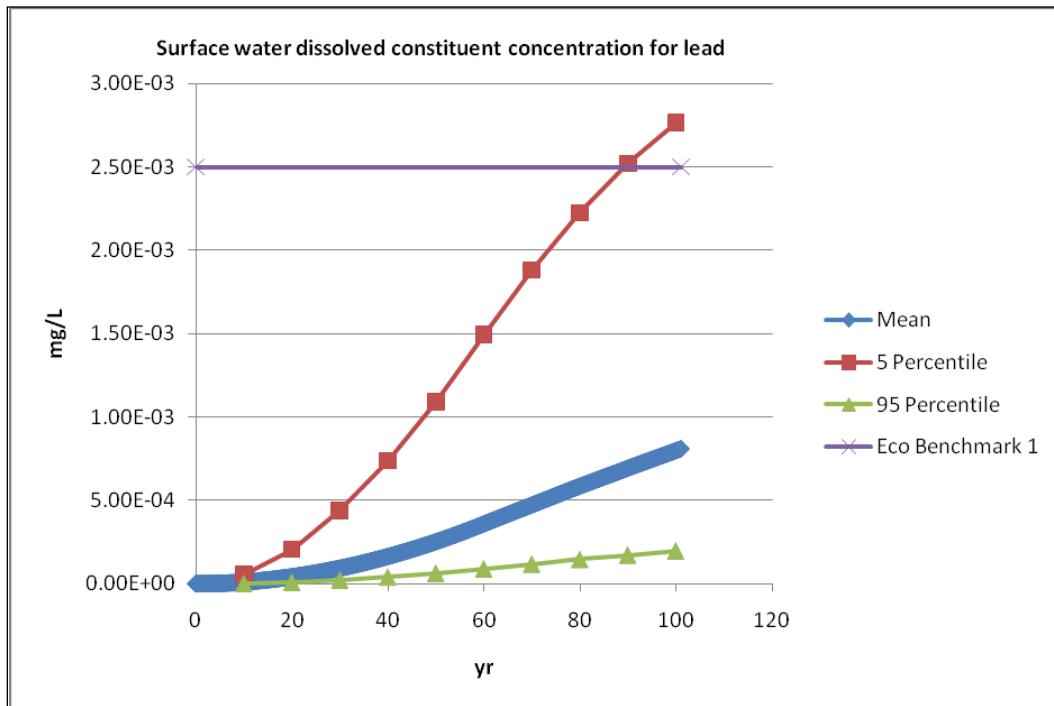


Figure 44. Tier 2 computed water-dissolved mean concentration and confidence bands of lead versus time for White Lake for Test 2 S/U analysis but with 10 Monte Carlo iterations instead of 500.

The sensitivity of inputs is reported for each time point that is output for each selected output variable. The plotted symbols in Figures 43 and 44 represent the output concentrations and corresponding time points. Although the sensitivity does vary over time, the sensitivity at the maximum output concentration is representative of the sensitivity at other times.

The input for the half-life of RDX in groundwater had the most influence on the variability of computed groundwater concentration of RDX, where this input contributed 70 percent of the variability at year 250. The next most sensitive inputs were AOI surface area and initial particle diameter of RDX residue in soil, which contributed about 4 and 6 percent of the variability, respectively. At year 100, the soil active layer thickness, lead solubility, and initial particle diameter of lead residue contributed 5, 41, and 20% of the variability, respectively.

Another S/U run was conducted that included lead $K_d$ for soil and surface water in addition to the other uncertain inputs. The distribution coefficients varied between 100 and 1,000 L/kg (with mean of 597) for soil with a normal distribution and between 400 and 10,000 L/kg (with mean of 4,000) for surface water with a log normal distribution. This run showed that the uncertainty in lead partitioning contributed less than 5% to the variability in dissolved lead concentrations in surface water.

In summary, the half-life of RDX in groundwater is a highly sensitive input affecting groundwater concentrations of RDX. Lead solubility and initial particle diameter of lead are fairly sensitive inputs affecting surface water concentrations of lead. It is noted that only seven inputs were treated as uncertain in this analysis. The partitioning of lead to soil and sediment was also investigated and was found to be relatively insensitive for lead water concentrations compared with lead solubility and initial particle diameter. However, there may be other inputs that affect output more than the inputs investigated, such as Darcy velocity and its effect on aquifer RDX concentrations, for example.

## Testing range management scenarios

Two hypothetical range management scenarios were run to demonstrate the utility of the Tier 2 approach for evaluating range management alternatives to avoid exceedence of protective benchmarks. Test 9 was selected as a basis for evaluation since both aquifer and surface water benchmarks are exceeded in that test. Test 9 was identical to Test 2 except that solid phase

MC particle erosion was activated, which reduced the time for metal concentrations to peak in surface water. The hypothetical management scenarios involved cycling of range use. Both 20- and 10-year cycles were tested. Instead of using the range for 60 years without any interruption, the range use was cycled every 20 and every 10 years. Thus, for the 20-year cycling, the range was used for years 0 to 19 and years 40 to 59, and the range was idle for years 20 to 39 and after year 60. These changes were implemented by altering the munitions use inputs on the Operational Inputs tab of the Site Conditions screen of the TREECS UI. Munitions use for years 0 to 19 and 40 to 59 were identical, and there were no rounds fired for years 20 through 39. The 10-year cycling was simulated the same way except with 10-year cycles of use and non-use. The models were run for 200 years rather than 100 years to help capture any transient features associated with cycling range use. Otherwise, all other inputs were the same as for Test 9.

The computed surface water dissolved lead concentration versus time plot is shown in Figure 45 for the 20-year cycling management scenario. Also shown in this figure for comparison are the results from Test 9 without range cycling and the protective health benchmark. The management scenario results in lower peak concentrations that are slightly greater than the benchmark. The range-use cycling is apparent in the plot as well. Peak concentrations are a little more than 1 ppb (or about 32%) lower for the management scenario compared with Test 9, but this reduction is due to the fact that about 1/3 less lead residue was loaded during the 60 years compared with Test 9.

The aquifer results are not presented with a figure, but the peak RDX and TNT concentrations are reduced from 1.02 and 3.84 ppb to 0.91 and 2.71 ppb, respectively, for the management scenario compared to Test 9. The shape of the concentration versus time curves did not change and is still bell-shaped, similar to the results shown in Figure 34. The management scenario reduced the aquifer peak concentrations for RDX and TNT, but they still exceed their protective human health benchmarks.

The second management scenario was tested where the range use was cycled on 10-year operational intervals rather than 20-year intervals. The 10-year intervals had little to no effect on reducing aquifer peak concentrations for the two explosives compared with the 20-year intervals. This result is probably due to the long response time for this aquifer. Surface water
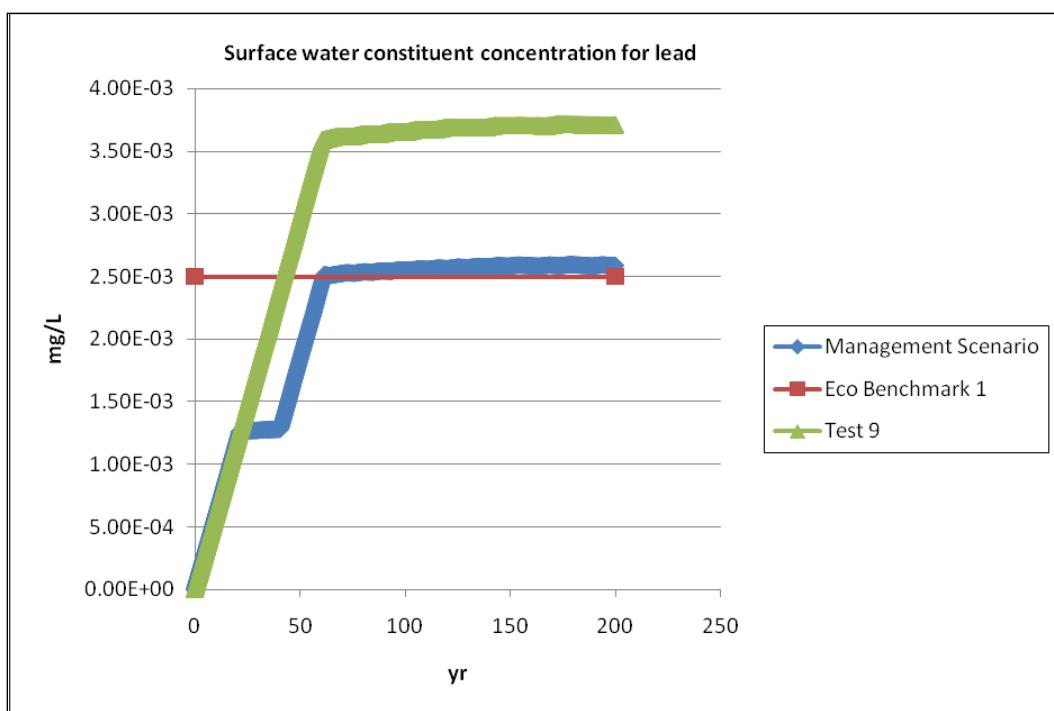
Figure 45. Tier 2 computed water dissolved concentration of lead versus time for White Lake for the range management scenario compared with Test 9 results and the protective health benchmark.

peak concentrations for the two metals are also about the same for the 10-year operational intervals compared with the 20-year intervals. However, the peak concentration in surface water for TNT was about 14% lower with the 10-year operational intervals compared with the 20-year intervals.

Thus, it appears that the time spacing of operational intervals is not important for groundwater at this site due to long response time. However, the time interval spacing does have some effect in surface water for more water-mobile MCs (such as explosives) but not for less mobile MCs (such as metals). The total MC residue mass loaded during the 60 years is more important than the range-use cycling intervals. The total residue mass that was loaded for both management scenarios was about 1/3 less than for Test 9. Range-use cycling interval should be important at sites that have faster natural attenuation and shorter groundwater response times. It is emphasized that these management runs, as well as Test 9, were conducted with no degradation of explosives, and degradation is expected to occur even if at low rates.

# 7  Summary and Recommendations

Tier 2 of TREECS was applied to Fort A.P. Hill, similar to the application
for Tier 1. The Tier 2 POC application addressed questions regarding the
practicality of the Tier 2 approach, and it provided a comparison against
Tier 1 results. Fortunately, the Tier 2 model development was far along
during this testing; thus, it was possible to also test model development
and implementation, which helped find and correct a number of errors,
programming bugs, and unanticipated problems.

It is emphasized that media concentrations are compared to benchmarks
in this report for illustrative purposes only and such comparisons are not
intended to guide decisions for further investigations or actions regarding
potential environmental health concerns. Some of the benchmarks used
for these comparisons may be lower or higher than those used in an actual
assessment. Comparisons of media concentrations with benchmarks are
primarily included to distinguish how results from Tier 2 differ from
results of Tier 1 analyses and to demonstrate how results might be used in
an actual assessment.

The inputs for the Tier 2 POC application are discussed in Chapters 3
and 4. The baseline results for the Tier 2 POC application are discussed in
Chapter 5. The Tier 1 POC application was repeated using updated inputs
as discussed in Chapters 4 and 5 to improve the reasonableness of results
and to make the comparisons between Tiers 1 and 2 more valid. Thus, the
updated Tier 1 POC results are discussed in Chapter 5 as well.

A wide range of sensitivity and other tests were conducted for Tier 2 and
are discussed in Chapter 6. The highlights of all application results are
summarized below, and recommendations are made where appropriate.
Additionally, recommendations for estimating solubility of metals as
discussed in Appendix A are summarized below.

## Tier 1 and baseline Tier 2 comparison

Since perchlorate is miscible and highly mobile in water, it responds nearly
identically for Tier 2 and Tier 1. Perchlorate soil concentrations, soil export
fluxes, sediment concentrations, and water total and dissolved concentra-
tions are almost identical for Tier 1 and Tier 2. All receiving media

concentrations are considerably less with Tier 2 compared to Tier 1 for the other four MCs due to the inclusion of the time domain in Tier 2 with attenuation effects associated with a finite MC loading period, solid phase dissolution, and aqueous phase adsorption. None of the five MCs exceeds protective health benchmarks for any media for the 100-year baseline simulation with Tier 2. Only lead slightly exceeds the surface water ecological benchmark after 600 years of simulation. For Tier 1, RDX, TNT, and lead exceeded the groundwater benchmarks, lead and copper exceeded the sediment benchmarks, lead exceeded the surface water human and ecological benchmarks, and copper exceeded the surface water ecological benchmark.

Lead and copper respond much differently under Tier 2 compared with Tier 1, especially for groundwater. Essentially zero concentrations were computed at the receptor well for thousands of years. The computed surface water and sediment concentrations for the two metals are two to four orders of magnitude less with Tier 2 compared to Tier 1. The explosives concentrations in sediment and surface water were about an order of magnitude lower for Tier 2 compared with Tier 1.

Although RDX and TNT concentrations did not exceed protective benchmarks for groundwater, their concentrations were within the same order of magnitude as the benchmarks. Thus, for different conditions, such as longer loading periods, these two MCs could potentially be a concern for groundwater at this site as demonstrated in sensitivity Test 2.

Overall, the two metals are not expected to ever be a concern in the groundwater of this site, whereas explosives, particularly RDX, could potentially be a concern in groundwater. TNT is less likely to be a concern due to the fact that it usually degrades much faster than RDX. Zero degradation was used for the baseline Tier 2 simulations. Lead is a potential concern for surface water at this site, but such concerns should not occur for many years (centuries). Explosives are not expected to be a concern in surface water and sediments. It is noted that very high loading rates were used for the metals. Lower loading rates were included in the sensitivity tests. Perchlorate is of no concern at this site for surface water or groundwater, since its loadings were estimated to be quite small for this site.

Although the user can input the depth of well intakes below the groundwater table, it is strongly recommended for conservatism (as explained in

Chapter 4) that this input parameter be set to zero. Values other than zero for well depth can result in computed concentrations that are much lower than those that could actually occur.

## Sensitivity tests

As with Tier 1, the MC residue loading rates are critically important regarding the resulting concentrations in receiving media since media concentrations vary linearly with residue loading rates. Additionally, the duration of residue loading is very important for Tier 2, which is not a factor in Tier 1 due to the steady-state assumptions of Tier 1. With the inclusion of the time domain in Tier 2, the timing and duration of loadings can be an important factor that potentially can be used to manage ranges to avoid exceedence of protective health benchmarks.

Soil interflow causes a diversion in loading fluxes from vadose zone to surface water causing higher surface water and sediment concentrations. Likewise, the effect of groundwater discharge to surface water is to increase surface water and sediment concentrations, but these increases occur much later resulting in succeeding surface water and sediment peak concentrations associated with the slower groundwater movement. These effects are manifested primarily for the more water-mobile MCs (RDX, TNT, and perchlorate), and the effects of groundwater discharge of metals are undetectable due to the extremely low metal concentrations in groundwater. The MC concentrations in the aquifer at the receptor well do not change with groundwater discharge since a diversion of aquifer mass flux does not affect aquifer concentrations. It is important to run the models long enough to determine the effects of groundwater discharge on surface water/sediment, which can require runs of hundreds of years.

Munitions constituents that are relatively mobile in water (i.e., low soil $K_d$ values) are insensitive to values specified (within a reasonable range) for the active soil layer thickness, whereas relatively immobile constituents (i.e., high soil $K_d$ values) respond almost linearly and inversely to the input thickness. Thus, halving or doubling the active soil layer thickness tends to nearly double or halve the receiving surface water and sediment concen-trations for metals. The active soil layer thickness should be treated as an uncertain variable for the more immobile MCs, such as metals.

For a constant MC loading to soil, the AOI surface area affects computed soil concentrations of MCs linearly and inversely, but it does not affect the

soil mass flux exports to surface water or groundwater, nor does it affect receiving surface water and sediment concentrations of MCs. Aquifer concentrations are inversely affected by AOI surface area that is input. For the Fort A.P. Hill application, reducing the AOI area by half nearly doubled the RDX aquifer concentrations. As stated above, the mass flux to ground-water does not change as AOI surface area is changed (assuming the loading of MCs to soil is the same). Thus, halving the surface area also halves the site groundwater percolation flow rate. The decrease in percolation flow rate increases the MC flux concentration entering the aquifer below the site, thus resulting in an increase in well concentrations. The effect of AOI surface area on aquifer concentrations is highly nonlinear such that the increase in aquifer concentrations greatly diminishes and asymptotically approaches a limit as surface area is greatly reduced. Regardless, it may be important to consider small AOIs for some range situations where water-mobile MCs are involved to ensure conservative projections for aquifer concentrations.

Activating solid phase particle erosion has little to no effect on computed soil and aquifer concentrations for all five MCs. However, activating this feature is quite important for the effect on metal concentrations in surface water/sediment, while it has little significance for explosives and other relatively water-mobile MCs. Turning on this feature increased receiving surface water and sediment concentrations by one to two orders of magnitude for lead and copper.

Decreasing the average initial solid phase particle diameter of MC residue has the effect of increasing MC dissolution rates and mobility in water. These changes result in lower soil concentrations and greater aquifer concentrations for relatively mobile MCs and greater surface water and sediment concentrations for all MCs. The less mobile MCs, such as metals, exhibit a greater increase in surface water and sediment concentrations as particle diameter is reduced. Similarly, increasing particle diameter has the inverse effect on mobility and receiving media concentrations. Receiving media concentrations are highly sensitive to the solid phase particle diameter of MC residue that is input for the Tier 2 soil model. Tenfold changes in the diameter can result in approximately tenfold changes in media concentrations.

Allowing MC degradation in soil for the two explosives reduces receiving media concentrations about equally for each media. A soil half-life of 90 days reduced media peak concentrations by approximately a factor

of 1.7. Degradation can also occur in the receiving media and will reduce the media concentrations even further, but this feature was not examined during sensitivity testing.

A tenfold increase in the solubility of the two metals causes nearly a tenfold increase in surface water and sediment concentrations. Thus, as expected, MC solubility is an important input, and the metal solubility is one of the most uncertain inputs. Thus, metal solubility should receive much scrutiny and should be assessed with S/U analyses.

Model results are insensitive to whether particles are declared as spheres or cylinders as long as the cylinder length is about the same as the diameter. If the length is much larger than the diameter, then dissolution rates are decreased as well as receiving media concentrations. The conservative approach is to treat MC residue particles as spheres.

The results for the Fort A.P. Hill POC application are relatively insensitive to the vadose zone model input values for vadose zone thickness and saturated hydraulic conductivity. There could be greater sensitivity to these inputs for other site conditions, so this should not be taken as an assumption for all sites.

Based on the 15 sensitivity tests, it is recommended that extra consideration be given to the following eight inputs and conditions when conducting an application:

1. MC residue loading rate and duration.
2. Occurrence of soil interflow and groundwater discharge.
3. Variations in the input for active soil layer thickness if modeling the fate of metals or highly adsorbing MCs in surface water/sediment.
4. Variations in the input for surface area of the AOI if modeling the fate of MCs in groundwater.
5. Activating (or not) solid phase particle erosion if modeling the fate of metals or other more immobile MCs in surface water/sediment.
6. Variations in the input for average, initial, solid phase particle diameter of MC residue.
7. Allowing degradation in soil (and perhaps other media) for MCs that can degrade, such as explosives, although zero degradation (very long half-life) is more conservative.

8. Variations in the input for MC solubility if it is less certain, such as for metals.

Other issues associated with several of the above uncertain input conditions were not considered in this study and may warrant future investigation. Regarding input condition number 5 above, a more mechanistic approach for computing solid phase particle erosion should be explored and tested, such as the Einstein and Brown equations discussed by Dortch et al. (2011). Regarding input condition number 6 above, more sensitivity testing of this input should be conducted to determine if it is worthwhile to implement multiple solid phase particle size classes within the Tier 2 soil model. Adding this feature would require substantial revisions to the soil model code and would increase the input data requirements.

## Testing of CMS

The results from CMS are very close to those for RECOVERY, since White Lake is a rather small lake of relatively short length. The two models should give comparable results when the water body is of short reach, and the water residence time is small. The residence time, or reach travel time, for the White Lake conditions is 0.57 day. The results of CMS are more prone to differ from those of RECOVERY for long, narrow water bodies, such as rivers. CMS results do exhibit a slight gradient of decreasing sediment and water concentrations along the length of the lake in the downstream direction.

## Testing Tier 2 soil model against laboratory data for lead

The description and results of this testing are presented in Appendix B and summarized in Chapter 6. The computed dissolved lead leachate was less than observed by a factor of 2 to 3, but this could be a result of using an assumed lead solubility that is lower than really occurred for the chemistry of the test soil. It is also suspected that very small solid phase lead particles may have passed with the leachate, which is a pathway the model does not simulate. Only dissolved phase MCs can move with leachate in the model. The computed and observed total lead in the runoff is of the same order of magnitude. The runoff lead is mostly solid phase lead particles according to the model. This seems reasonable since the 16-week test period was probably not long enough to generate much lead corrosion and dissolution, which is required to feed the other soil export processes.

If very small, solid phase metal particles, or colloidal metal, exist in SAFR soils, then this colloidal material could potentially move as if it is dissolved. In this case, the Tier 2 soil model could be modified to include an additional term to account for solid phase mass that is small enough to function as dissolved mass. However, the easiest way to represent the additional leached flux due to colloidal metal is to decrease the soil $K_d$ for the metal, which can be done as part of an S/U analysis. The greatest difficulty will be estimating the fraction of solid phase mass that is colloidal size and how that alters the apparent $K_d$ that is required to represent the effect of colloids.

## Testing of S/U

The S/U feature of Tier 2 TREECS was tested for RDX and lead using the Test 2 conditions with the addition of RDX degradation in soil and groundwater. Seven input parameters were treated as uncertain. Mean and the upper and lower 5% confidence bands for results were presented for surface water and aquifer. The S/U feature worked properly as anticipated. It was determined for this test case that very similar results can be obtained with only 10 Monte Carlo simulation iterations compared with 500 iterations, but the value of the random seed becomes very important when few iterations are used. Therefore, it is best to use a sufficiently large number of iterations.

Seven uncertain inputs were selected to evaluate their sensitivity on two outputs, RDX groundwater concentration and dissolved concentration of lead in surface water, and to develop confidence bands on these output concentrations. The half-life of RDX in groundwater was determined to be a highly sensitive input affecting groundwater concentrations of RDX. Lead solubility and initial particle diameter of lead residue are relatively sensitive inputs affecting surface water concentrations of lead. The partitioning of lead to soil and sediment was also investigated as uncertain and was found to be relatively insensitive for lead water concentrations compared with lead solubility and initial particle diameter. However, there may be other inputs that affect output more than the inputs investigated, such as Darcy velocity and its effect on aquifer RDX concentrations.

## Testing range management scenarios

Two hypothetical management scenarios were tested that involved cycling of range use. Test 9 conditions were used, but instead of using the range for 60 years without any interruption, range use was cycled every 20 and every

10 years. For the 20-year cycling, the range was used from years 0 to 19 and years 40 to 59, and the range was idle for years 20 to 39 and after year 60. Range use was cycled every 10 years for the 10-year interval scenario. Range cycling resulted in 1/3 less MC residue total load compared with Test 9.

Computed aquifer receptor well peak concentrations for RDX and TNT were reduced 11 and 29 percent, respectively, for the 20-year cycling compared with Test 9 results. The peak concentration in groundwater associated with the 10-year cycling was no lower than the peak for the 20-year cycling due to the long response times of this aquifer. Computed surface water peak dissolved lead concentration was reduced 32 percent for the 20-year cycling compared with Test 9, but the 10-year cycling did not reduce these peaks any lower than the 20-year cycling results. The reductions in media peak MC concentrations were due mostly to the 1/3 reduction in MC residue loading. However, the 10-year cycling did reduce the TNT peak concentration in surface water about 14 percent lower than the results for the 20-year cycling, which shows that the range-use cycling interval can impact peak concentrations in receiving media.

These tests demonstrated the utility of using TREECS Tier 2 for evaluating the effectiveness of range-use strategies. Although variations in the range-use cycling interval were not found to be highly effective at this site for controlling media concentrations, these variations could be more effective at other sites that have faster natural attenuation where MCs are more mobile.

## Estimating solubility of metals

It was possible to apply Visual Minteq (VM) to estimate lead and copper solubility for Fort A.P. Hill. The approach was to start with background soil conditions and ionic component concentrations in soil and then adjust downward the ionic component concentrations towards values expected in soil pore water to obtain the measured background pH. This was done by exposing the system to atmospheric $CO_2$, allowing solid phase precipitation, and computing pH from mass balance, not mass and charge balance. Ionic concentrations were adjusted until a low charge difference of about 1% was reached. With the adjusted soil pore-water ionic component concentrations, the dissolved metal value was calculated with the following allowances:

1. Addition of solid phase metal.

2.  System open to atmospheric $CO_2$.
3.  Allowance for changing pH while enforcing charge balance.

Spreadsheet models obtained on the Internet from the Stevens Institute of Technology were also used to estimate lead and copper solubility. With pH, TDS, and alkalinity as inputs and with values calculated from VM for these inputs, the Stevens spreadsheet model computed lead solubility of 3.03 mg/L, which is quite close to the value of 2.24 computed by VM. However, it is stressed that the values of pH and alkalinity are different with and without the presence of lead or copper. The metals tend to increase the pH. If the background soil pH of 5.5 is used with an alkalinity of about zero, the spreadsheet model computed a lead solubility of 251 mg/L, or two orders of magnitude greater than that calculated with VM. The spreadsheet model for copper solubility computed a value of 18.4 mg/L using VM results for pH, TDS, and alkalinity. This value is much higher than the copper solubility of 0.5 computed with VM. When the lower background soil pH of 5.5 was used in the spreadsheet model, the computed copper solubility was 440 mg/L. Thus, it is easy to see why it is important to have a more accurate estimate of pH in the presence of lead or copper as provided by VM.

The spreadsheet model will be distributed within the TREECS tools for estimating lead and copper solubility. However, it should be recognized that the spreadsheet model will provide higher solubility estimates than may actually occur although inflated estimates are more conservative for modeling metal fate. Spreadsheet model estimates can be inflated by as much as three orders of magnitude. For this reason, uncertainty analysis for metal solubility should be conducted during the TREECS model applications where solubility estimated with the spreadsheet model is decreased by about two or three orders of magnitude. The two primary reasons for the inflated estimates with the spreadsheet model are that the spreadsheet model does not consider metal precipitation, and the soil-water pH can be greater than the background pH with the presence of lead or copper. Application of VM can be a better alternative to estimating metal solubility, but application of this model requires a fairly good understanding of geochemistry.

## Concluding remarks

Overall, Tier 2 of TREECS performed as expected and was found to provide extremely valuable insight into the fate of MCs on and exported from firing ranges. The inclusion of time in the modeling has a crucial impact on MC

fate, resulting in phasing and attenuation of media concentrations. It is anticipated that training will be required for proper application of Tier 2, but the improved accuracy and other benefits of Tier 2 should far outweigh any training requirements. Although Tier 2 requires substantially more time and data to apply than Tier 1, the benefits of Tier 2 over Tier 1 should prove to be far greater than the additional time and cost to apply it.

# References

Army Environmental Command (AEC). 2009. Personal communication with staff of AEC.

Castleton, K. J., G. Whelan, and B. L. Hoopes. 2006. *FRAMES Software System: Linking to the Statistical Package R.* Report PNNL 16781. Richland, WA: Pacific Northwest National Laboratory.

Clausen, J. L., N. Korte, B. Bostick, B. Rice, M. Walsh, and A. Nelson. 2007. *Environmental assessment of lead at Camp Edwards, Massachusetts, small arms ranges.* ERDC/CRREL TR-07-11. Hanover, NH: U.S. Army Engineer Research and Development Center.

Dortch, M. S., S. Fant, and J. A. Gerald. 2007. Modeling fate of RDX at Demolition Area 2 of the Massachusetts Military Reservation. *J. of Soil and Sediment Contamination* 16(6), 617-635.

Dortch, M. S., J. A. Gerald, and B. E. Johnson. 2009. *Methods for Tier 1 modeling with the Training Range Environmental Evaluation and Characterization System.* Technical Report ERDC/EL TR-09-11. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Dortch, M. S., B. E. Johnson, and J. A. Gerald. 2010. *Proof-of-concept application of Tier 1 modeling approach within the Training Range Environmental Evaluation and Characterization System.* Draft Technical Report ERDC/EL TR-10-19. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Dortch, M. S., B. E. Johnson, Z. Zhang, and J. A. Gerald. 2011. *Methods for Tier 2 modeling within the Training Range Environmental Evaluation and Characterization System.* Draft Technical Report ERDC/EL TR-11-2. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

E.A. Engineering, Science, and Technology, Inc. 2006. *Operational Range Assessment Program, Phase I Qualitative Assessment Report, Fort A.P. Hill, Bowling Green, Virginia.* Draft final report prepared for the U.S. Army Engineer District, Baltimore and the U.S. Army Environmental Command, Sparks, MD.

Fairhall, L.T. 1924. The solubility of various lead compounds in blood serum. *J. of Biological Chemistry*, LX (3), 481-484.

Julien, Pierre Y. 1995. *Erosion and sedimentation.* New York, NY: Press Syndicate of the University of Cambridge.

Larson, S., B. Tardy, K. Rainwater, and J. Tingle. 2005. *Rainfall lysimeter evaluation of leachability and surface transport of heavy metals from six soils with and without phosphate amendment.* Technical Report ERDC TR-05-9, Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Maidment, D. R. (editor in chief). 1993. *Handbook of Hydrology.* New York, NY: McGraw-Hill, Inc.

Pennington, J. C. T. F. Jenkins, S. Thiboutot, G. Ampleman, J. Clausen, A. D. Hewitt, J. Lewis, M. R. Walsh, M. E. Walsh, T. A. Ranney, B. Silverblatt, A. Marois, A. Gagnon, P. Brousseau, J. E. Zufelt, K. Poe, M. Bouchard, R. Martel, D. D. Walker, C. A. Ramsey, C. A. Hayes, S. L. Yost, K. L. Bjella, L. Trepanier, T. E. Berry, D. J. Lambert, P. Dubé, and N. M. Perron. 2005. *Distribution and fate of energetics on DoD test and training ranges: Interim Report 5*. Technical Report ERDC TR-05-2. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

Stumm, W., and J. J. Morgan. 1981. *Aquatic chemistry, an introduction emphasizing chemical equilibria in natural waters.* New York, NY: John Wiley & Sons.

Taylor, S., J. Lever, M. Walsh, M.E. Walsh, B. Bostick, and B. Packer. 2004. *Underground UXO: Are they a significant source of explosives in soil compared to low- and high-order detonations?* Technical Report ERDC/CRREL TR-04-23, Hanover, NH: U.S. Army Engineer Research and Development Center.

U.S. Department of Agriculture (USDA) Soil Conservation Service (SCS). 1983. *National Engineering Handbook*, Section 3, Sedimentation, 2d. ed.

U.S. Environmental Protection Agency (USEPA). 2003. *TRW recommendations for performing human health risk analysis on small arms shooting ranges*. OSWER #9285.7-37, Office of Solid Waste and Emergency Response, Washington, DC.

# Appendix A: Estimating Metal Solubility with Visual Minteq

The equilibrium chemistry modeling software Visual Minteq (http://www.lwr.kth.se/English/OurSoftware/vminteq/ can be used to estimate the reaction products of metals and metal solubility. Visual Minteq was explored for computing water solubility of lead and copper.

## General approach

Visual Minteq (VM), version 2.61, was applied repeatedly to gain an understanding of how to best apply the model to estimate lead and copper solubility. The general recommended approach is described below.

Modeling metal equilibrium chemistry using VM requires specifying the following: available and common ionic components; either a finite or an infinite amount of solid phase metal; either fixed or calculated pH; and calculated ionic strength. After much experimentation with VM, it was concluded that it was better to let the model calculate the pH from mass balance. There is an option to compute pH from mass and charge balance, but this approach did not always produce reliable results. If selecting only mass balance, it is necessary to adjust the input ionic species concentrations to balance charge. Generally, the difference in charge balance should be small, e.g., less than 10%. Using fixed pH also requires balancing the charge, which was very difficult or impossible to accomplish for fixed pH even when using unrealistically high concentrations for various anion components to try to balance unrealistically high dissolved metal concentrations. Additionally, measurements of soil pH over soil depth within firing range berms indicated that pH is elevated near the surface where lead concentration is high, indicating that lead oxidation and carbonation increase pH. Therefore, it seems logical that pH should be allowed to vary and be calculated by the model.

The main screen of the VM user interface is shown in Figure A1. Under the *Parameters* tab, which is on the user interface menu bar of the main screen, ensure that alkalinity is not specified. Specifying alkalinity seems to over-constrain the problem. Also, under *Parameters/Various default settings*, select the options as shown in Figure A2. One of these options is to allow precipitation of over-saturated species during each model iteration.

The system should be at equilibrium with atmospheric $CO_2$, i.e., open to the atmosphere. This is done by clicking the *Gases* tab in the user interface menu bar and making sure that the *Specify fixed CO2 partial pressure* option is chosen and the two default values of 0.00038 atm and 1.0 x atm are in the input boxes. The box to enter as a possibly fixed species should not be checked. Finally, the *Add* button should be clicked on the interface screen so that $CO_2$ is added as a fixed species. The Gases input screen for setting an open atmospheric condition is shown in Figure A3.

The primary cations that affect soil-water chemistry are calcium ($Ca^{+2}$), magnesium ($Mg^{+2}$), potassium ($K^+$), sodium ($Na^+$), hydrogen ($H^+$), and aluminum ($Al^{+3}$), where the first four are base-forming cations, and the latter two are acid-forming cations. Sodium is usually at lower concentrations than calcium and magnesium and has little to no effect on computed pH and alkalinity. Thus, sodium can be left out of the component list for practical purposes. Hydrogen must be in the component list and will be automatically added as a result of computing pH. Aluminum concentrations are generally low compared with other ions, but aluminum can have a pronounced effect by lowering pH and affecting the charge balance.
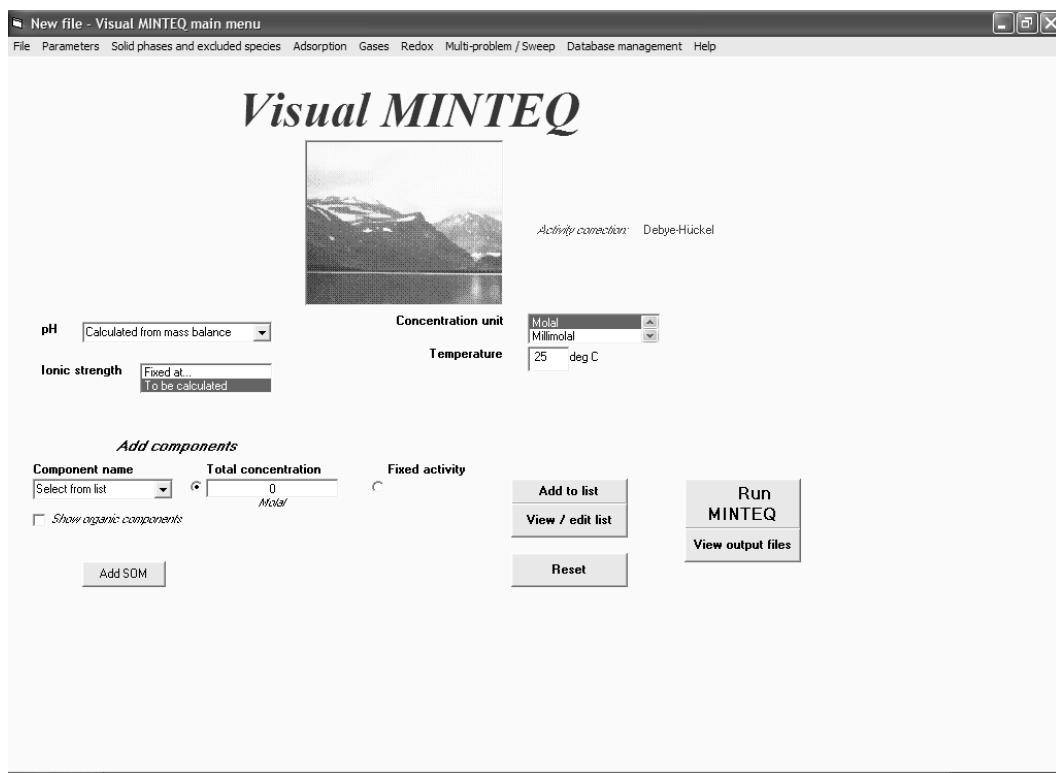


Figure A1. VM main input screen.
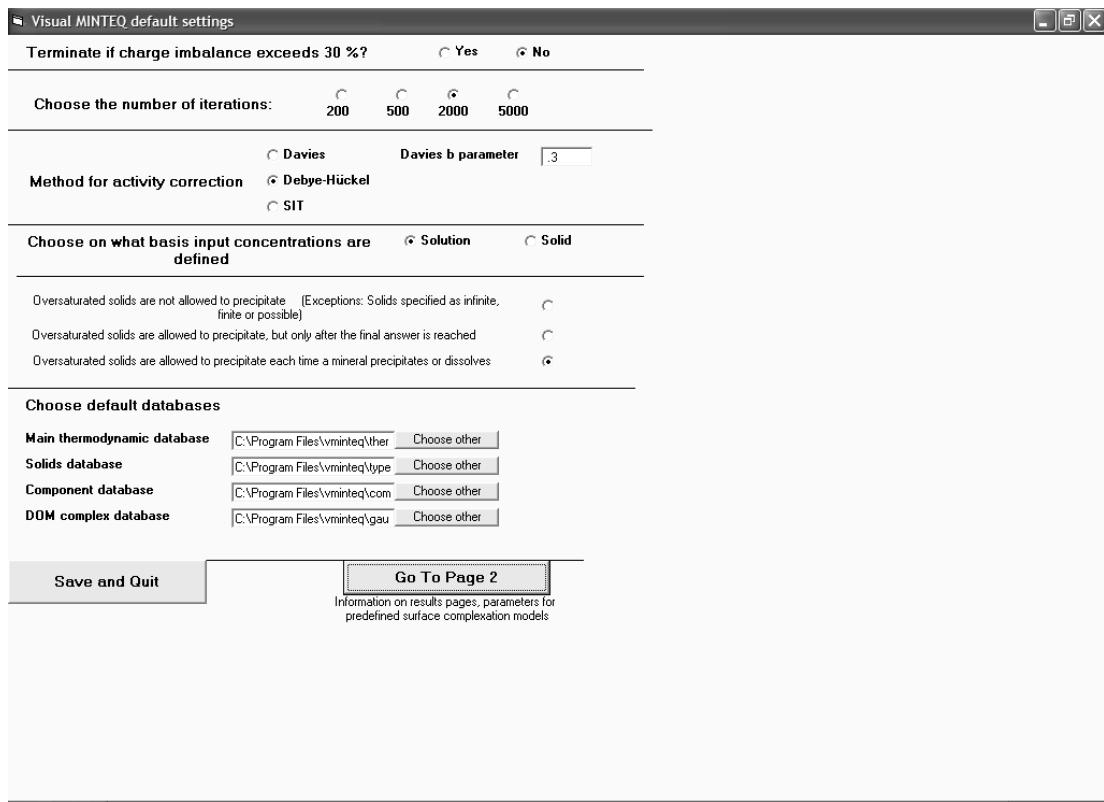
Figure A2. VM various default settings screen.
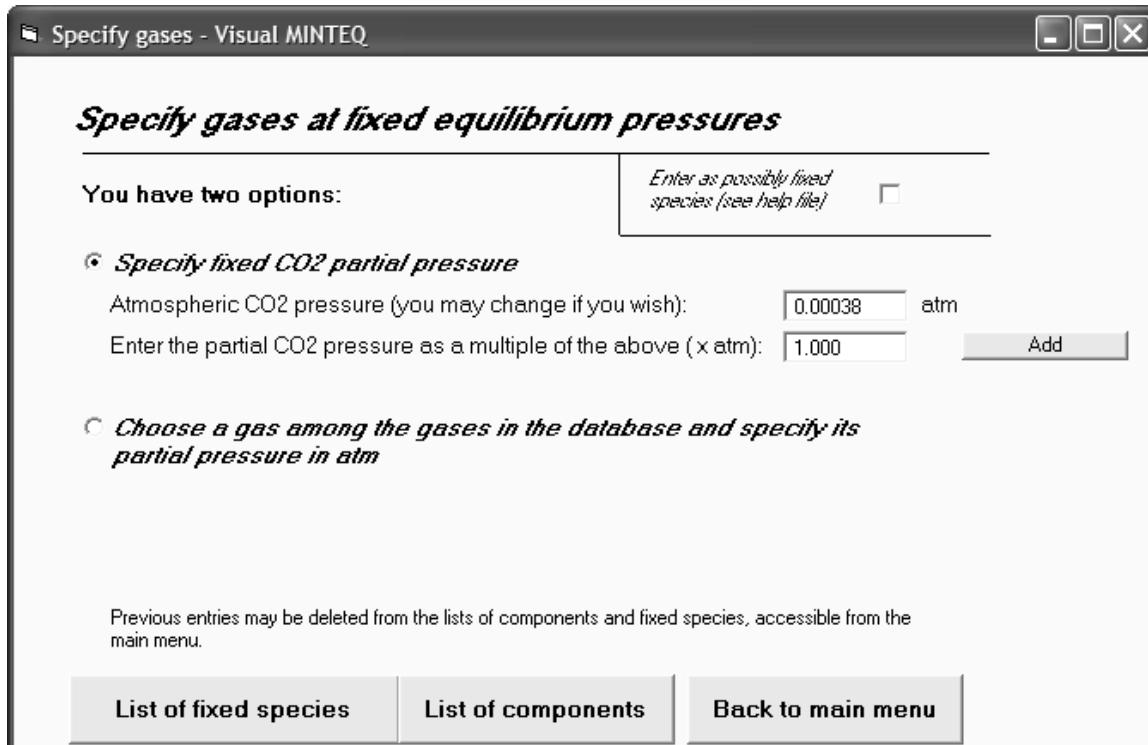


Figure A3. VM input screen for gases.

The primary anions affecting soil-water chemistry are bicarbonate and carbonate ($HCO_3^-$ and $CO_3^{-2}$), sulfate ($SO_4^{-2}$), and chloride ($Cl^{-1}$). Nitrogen and phosphorus anionic forms of nutrients, such as nitrate ($NO_3^-$) and phosphate ($PO_4^{-3}$), are important for plant growth, but are usually at much lower concentrations than carbonates, sulfates, and chlorides. Carbonate is automatically added to the component list due to electing the option of forcing the system to be open to atmospheric $CO_2$.

Therefore, each of the following major components and their respective concentrations should be added via the *Add components* feature on the main input screen: sulfate, chloride, calcium, magnesium, potassium, and aluminum.

## Background conditions

The background soil chemistry conditions without any lead or copper had to be modeled first in order to determine the appropriate input conditions for modeling with the addition of lead and copper. The primary input variables for background conditions are the ionic component concentrations discussed above.

The objective was to use conditions at Fort A.P. Hill, but data were not found for ion concentrations at this site. However, Larson et al. (2005) did measure major ion concentrations for six soils. The soil they called silty sand B was the closest to the soil conditions at Fort A.P. Hill. The characteristics of the silty sand B soil and the Fort A.P. Hill soils are summarized in Table A1. Given the lack of more detailed chemical data for Fort A.P. Hill soils, the measured chemical characteristic of the silty sand B soils were used. The ion concentrations of the silty sand B soils, which are shown in Table A2, were entered into the VM component input. There were no measurements for soil aluminum concentration.

Table A1. Comparison of soil properties.

| Soil | Percent sand | Percent fines | Cation Exchange Capacity, meq/100 g | pH | Percent TOC |
|---|---|---|---|---|---|
| Silty sand B (Larson et al. 2005) | 77 | 23 | 8 | 5.5 | 1.2 |
| Fort AP Hill (from Web Soil Survey) | 65 | 35 | 6-8 | 5.5 | 0.7 |

Table A2. Ion concentrations (mg/kg) for silty sand B soil (Larson et al. 2005)

| Cl⁻ | $SO_4^{-2}$ | $Ca^{+2}$ | $Mg^{+2}$ | $K^+$ |
|---|---|---|---|---|
| 36 | 19 | 152 | 26.4 | 12.7 |

Although the ion concentrations of Table A2 are for soil, these values were initially entered into VM assuming parts per million or mg/L for soil-water. With these values and with the other input conditions (e.g., open atmospheric $CO_2$, allowing species precipitation, and pH calculated from mass balance), the computed pH was 5.61, but the charge balance difference was off by 77 percent with too much cationic concentration. This is without including aluminum. Thus, it was necessary to adjust downward the input concentrations for the cations. This type of adjustment is very reasonable since the measured concentrations in Table A2 are for soil and not for the water in contact with the soil. Soils have an attraction to hold cations rather than releasing all of them to the soil water. This attraction is referred to as the cation exchange capacity or CEC. For a CEC of 6 to 8 meq/100 g, a portion of the cations will be retained by the soil, and the remainder will be released to the soil water. Thus, it is reasonable to assume that the soil water cation concentrations will be less than the soil concentrations in Table A2.

The cation concentrations were repeatedly adjusted until the charge difference was low. However, the concentration ratios of magnesium to calcium and potassium to calcium were kept about the same as those in Table A2. With concentrations of 20, 4, and 2 mg/L for calcium, magnesium, and potassium, respectively, the computed pH was 5.62 and the charge difference was 1.2 percent with slightly excess cationic charge. It is noted that the computed pH of 5.62 is fairly close to the observed background soil pH of 5.5.

Adding just a small amount of aluminum has a profound effect on lowering the pH. With the addition of only 0.01 mg/L of aluminum, the calculated pH dropped to 5.53 with a charge difference of 1.2 percent, but with excess anions this time. With an aluminum concentration of 0.1 mg/L, the pH is about 5, and only a small amount of cations can be added to balance the charge. Although the true aluminum concentration is unknown, freshwater has concentrations in parts per billion rather than parts per million. Thus, setting a concentration of 0.01 mg/L seems reasonable and provides the proper pH without disrupting the charge balance. The only precipitated

solid was diaspore, an aluminum oxide hydroxide. The final background component concentrations are shown in Table A3. The values in Table A3 are similar to values typically found in freshwater systems.

Table A3. Ion concentrations (mg/L) for background soil-water conditions.

| $Cl^-$ | $SO_4^{-2}$ | $Ca^{+2}$ | $Mg^{+2}$ | $K^+$ | $Al^{+3}$ |
|---|---|---|---|---|---|
| 36 | 19 | 20 | 4 | 2 | 0.01 |

## Lead solubility

The weathering crust around lead projectiles is the result of oxidation and carbonation and typically results in a mixture of hydrocerussite [$Pb_3(CO_3)_2(OH)_2$], cerussite ($PbCO_3$), anglesite ($PbSO_4$), and massicot (PbO) (Clausen et al. 2007). These crusts can further react with soil-water and associated anions resulting in equilibrium reaction products. The sum of the dissolved $Pb^{+2}$ components is the lead solubility.

If it is assumed the lead crust forms much quicker than it dissolves, then there is always a large, or infinite, supply of solid phase lead available for solution reactions. Bullets used on military firing ranges are often jacketed with a copper/zinc alloy surrounding a lead alloy core that is predominantly lead. The metal coupling can create a galvanic effect, which can accelerate corrosion (U.S. Environmental Protection Agency (USEPA) 2003). Thus, the choice of an infinite supply of solid phase lead should be a reasonable approach for estimating maximum solubility. As discussed above under the section titled "General Approach," the VM model has the option to assume an infinite or a finite supply of solid phase component mass. This is accomplished under the *Solid phases and excluded species* tab of the user interface menu bar. For an infinite supply, select the *Specify infinite solid phases* option. A scroll list within the interface input screen can be used to select the appropriate solid.

The solid phase species list included the four solids mentioned above (e.g., hydrocerussite, cerussite, anglesite, and massicot). Additionally, there were other similar species available in the list, which included:

- $Pb(OH)_2$
- $Pb_2O_3$
- $Pb_{10}(OH)_6O(CO_3)_6$
- $Pb_2OCO_3$

- $Pb_2O(OH)_2$
- $Pb_3O_2CO_3$
- $Pb_3O_2SO_4$
- PbO: $0.3H_2O$
- Pb metal

Each of the four lead solids believed to be in weathered crust and all of the lead solids in the above list were tested individually as an infinite solid mass. Specifying infinite solid phase lead with the background conditions of Table A3 produced reasonable results for hydrocerussite and anglesite, but VM would not execute successfully for massicot and cerussite. The results for infinite mass of hydrocerussite were particularly interesting, producing a pH of 6.59, I = 0.0022, charge difference of 1.15 %, $Pb^{+2}$ = 1.08 E-5 mol/L, and no precipitates of lead. Specifying infinite amount of mass for each of the other lead solids in the list above did not produce reasonable results for any of the species. In most cases, the results were incomplete. This was true even when the aluminum was removed.

After similar experimentation with the finite solid phase option, it was decided that $Pb(OH)_2$ provided the most reasonable results for the species in the list above. Thus, VM was run with varying amounts of finite lead hydroxide and with the background component concentrations of Table A3. With lead hydroxide concentrations of 100 micro mol/L ($\mu$mol/L), VM results were meaningless, such as negative pH. For a lead hydroxide concentration of 10 $\mu$mol/L, reasonable results were obtained, which consisted of pH = 6.48, ionic strength (I) = 0.0022, charge difference = 1.15 %, and $Pb^{+2}$ = 8.53 E-6 mol/L. Reasonable results were also obtained for a lead hydroxide concentration of 1 $\mu$mol/L, which consisted of pH = 5.69, I = 0.0022, charge difference = 1.16 %, and $Pb^{+2}$ = 9.08 E-7 mol/L. Likewise, smaller concentrations of lead hydroxide resulted in reasonable results that approached the background conditions with less soluble lead. Thus, a finite amount of lead hydroxide in the range of 10 to 100 $\mu$mol/L provides reasonable results while maximizing lead solubility. After making several more runs with varying amounts of lead hydroxide, it was found that 60 $\mu$mol/L of lead hydroxide maximized the computed soluble lead while providing reasonable results, including pH = 6.59, I = 0.0022, charge difference = 1.15 %, and $Pb^{+2}$ = 1.08 E-5 mol/L, or 2.24 mg/L. The solid hydrocerussite was also precipitated. These results are identical to the run discussed above with an infinite amount of

hydrocerussite solid. Thus, a lead solubility of 2.24 mg/L seems quite reasonable for the conditions of Table A3.

A spreadsheet for estimating lead solubility from a Stevens Institute Web site, http://personal.stevens.edu/~dvaccari/metals.html, was applied as a comparison. The spreadsheet model requires pH, TDS, and alkalinity as $CaCO_3$ as input. The input pH was set to 6.59 as computed by VM. The input TDS was 88 mg/L based on I of 0.0022 as computed by VM. The alkalinity, which was calculated using the VM-computed molal concentrations of carbonate, bicarbonate, hydrogen, and hydroxide, was 2.34 E-5 mol/L, or 1.17 mg/L as $CaCO_3$. With these inputs, the spreadsheet model computed lead solubility of 3.03 mg/L, which is quite close to the value of 2.24 computed by VM. The problem with using the spreadsheet model is that the value of pH with the presence of lead was not known without applying VM. The spreadsheet model does not account for metal precipitation.

Higher, but more conservative estimates will be obtained with the spreadsheet model if background values for inputs are used. For example, using the background value for pH = 5.53 and VM computed value for I = 0.0022 or TDS = 88 mg/L, and associated alkalinity of zero [for pH values this low, alkalinity is expected to be negligible (Stumm and Morgan 1981)], the spreadsheet model calculated a lead solubility of 251 mg/L. This result is two orders of magnitude greater than the estimates with VM or the spreadsheet model using conditions computed by VM.

VM is considered to be more accurate than the spreadsheet model since it includes more reactions, precipitation, and requires an iterative solution. However, to apply VM requires more information in terms of major ion concentrations and a fairly good understanding of geochemistry.

## Copper solubility

Copper is usually very resistant to corrosion; for this reason it is used in water pipes. This is also the reason that ancient copper artifacts have lasted thousands of years. However, copper corrosion can occur. The predominant solid phase products of copper oxidation/corrosion are copper oxides and hydroxides.

VM was applied to explore copper solubility using the same basic approach used for lead, which was to specify an infinite and finite solid phase copper, expose the system to atmospheric $CO_2$, allow precipitation, and

compute pH (from mass balance) and ionic strength. The background ionic component concentrations were set to match the values used for lead in Table A3.

After experimenting with the various forms of copper specified as an infinite solid phase, it was determined that specifying infinite copper solid components produced unreasonable or incomplete solutions in all but two cases. One case was for infinite cuprite, or $Cu_2O$. However, cuprite involves the less stable valence state of +1 for copper, i.e., $Cu^{+1}$, rather than the more stable valence of +2. The other case was for infinite tenorite (CuO). This model run resulted in a lower pH of 5.31, I = 0.0065, charge difference = 0.35 %, and a rather high $Cu^{+2}$ concentration of 1.42 E-3 mol/L. The solid brochantite, $CuSO_4 \bullet 3Cu(OH)_2$, was precipitated along with diaspore. The low pH and the rather high copper solubility prompted the decision to explore various amounts of finite copper solid mass.

Testing with finite amounts of the solid $Cu(OH)_2$ revealed that concentrations greater than 120 μmol/L resulted in incomplete model solutions due to poor initial activity guesses. Values less than 9 μmol/L of copper hydroxide resulted in varying results depending on the amount of copper hydroxide. As the amount of fixed solid copper hydroxide was reduced below 9, the pH decreased towards the background value of 5.53, and the soluble copper ($Cu^{+2}$) decreased. Also, there was no precipitated copper species for copper hydroxide below 9 μmol/L. For values of copper hydroxide between 9 and 120 μmol/L, results were constant with pH = 6.42, I = 0.0022, and $Cu^{+2}$ = 7.81 E-6 mol/L. The amount of precipitated tenorite (CuO) increased as copper hydroxide was increased between 9 and 120 μmol/L. The charge difference was 1.15 % for all results between 9 and 120 μmol/L of copper hydroxide.

It was also found that finite copper hydroxide results in the range of 9 to 120 μmol/L could be obtained using finite tenorite (CuO) in the same concentration range. Therefore, either finite copper hydroxide or finite tenorite of approximately 9 to 120 μmol/L produces reasonable results with pH = 6.42, I = 0.0022, and $Cu^{+2}$ = 7.81 E-6 mol/L, or copper solubility of 0.5 mg/L.

The Stevens spreadsheet for copper was applied using the pH, TDS, and alkalinity calculated from VM as inputs. The Stevens spreadsheet model

computed copper solubility of 18.4 mg/L. However, the spreadsheet model does not account for the precipitation.

## Solubility for lead and copper combination

Tests were conducted for the background conditions of Table A3 with varying amounts of hydrocerussite and tenorite. For an infinite amount of both, the computed pH was 5.32, I = 0.0066, and the charge difference = 0.35 %. However, the computed soluble copper was quite high with $Cu^{+2}$ = 1.39 E-3 mol/L. The computed $Pb^{+2}$ was reasonable with a value of 2.27 E-5 mol/L, which is close to the value computed for lead alone.

A model run was made with infinite hydrocerussite and finite tenorite of 10 μmol/L. This run was incomplete due to an estimate of zero activity for some components. Increasing or decreasing the finite tenorite concentration by an order of magnitude produced the same result. Specifying finite amounts of both solids produced unreasonable results, such as pH values lower than expected (such as 4.5 and less) and rather high solubility for the higher values of finite solid input. It is not known why the combination of the two metals had such an unexpected effect on pH. At this time, it is suggested that results only be considered with each metal treated individually.

## Conclusions and recommendations

It was possible to apply VM starting with background conditions of silty sand soil B and adjusting downward the ionic component concentrations towards values expected in soil water, to obtain the measured background pH. This was done by exposing the system to atmospheric $CO_2$, allowing precipitation, and computing pH from mass balance, not mass and charge balance. Ionic concentrations were adjusted until a low charge difference (about 1 percent) was reached.

With the addition of a finite amount of solid lead hydroxide of 60 μmol/L, the computed soluble lead was maximized while providing reasonable results, including pH = 6.59, I = 0.0022, charge difference = 1.15 %, and $Pb^{+2}$ = 1.08 E-5 mol/L, or 2.24 mg/L. The same result was achieved by specifying an infinite amount of hydrocerussite solid. With the pH, TDS, and alkalinity calculated from VM as inputs, the Stevens spreadsheet model computed lead solubility of 3.03 mg/L, which is quite close to the value of 2.24 computed by VM.

The addition to the background conditions of either copper hydroxide or copper oxide (tenorite) in the range of 9 to 120 µmol/L resulted in reasonable results with pH = 6.42, I = 0.0022, and $Cu^{+2}$ = 7.81 E-6 mol/L, or copper solubility of 0.5 mg/L. The amount of precipitated tenorite (CuO) increased as either copper hydroxide or tenorite was increased from 9 to 120 µmol/L, and the charge difference was constant at 1.15 %. With the pH, TDS, and alkalinity calculated from VM as inputs, the Stevens spreadsheet model computed copper solubility of 18.4 mg/L.

A successful method was not found for estimating solubility using VM with both solid phase lead and copper present. Thus, it is recommended that the results for each metal tested individually be used at this time.

Use of VM requires much more information and understanding of soil-water chemistry than use of the spreadsheet model, but VM can provide more accurate estimates of solubility. The spreadsheet model will be distributed within TREECS tools for estimating lead and copper solubility. However, it should be recognized that the spreadsheet model will provide higher solubility estimates than can actually exist although inflated estimates are more conservative for modeling metal fate. As an example, the spreadsheet model estimates copper solubility of 440 mg/L for the background soil pH of 5.53 compared to the estimate of 0.5 mg/L for copper solubility computed with VM. Thus, estimates from the spreadsheet model can be inflated by as much as three orders of magnitude. For these reasons, sensitivity of metal solubility should be conducted during the TREECS model applications where solubility estimated with the spreadsheet model is decreased by about two or three orders of magnitude. The two primary reasons for the inflated estimates with the spreadsheet model are that the spreadsheet model does not consider metal precipitation, and the soil-water pH can be greater than the background pH with the presence of lead or copper.

# Appendix B: Testing the Soil Model Against the Laboratory Rainfall Lysimeter Study for Lead

## Background

A study of leachability and surface runoff of heavy metals from six soils was conducted by Larson et al. (2005) using laboratory rainfall lysimeter test cells. The results for lead obtained from the control test cell (i.e., without phosphate amendment) for the silty sand B soil were used for testing the Tier 2 soil model. This model test was conducted to see how well the model would perform for predicting the leached dissolved lead mass and total lead mass in runoff. The laboratory test conditions, methods, and results reported by Larson et al. (2005) are discussed below.

## Test conditions

The lysimeter test cells were filled with test soil and were placed under a rainfall simulator on a slope of 0.0625 to create runoff. Each lysimeter was configured to allow collection of runoff water and leachate water. Rainfall, which was water treated through reverse osmosis (RO), was applied for 16 weeks at a rate of 18 L per week, which amounted to an annual rainfall rate of 0.467 m/yr. Rainfall was applied weekly over a period of about 26 minutes.

The lysimeter test cell was 78.7 cm on each side and 61 cm deep. Following lead enrichment, soil was added to the cell to a depth of approximately 23 cm. The lead-enriched soil was prepared by firing 3,293 M855 rounds (5.56-mm bullets) from a distance of 98.5 m into 660 kg of the sand B soil in a catch box. The soil was sieved to remove particles larger than 26.5 mm before placement in the test cell. Below the soil layer was a 7.6-cm layer of sand, and below the sand was a 7.6-cm layer of pea gravel with a geotextile cloth between the sand and gravel.

The prepared soil was sampled with nine replicates and analyzed for lead concentrations. The average lead concentration in the 1.7-mm fraction and smaller soil was 5,930 mg/kg compared with a theoretical maximum of 10,000 mg/kg based on the number of bullets fired with a mass of 1.9 g of

lead in each bullet. The 1.7-mm and smaller fraction of soil contained approximately 60 percent of the lead mass according to an analysis of lead content for soil samples sieved with varying sieve sizes. Thus, the total concentration of lead was probably closer to 9,884 mg/kg, which is close to the theoretical concentration. This latter lead concentration results in a computed initial lead mass in soil of 2,098 g using the cell dimensions, an initial soil depth of approximately 0.23 m, and a soil bulk density of 1.49 g/ml for silty sand.

The measured lead soil-water partition coefficient was 157 L/kg for the silty sand B soil. The volumes of runoff and infiltrated water over the 16-week test were measured. The measured runoff and infiltration of 82.7 L and 162.7 L, respectively, translate into annual rates of 0.134 and 0.263 m/yr, which is 85 percent of the rainfall rate. Since rainfall was applied weekly over a period of about 26 minutes, it is likely the difference in rainfall and losses from runoff and infiltration of 43 L can be attributed to evaporation.

The silty sand B soil consisted of 77.2 percent sand and 22.3 percent fines. The measured specific gravity was 2.62. Since measurements of soil porosity and/or dry bulk density were not available and other information on soil texture (percent sand, silt, and clay) was lacking, assumptions had to be made for further definition of soil characteristics. It was assumed that the silty sand B soil was similar to a loamy sand texture, which has about 83, 11, and 6 percent of sand, silt, and clay, respectively. This soil texture has a sediment porosity, sediment dry bulk density, and water field capacity of 43.7 percent, 1.49 kg/L, and 12 percent, respectively. Although this soil texture is not exactly the same as the sand B soil, it was considered similar enough for the purposes of comparing the model with laboratory data.

## Erosion results

The measured total suspended solids (TSS) mass in runoff and leachate from the lead-enriched, non-amended, sand B soil test cell was 125.9 and 6.2 g, respectively. It is not clear why there would be any solids in the leachate given that the leachate had to pass through layers of sand, geotextile cloth, and pea gravel. It is possible that the use of RO rainwater could have caused some stripping of ions with increased soil dispersion, resulting in leaching of very fine soil particles. Using the measured TSS mass eroded over 16 weeks, a soil dry bulk density of 1.49 kg/L, and a test cell surface area of 0.619 m² results in an erosion rate of 4.43 E-4 m/yr. The Universal Soil Loss Equation (USLE) was applied within the Hydro-Geo-

Characteristics Toolkit (HGCT) of TREECS using estimated parameter values of 50 for the rainfall factor $R$, 0.1 for the soil erodibility factor $K$, 0.2 for the soil length-gradient factor $LS$, 0.45 for the crop management factor $C$, and 1.0 for the conservation practice factor $P$. The USLE resulted in an estimated erosion rate of 0.45 ton/acre/year, which translates into 6.77 E-5 m/yr, which is a factor of six smaller than the measured rate based on TSS mass collected from runoff. It is noted that the USLE was never intended for application to a scale as small as the laboratory lysimeter test cell. Thus, the measured erosion rate was used for applying the model.

## Leachate results

The 16-week accumulated total lead in leachate was reported to be approximately 0.05 g. The accumulated dissolved lead in leachate was not reported. However, the 16-week averages for dissolved (i.e., passing a 0.45-micron filter) and total lead in collected leachate samples were reported and were 96 and 423 µg/L, respectively. Using the ratio of these dissolved to total concentrations times the accumulated total lead in leachate resulted in an estimated accumulated dissolved lead in leachate of 0.01 g. If the average dissolved lead in leachate concentration of 96 µg/L is multiplied by 18 L/week and by 16 weeks, then the estimated accumulated leached dissolved lead is 0.028 g, which is nearly three times the first estimated value. Since there was considerable variance in the reported mean concentrations, the first estimate (i.e., 0.01 g) is assumed to be the better estimate of the cumulative leached dissolved lead mass.

The TREEC Tier 2 soil model, which is described by Dortch et al. (2011), was applied to the test cell conditions using information described in the preceding sections. Additionally, information on lead solubility in water, lead solid phase mass density, average initial lead particle size, and soil volumetric moisture content was required for computing dissolution and leaching in the model. The soil moisture content was assumed to equal the field capacity (12 percent).

Lead solubility can vary widely depending on the local geochemistry and lead salts that form. Lead carbonate is a fairly common form of lead. A rather dated laboratory study (Fairhall 1924) showed that the solubility of lead carbonate in water at 18 °C was 17 mg/L, but this result does not take into account pH, alkalinity, total dissolved solids, and ion concentrations that can affect lead solubility. For the reported pH of this soil of 5.48, it is possible that the lead solubility could be higher. However, for this analysis,

a lead solubility of 17 mg/L was assumed. Testing with the Stevens spreadsheet for lead (see Appendix A) indicated that this value is lower than those estimated with the spreadsheet. However, the spreadsheet does not take into account precipitation and other factors that lower the solubility.

Larson et al. (2005) analyzed multiple wet-sieved samples of the sand B soil to determine the relative particle size distribution of the lead. The relative particle size of lead was determined from a plot of percent of lead in particle size class or larger versus sand B particle size class. From this plot, it was found that the soil particle size containing approximately 50 percent of the lead was 500 μm. Thus, an initial solid phase lead particle size of 500 microns was used for the model. The density of solid phase lead is 11.35 g/cm³. The initial solid phase lead mass was specified as 2,098 g as discussed above.

The cumulative leached dissolved lead mass after 16 weeks computed by the model was 0.0041 g compared with 0.01 g as the estimated observed amount. Thus, the computed leached dissolved lead mass was approximately two to three times smaller than the measured mass. The reason for this much difference is not known. The most sensitive, unknown input parameter is lead solubility. Results are just as sensitive to the initial solid phase lead particle size as solubility, but there was an effort to measure particle size. If the solubility was a factor of 2 or 3 greater than the assumed value, the model would agree with the measurement. It is recognized that assumed solubility could be quite different than the true solubility since lead solubility is highly variable and dependent on local chemistry. The model does not compute a particulate leachate flux; thus, there was no attempt to compare with that measurement or the total leached mass. Evidently, the pore spaces in the sand, filter cloth, and pea gravel of the test cell are large enough to pass particulate or solid phase lead particles and colloids with the leached water.

## Runoff results

The measured cumulative runoff mass of total lead over the 16 weeks was 2.2 g. The model-computed cumulative runoff mass of total lead for 16 weeks was 1.25 g, which is the same order of magnitude as measured, although about half the value. The computed and measured cumulative runoff masses are reasonably close considering that the model assumes that the solid phase lead concentration is homogenous throughout the test soil, which may not have been the case.

The model cumulative runoff mass is the sum of the computed cumulative mass exports for rainfall-extracted pore water, erosion of soil with adsorbed aqueous phase lead, and erosion of solid phase lead particles. However, the cumulative runoff mass for the first two fluxes was only 0.002 g compared with 1.245 g for the erosion of solid phase lead particles. Over longer time frames, it is expected that the first two fluxes would become more important due to longer time for dissolution to occur. Considering the rather simple method used to estimate solid phase particle erosion and the fact that all of the lead particles were represented with one particle size, it is encouraging that the computed cumulative runoff mass is within half of that observed.

## Conclusions

The computed dissolved leachate lead was less than observed by a factor of 2 to 3, but this could be a result of using an assumed lead solubility that is lower than really occurs for chemistry of the test soil. It is also suspected that very small particulate solid phase lead may have been passed with the leachate, which is a pathway the model does not simulate. Only dissolved phase MC can move with leachate in the model.

The computed and observed total lead in the runoff is of the same order of magnitude. The runoff lead is mostly solid phase particulate lead according to the model. This seems reasonable since the 16-week test period is not expected to have been long enough to generate much lead corrosion and dissolution, which are required to feed the other soil export processes.

# Appendix C: Revisions to the Erosion and Hydrology Estimation Methods in TREECS

Methods that are built into the HGCT for estimating erosion rate and hydrologic variables, such as average annual runoff and infiltration rates, were modified between the POC evaluation of Tier 1 and Tier 2. The modifications will apply to both Tier 1 and Tier 2 applications of TREECS in the future. The modifications and how they vary from the descriptions provided in previous reports (Dortch et al. 2009, 2010) are described below.

## Erosion rate

The LS factor on the USLE was first estimated using the graphs in Figure C1 along with the slope length and percent slope. This procedure can result in excessively large LS factors, which leads to unrealistically high soil erosion rates if the LS value falls along the dashed line. Thus, the procedure was changed to compute LS using an equation presented by Julien (1995),

$$LS = \sqrt{X_r}\left(0.0076 + 0.53S_o + 7.6S_0^2\right) \tag{C1}$$

where $X_r$ is land slope length (ft), and $S_0$ is the land slope (ft/ft). The value of $X_r$ is limited to 400 ft in applying Equation C1 based on engineering judgment since a length greater than that is moving away from overland sheet flow and erosion and into the realm of rill and gully flow.

## Hydrology

The revised hydrology module has been modified to account for evapotranspiration ($ET$) and snow accumulation and melting in addition to computing dissolution days and rainfall impact days. Introducing $ET$ and snow accumulation and melting impacts the previous runoff and infiltration computations; however, these additions allow for more accurate runoff and infiltration computations as well as broadening the applicability of the model over more diverse climate zones. Within the hydrology model, a dissolution day is defined as a day where water movement occurs in the soil due to rainfall or snowmelt, and the contaminant is exposed to dissolution. A rainfall impact day is defined as a day where rainfall occurs and hits the bare ground extracting $MC$ from the soil pore water. Thus, the ground must be free of any snowpack for rainfall impact to occur.
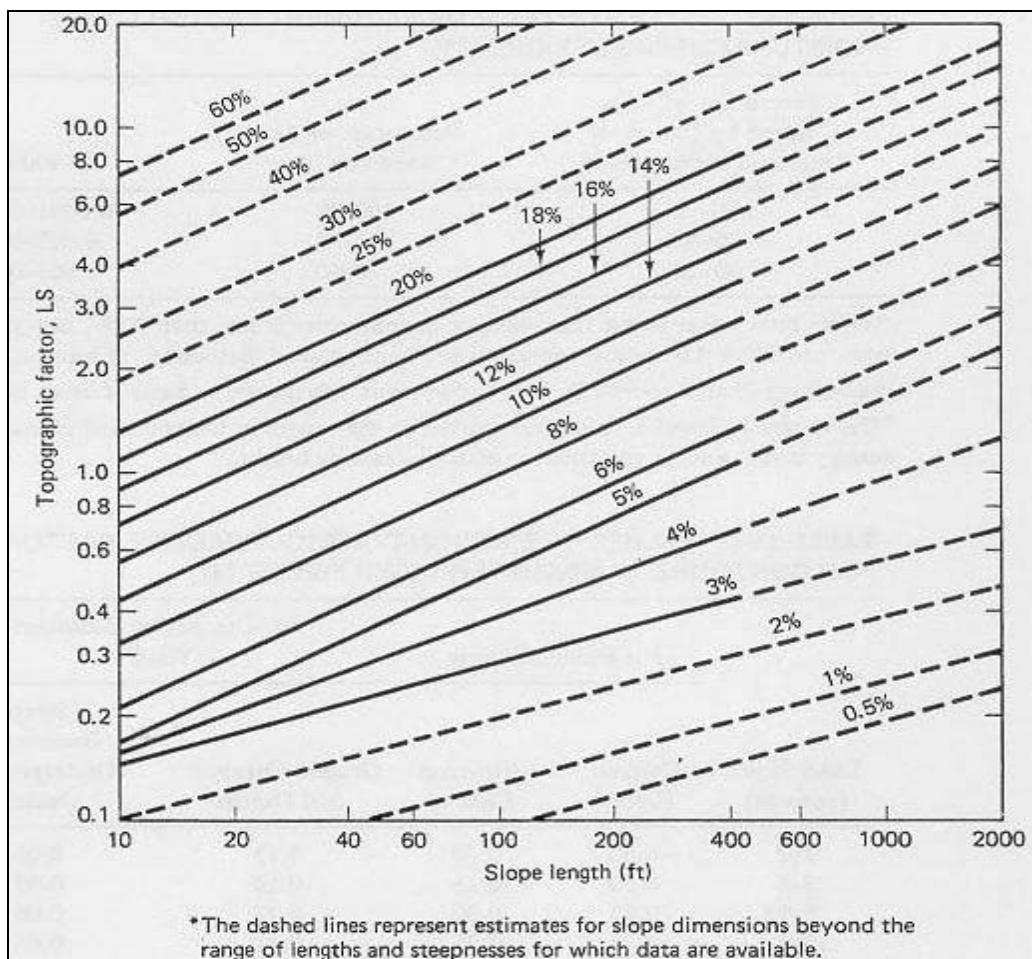
Figure C1. Topographic factor, LS, in USLE (U.S. Department of Agriculture (USDA) Soil Conservation Service (SCS) 1983)

When computing the average annual runoff, it is first necessary to determine the AOI drainage area and the hydrologic abstractions (e.g. infiltration, evapotranspiration, etc.) of the catchment, Figure C2. The hydrologic abstractions are represented by the SCS Curve Number (*CN*). Once these two items have been determined, the period of record daily precipitation amounts are input into the module. A running total of the previous five-day precipitation amount is computed and based upon this value, the Antecedent Moisture Content (*AMC*) level is determined. An *AMC I* is a dry condition, an *AMC II* is an average condition, and an *AMC III* is a wet condition. Once the *AMC* level has been determined, then the *CN* is adjusted, if necessary, and the daily runoff (*Q*) is computed. As the computations proceed, monthly and yearly average flows are computed for the period of record precipitation. Once the yearly average flow has been computed for each year of the period of record, then an average annual runoff computation can be made for the entire period of record.
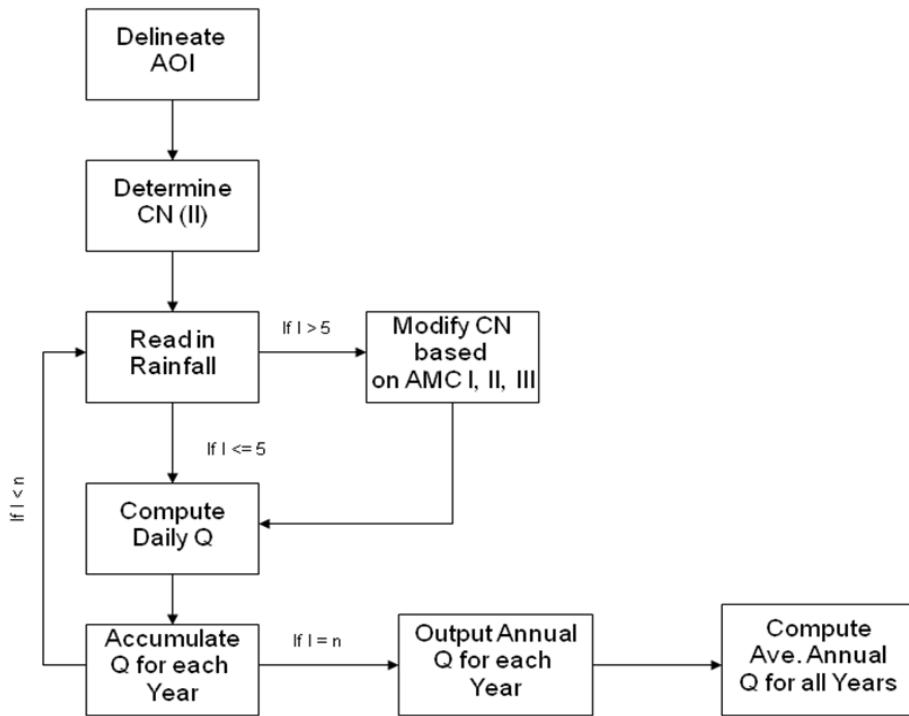
Figure C2. Average annual runoff flowchart

Once $Q$ has been computed, it is necessary to determine how much of the hydrologic abstraction infiltrates ($I$) and how much is lost due to $ET$, Figure C3. Since $ET$ is computed on a monthly basis, the daily flows are accumulated on a monthly basis so that monthly infiltration and monthly $ET$ can be estimated.

The Thornthwaite Method, which is a heat index method, is used to compute monthly potential evapotranspiration ($PET$) as follows,

$$I_t = \left(\frac{T}{5}\right)^{1.514} \tag{C2}$$

where

$I_t$ = monthly heat index
$T$ = mean monthly temperature (degree Celsius)

Mean monthly $PET$ at $0^0$ latitude is computed by:
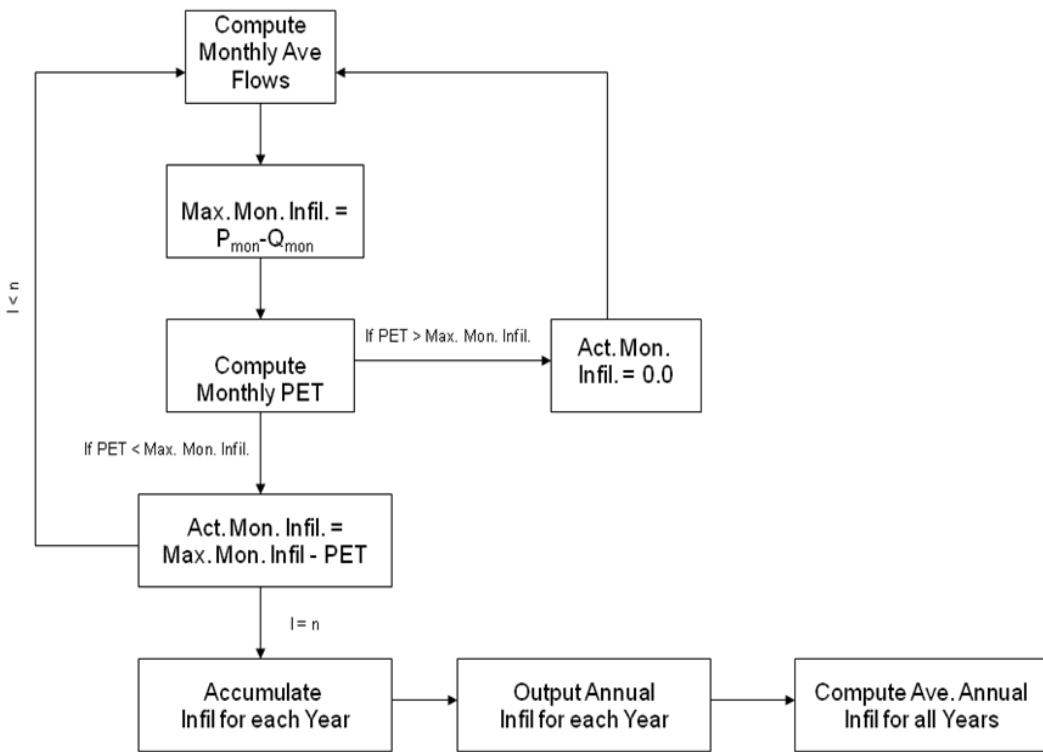
Figure C3. Average annual hydrologic abstractions flowchart

$$PET(0) = 1.6\left(\frac{10T}{J}\right)^{c} \tag{C3}$$

$$c = 0.000000675\,J^{3} - 0.0000771\,J^{2} + 0.01792\,J + 0.49239 \tag{C4}$$

where $J$ = sum of 12 monthly values of heat index ($I_t$)

At latitudes other than $0^0$, $PET$ is calculated by:

$$PET = K \times PET(0) \tag{C5}$$

where $K$ is a constant for each month of the year, varying as a function of latitude (Table C1).

In addition to runoff, infiltration, and ET, the TREECS hydrology module also computes snow accumulation and snow melt. In deciding whether precipitation occurs in the form of rainfall or snowfall, the module evaluates the daily temperature to see if the temperature is above or below the freezing level.

Table C1. Constant K in Thornthwaite Method

| Lat | Jan | Feb | Mar | Apr | May | Jun | Jul | Aug | Sep | Oct | Nov | Dec |
|------|------|------|------|------|------|------|------|------|------|------|------|------|
| 60°N | 0.54 | 0.67 | 0.97 | 1.19 | 1.33 | 1.56 | 1.55 | 1.33 | 1.07 | 0.84 | 0.58 | 0.48 |
| 50°N | 0.71 | 0.84 | 0.98 | 1.14 | 1.28 | 1.36 | 1.33 | 1.21 | 1.06 | 0.90 | 0.76 | 0.68 |
| 40°N | 0.80 | 0.89 | 0.99 | 1.10 | 1.20 | 1.25 | 1.23 | 1.15 | 1.04 | 0.93 | 0.83 | 0.78 |
| 30°N | 0.87 | 0.93 | 1.00 | 1.07 | 1.14 | 1.17 | 1.16 | 1.11 | 1.03 | 0.96 | 0.89 | 0.85 |
| 20°N | 0.92 | 0.96 | 1.00 | 1.05 | 1.09 | 1.11 | 1.10 | 1.07 | 1.02 | 0.98 | 0.93 | 0.91 |
| 10°N | 0.97 | 0.98 | 1.00 | 1.03 | 1.05 | 1.06 | 1.05 | 1.04 | 1.02 | 0.99 | 0.97 | 0.96 |
| 0° | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| 10°S | 1.05 | 1.04 | 1.02 | 0.99 | 0.97 | 0.96 | 0.97 | 0.98 | 1.00 | 1.03 | 1.05 | 1.06 |
| 20°S | 1.10 | 1.07 | 1.02 | 0.98 | 0.93 | 0.91 | 0.92 | 0.96 | 1.00 | 1.05 | 1.09 | 1.11 |
| 30°S | 1.16 | 1.11 | 1.03 | 0.96 | 0.89 | 0.85 | 0.87 | 0.93 | 1.00 | 1.07 | 1.14 | 1.17 |
| 40°S | 1.23 | 1.15 | 1.04 | 0.93 | 0.83 | 0.78 | 0.80 | 0.89 | 0.99 | 1.10 | 1.20 | 1.25 |
| 50°S | 1.33 | 1.19 | 1.05 | 0.89 | 0.75 | 0.68 | 0.70 | 0.82 | 0.97 | 1.13 | 1.27 | 1.36 |

The snowfall mass balance equation is:

$$Sacc_i = Sacc_{i-1} + S_i - E_i - SM_i \qquad \text{(C6)}$$

where

$Sacc_i$ = snow accumulation for current day (mm $H_2O$)
$Sacc_{i-1}$ = snow accumulation for previous day (mm $H_2O$)
$S_i$ = snowfall for current day (mm $H_2O$)
$E_i$ = evaporation (Sublimation) for current day (mm $H_2O$)
$SM_i$ = snowmelt for current day (mm $H_2O$)

From "Handbook of Hydrology," (Maidment 1993), $E_i$ for an 8-hr period at an open site is estimated to be: average = 0.30 mm; maximum = 0.76 mm; and minimum = 0.02 mm. Given that sublimation only occurs during daylight hours, and 8 hr of sunlight are assumed, these values would be the daily sublimation depth.

Snow melting is estimated by

$$SM_i = b_{mlt} \times sno_{cov} \times \left[ \frac{T_{snow_i} + T_{mx_i}}{2} - T_{mlt} \right] \qquad \text{(C7)}$$

where

$b_{mlt}$ = melt factor (mm $H_2O$/day-$^oC$)

$sno_{cov}$ = fraction of area covered by snow (0 to 1.0)

$T_{snow_i}$ = snowpack temperature for current day, i ($^oC$)

$T_{mx_i}$ = maximum air temperature for current day, i ($^oC$)

$T_{mlt}$ = base temperature above which snowmelt will occur ($^oC$)

From the Soil and Water Assessment Tool (SWAT), $b_{mlt}$ for rural areas is estimated to vary from 1.4 to 6.9 mm $H_2O$/day-$^oC$. Modeling assumptions made in the snow calculations are:

- $sno_{cov}$ = 100% (1.0) since we are working with small open areas
- $T_{mlt}$ = 0 $^oC$

Applying these assumptions and recognizing that snowmelt occurs only when $(T_{snow} + T_{mx})/2$ is greater than $T_{mlt}$ (otherwise $SM_i$ is zero), Equation C7 reduces to

$$SM_i = b_{mlt} \left[ \frac{T_{snow_i} + T_{mx_i}}{2} \right] \tag{C8}$$

The temperature of the snowpack can be estimated from

$$T_{snow_i} = T_{snow_{i-1}} \left( 1 - l_{sno} \right) + T_{av} \times l_{sno} \tag{C9}$$

where $l_{sno}$ is the lagging factor, which assigns how much weight to put on the previous day's snowpack temperature versus the current day's mean daily air temperature, and $T_{av}$ is the mean daily air temperature (oC). As the lagging factor approaches 1.0, more weight is placed on the current day's mean daily air temperature.

The final computations made by the TREECS hydrology module are the number of rainfall impact days per year and the number of dissolution days per year that one can expect to occur on average over the total period of record. The flowchart for these computations is shown in Figure C4.

## Rainfall Impact Days and Dissolution Days
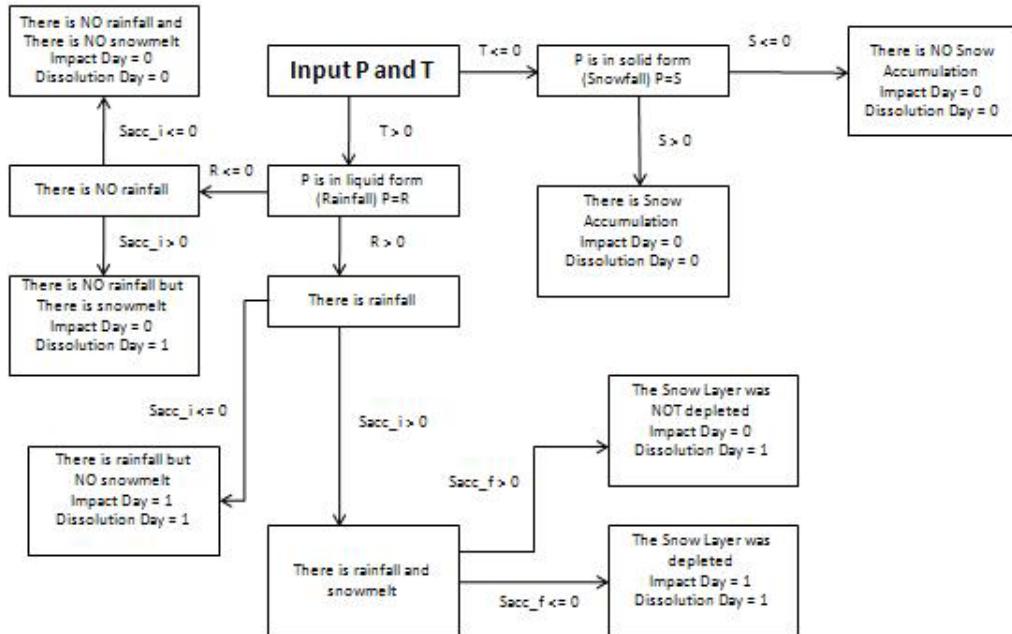


Figure C4. Flowchart for rainfall impact and dissolution days.

MC dissolution can occur due to rainfall or snowmelt; however, snow pack must exist for there to be snowmelt. In Figure C4, $Sacc\_i$ represents the accumulated snowpack depth at the beginning of the day and $Sacc\_f$ represents the accumulated snowpack depth at the end of the day. As the computations proceed, $Sacc\_f$ becomes $Sacc\_i$ for the following day. For rainfall impact (i.e., rainfall extracted runoff) to occur there must be no remaining snow pack. From Figure C4, each day's precipitation and mean daily temperature are evaluated along with whether or not a snowpack exists to determine whether or not rainfall impact and/or dissolution occur on that particular day. If the rainfall Impact Day and/or the Dissolution Day designation integer are equal to zero, then the module assumes that those processes did not occur that day. If the Impact Day and/or the Dissolution Day designation integer are equal to one, then the module assumes that those processes did occur that day and each counter is incremented accordingly.

# REPORT DOCUMENTATION PAGE

| 1. REPORT DATE *(DD-MM-YYYY)* <br> August 2011 | 2. REPORT TYPE <br> Final report | 3. DATES COVERED *(From - To)* |
|---|---|---|

**4. TITLE AND SUBTITLE**

Proof-of-Concept Application of Tier 2 Modeling Approach within the Training Range Environmental Evaluation and Characterization System

**5a. CONTRACT NUMBER**

**5b. GRANT NUMBER**

**5c. PROGRAM ELEMENT NUMBER**

**6. AUTHOR(S)**

Mark S. Dortch, Billy E. Johnson, Jeffrey A. Gerald, Zhonglong Zhang, and Andrew P. Simmons

**5d. PROJECT NUMBER**

**5e. TASK NUMBER**

**5f. WORK UNIT NUMBER**

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

U.S. Army Engineer Research and Development Center,
Environmental Laboratory,
3909 Halls Ferry Road,
Vicksburg, MS 39180-6199

**8. PERFORMING ORGANIZATION REPORT NUMBER**

ERDC/EL TR-11-10

**9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

U.S. Army Corps of Engineers
Washington, DC 20314-1000

**10. SPONSOR/MONITOR'S ACRONYM(S)**

**11. SPONSOR/MONITOR'S REPORT NUMBER(S)**

**12. DISTRIBUTION / AVAILABILITY STATEMENT**

Approved for public release; limited distribution.

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT**

The Training Range Environmental Evaluation and Characterization System (TREECS) is being developed for the Army to forecast the fate of and risk from munitions constituents (MCs), such as high explosives (HE), within and transported from firing/training ranges to surface water and groundwater. The overall objective is to provide environmental specialists with tools to assess the potential for migration of MCs into surface water and groundwater systems and to assess range management strategies to protect human and environmental health. Tier 1 consists of screening-level methods that assume highly conservative, steady-state MC loading and fate. Tier 1 requires minimal data input and can be easily and quickly applied by environmental staff. If MC concentrations predicted with Tier 1 exceed protective health benchmarks at receptor locations, then further evaluation with Tier 2 is recommended to obtain more definitive results.

Tier 2 provides time-varying analyses since it does not make the highly conservative assumptions of steady-state (time-invariant) conditions with no MC loss or degradation as used for Tier 1. Tier 2 solves mass balance equations for both solid and non-solid phase MC with dissolution. MC residue loadings to the range soil can vary from year to year based on munitions use; thus, media concentrations computed with Tier 2 should be closer to those expected under actual conditions. Media concentrations will also reflect time phasing associated with time-varying MC loading conditions and transport arrival times, which can be greatly extended for the vadose zone and groundwater. Having time as a dimension in the analysis provides a powerful tool for examining range management strategies to promote attenuation of media concentrations.

This report describes the proof-of-concept application of the prototype TREECS Tier 2 modeling approach and provides recommendations for final implementation and use of those methods.

**15. SUBJECT TERMS**

| Human and environmental health <br> Fort A.P. Hill | Fate of munitions constituents (MCs) <br> Range management strategies | Training Range Environmental Evaluation and Characterization System (TREECS) |
|---|---|---|

| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 18. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON |
|---|---|---|---|---|---|
| **a. REPORT** <br> UNCLASSIFIED | **b. ABSTRACT** <br> UNCLASSIFIED | **c. THIS PAGE** <br> UNCLASSIFIED | | 140 | **19b. TELEPHONE NUMBER** *(include area code)* |