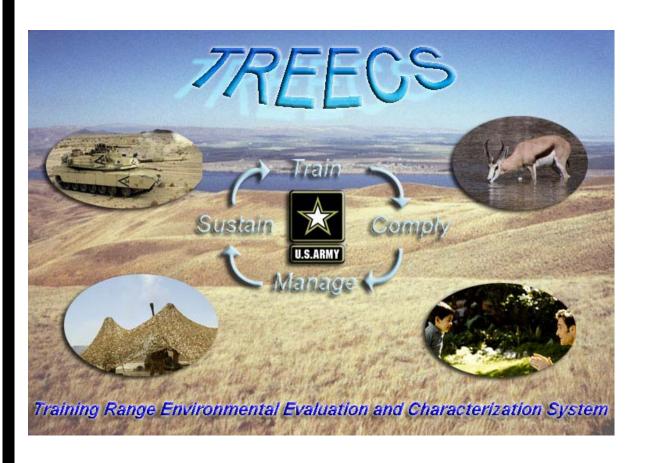


# Proof-of-Concept Application of Tier 1 Modeling Approach Within the Training Range Environmental Evaluation and Characterization System

Mark S. Dortch, Billy E. Johnson, and Jeffrey A. Gerald

October 2010



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#### Final report

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**Abstract:** 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 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 Army 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 will consist of screening-level methods that require minimal data input requirements and can be easily and quickly applied by environmental staff to assess the potential for migration into surface water and groundwater. Any predicted surface water and/or groundwater MC concentrations that exceed protective health benchmarks at receptor locations would require further action such as evaluation using TREECS Tier 2.

Highly conservative assumptions of steady-state (time-invariant) MC conditions and no MC degradation are used in the Tier-1 modeling approach. Thus, MC loadings to the range are constant over time, and fluxes to and concentrations within receiving water media reach a constant MC concentration for comparison with protective ecological and human health benchmarks. Tier 1 includes an analytical soil model with computed leaching flux linked to a semi-analytical-numerical aquifer model. The computed runoff-erosion fluxes are linked to a numerical surface-water and sediment model. Tier 1 also includes a hydro-geo-characteristics toolkit for estimating input parameters.

This report describes the proof-of-concept application of the prototype TREECS Tier-1 modeling approach and provides recommendations for final implementation and use of these methods.

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# **Preface**

This study was funded by the U.S. Army's Environmental Quality and Installations (EQI) Research Program. The application reported herein was conducted by Dr. Mark Dortch of MSD Engineering Consulting, under contract to the U.S. Army Engineer Research and Development Center (ERDC). This report was written by Drs. Dortch and Billy Johnson and Jeffrey Gerald of the Water Quality and Contaminant Modeling Branch (WQCMB), Environmental Processes and Effects Division (EPED), Environmental Laboratory (EL), ERDC. The study was conducted under the general direction of Dr. Beth Fleming, Director, EL; Dr. Richard Price, Chief, EPED, and Dr. Quan Dong, Chief, WQCMB. Dr. John Cullinane was Director of the EQI Program.

Personnel from the Army Environmental Command and the Army Center for Health Promotion and Preventive Medicine (CHPPM) provided valuable information, reviews, comments, and recommendations during this study that helped to improve and refine Tier 1 methods. Their assistance and participation are greatly appreciated.

COL Gary E. Johnston was Commander and Executive Director of ERDC. Dr. Jeffery P. Holland was Director. This report is approved for limited distribution.

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# **Unit Conversion Factors**

Multiply	Ву	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
slugs	14.59390	kilograms
square feet	0.09290304	square meters
square miles	2.589998 E+06	square meters

# 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 (HEs) and metals, within and transported from firing/training ranges to surface water and groundwater. The overall objective is to provide Army 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.

TREECS will be accessible on the internet and initially will have two tiers for assessments. Tier 1 includes screening-level methods that require minimal data input requirements and can be easily and quickly applied to assess potential for MC migration into surface and/or groundwater at concentrations that exceed 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 Tier 1 analysis, proceeding to Tier 2 to obtain a more definitive assessment is warranted. 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 application knowledge and skill, but can be used by local environmental staff with a moderate understanding of multi-media fate and transport. The Tier 2 approach will allow time-varying analyses, which should provide more accurate predictions with generally lower concentrations because of mediating effects of transport phasing and dampening. 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 1 modeling approach and provides recommendations for its

implementation and use. The POC application was required to evaluate the reasonableness of approach, ascertain missing elements, delineate methods to obtain various inputs, and determine those parts that required revision. Details of the Tier 1 modeling approach are not included in this report but can be found in the report by Dortch et al. (2009). The POC application was not intended to validate model accuracy; this process will be undertaken later through various applications to field-study sites.

Use of the POC application was required for an Army installation 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 off-range migration that may pose 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. Ft. A. P. Hill is being evaluated as a pilot study and was chosen for this POC application.

A primary goal of TREECS development is provision of cost-effective tools to rapidly facilitate better understanding of each site when conducting ORAP Phase II. TREECS Tier 1 application results could show that some ranges presently categorized as inconclusive should be re-categorized as unlikely, whereas other results might show that some ranges in the inconclusive category require closer attention or higher priority.

# 2 Approach

The general approach consisted of selection of a study site and application of a preliminary version of Tier 1 formulations to that site, as described in this report.

#### Site selection and description

Ft. A.P. Hill was selected as the study site for POC application. Reasons for this site selection included the following.

- This site had been selected for pilot study under Phase II ORAP.
- Numerous firings per year had occurred for both HE and small arms.
- Site-characterization data quality was good.
- A good record of range use with quantity of rounds fired for each munitions type was available for the period between 2000 and 2006.
- Notable potential receptor locations were present outside the installation in close proximity to the installation boundary.

As described by EA, Engineering, Science, and Technology, Inc. (EA) (2006), Ft. 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. Ft. A.P. Hill was established in 1941 as an Army training facility for use in troop and artillery training on land purchased by the U.S. government. Currently, Ft. 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 active and reserve troops of the U.S. Army, Navy, Marines, and Air Force, as well as other government agencies. Ft. A.P. Hill currently conducts training in 128 training areas in 98 firing ranges and three impact sites. Other information regarding this installation, as well as an ORAP Phase-I assessment, can be found in the EA report (2006). Other site descriptions and characterization information required for modeling are discussed in this report in pertinent sections.

# **Modeling approach**

Following development of the Tier 1 modeling approach (Dortch et al. 2009), soil-model formulations were coded into a spreadsheet for testing

on Ft. A.P. Hill. Leaching export-flux output from the spreadsheet was then transferred to inputs for the MEPAS aquifer model, and the export fluxes for rainfall-ejected runoff and erosion were transferred to the inputs for the RECOVERY surface-water model. The aquifer model and RECOVERY model are described by Dortch et al. (2009), and both models reside within the Adaptive Risk Assessment Modeling System (ARAMS), which can be accessed at <a href="http://el.erdc.usace.army.mil/arams/arams.html">http://el.erdc.usace.army.mil/arams/arams.html</a>. This procedure provided a way to rapidly test the modeling approach prior to final software development in TREECS. The final Tier-1 soil model was coded into C# language and will be an executable linked with executables for the MEPAS aquifer and RECOVERY surface-water/sediment models within TREECS. The Tier 1 soil model spreadsheet also served as a means of verifying the correctness of the C#-coded soil model.

The first step of the modeling application was to establish the area of interest (AOI). Early in the application, difficulties in separating out the fate of MC residual mass were noted because of the operation of individual firing ranges. Many firing ranges may use the same impact area. For example, at Ft. A.P. Hill there are 98 firing ranges but only three impact areas. Rather than assessing each range with TREECS, assessing an AOI, which would typically be an impact area for HEs or a bermed target area for a small-arms firing range (SAFR), would be more logical. For this application, a single AOI for HEs and metals from SAFRs was considered.

Estimation of the amount of MC mass residue deposited onto the AOI on an annual basis was required. Range-firing records were used for this task, as described in the next chapter.

The next step was to set up inputs for the Tier-1 soil fate-and-export model. This step required estimating hydrologic variables used in input. After the soil model was run, its output and other parameter inputs were created for the aquifer and surface-water models. Subsequently, computed concentrations of these models were compared with health benchmarks. All inputs and their estimation methods are described in Chapter 4 of this report, and model output is described in Chapter 5. Modeling sensitivity tests are discussed in Chapter 6.

# 3 MC Residual-Mass Loadings

MC residual-mass loadings were determined for RDX, TNT, lead, copper, and perchlorate. HE loadings were quantified for large- and mediumcaliber firings. Large-caliber munitions include those greater than 60 mm, and medium caliber are between 20 and 60 mm. Perchlorate loadings were potassium perchlorate (KClO<sub>4</sub>) associated with practice rounds and simulators. Supplementary information (Army Environmental Command (AEC) 2009) to the ORAP Phase I report on Ft. A.P. Hill (EA, Inc. 2006) was used to estimate MC mass loadings. Supplementary information contained the Department of Defense Identification Code (DODIC) of munitions fired on each range, as well as number of rounds fired each year for the years 2000 through 2006. The Munition Items Disposition Action System (MIDAS) was accessed to determine the mass of MCs delivered to the impact area for each DODIC and each round fired. Determination of the annual residual-mass loading for each of the five constituents is described below. It was assumed that all residual-mass loading was deposited into the single AOI.

# **HE** loadings

Records provided by AEC (2009) were examined to determine the total number of predominate munitions fired for large and medium calibers. Attention was then focused on DODICs that were most often fired. For each of those DODICs, the number of rounds fired was summed for all ranges and all years to determine the total fired for the DODIC over the 7-year period. This total was divided by seven to determine the average number of rounds fired per year. The predominant large- and mediumcaliber munitions fired are shown in Table 1 and Table 2, respectively, as well as the mass of TNT and RDX in each round delivered to the impact area and the total calculated residual TNT and RDX loading. To calculate residual HE mass loading, it was assumed that all residual mass was because of low-order detonations, with a 2% occurrence rate and a 50% yield for each occurrence; i.e., half was exploded and half was unexploded. The actual, low-order occurrence rate could be less than the assumed rate, but the value used was adequate for conducting the POC application. The RDX total-residual loading per year is the sum of the grand total rates, or 15,201 g/year, in Table 1 and Table 2.

DODIC	Size, mm	TNT, g/round	RDX, g/round	Number fired /year	TNT loading, g/year	RDX loading, g/year
D544	155	6,756	0	861	58,169	0
C445	105	948	1,252	270	2,560	3,380
Grand totals					60,729	3,380

Table 1. Primary large caliber firings and loadings of HE.

Table 2. Primary medium caliber firings and loadings of HE.

DODIC	Size, mm	RDX, g/round	Number fired/year	RDX loading, g/year
B546	40	44.73	5,429	2,428
B470	40	54.41	9,286	5,052
B542	40	37.36	11,286	4,216
B103	30	3.95	3,143	124
Grand total				11,821

## **Metals loadings**

Only small-arms firings were considered for metals loadings. Most of the small-arms rounds fired were 5.56 mm. The most-often used, live 5.56-mm round was DODIC A059, which has 0.005 and 0.003 lb of lead and copper, respectively, in the projectile and jacket, according to the MIDAS database. The ORAP Phase I report on Ft. A.P. Hill (EA, Inc. 2006) stated that approximately 22,000,000 small-arms rounds are fired per year. This amount seems too high and may be an error in the report. An examination of range-firing records indicated that this may have been the total number of small-arms rounds fired over the 7-year period from 2000 - 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/year of lead and copper loading, respectively, deposited into SAFRs. A mass of 50,000,000 g is equal to 55 English tons, which is a considerable amount of lead deposited each year. The reported value of 22,000,000 rounds per year is used for this POC analysis, but this amount may be inflated by a factor of seven.

Difficulty occurs in assessing metals associated with SAFRs because many ranges are scattered throughout the installation, whereas most HE is exploded within a few large impact areas. Small arms may be fired into

targets with backdrop berms or at targets in open areas. Obviously, the total impact mass for metals from small-arms firing is considered to be residual.

## **Perchlorate loadings**

Table 3 shows predominant DODICs used that contained perchlorate, as well as numbers fired per year and estimated residual loadings. Estimated residual loadings were computed using an assumed emission factor of 0.01, which means that 1% of total perchlorate within munitions was deposited as unexpended residue. The 1% assumption is purely a guess, and thus, emission factors require further research. As with metals, the deposition of perchlorate can be spread over a large area. All perchlorate in these munitions was in the form of potassium perchlorate.

Table 3. Primary DODICs used containing perchlorate, with firings and estimated loadings.

DODIC	Perchlorate, g/round	Number fired/ year	Perchlorate loading, g/year
B584	0.68	8,282	56.3
L601	14.74	68	10
L594	38.87	16	6.2
H975	13.04	10	1.3
Grand total	•		74

# 4 Site Characterization and Model Inputs

Various site characteristics and other inputs must be determined or estimated to apply TREECS Tier 1 models. These data fit into the general categories of site dimensions, physical, soil, hydrologic characteristics, and fate-and-transport parameters. Each of the required variables and their estimation methods within these categories are discussed below.

#### Site dimensions and physical characteristics

The AOI dimensions (length and width) and area must be determined for model input. For the Tier 1 soil fate-and-export model, AOI dimensions and area do not affect the export fluxes, but area does affect the computed AOI soil concentration of MC residue, and the dimensions can affect aquifer concentrations. Thickness of the surface-soil layer containing MC residue drops out of the equations and is not required.

Aquifer concentrations computed by the MEPAS aquifer model can be affected by AOI dimensions, especially when the receptor well is located in close proximity to the AOI. The AOI width, W<sub>f</sub>, is the AOI dimension that is perpendicular to the groundwater flow. The AOI length, L<sub>f</sub>, is the AOI dimension that is parallel to groundwater flow. Aquifer concentrations are affected by AOI dimensions when the downstream longitudinal distance to the receptor well is less than approximately 10 x W<sub>f</sub>. The downstream longitudinal distance of the well is measured from the AOI centroid, or at one half the AOI length, L<sub>f</sub>. As a rule of thumb, the well should not be closer than 1.5 L<sub>f</sub> 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. 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<sub>f</sub> and L<sub>f</sub>; rather it is the area of the polygon.

Determining AOI shape and dimensions can be difficult even for a single impact area because impact areas are rather large and heterogeneous. At Ft. A.P. Hill, there are three dudded impact areas, 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 direct and indirect firing points. These areas are subject to each type of live-fire munitions and pyrotechnics.

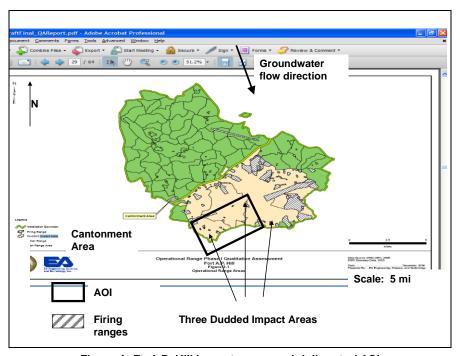


Figure 1. Ft. A.P. Hill impact areas and delineated AOI (modified from EA, Inc. 2006).

For Ft. A.P. Hill, the primary impact area, and thus the AOI, was depicted by examination of supplementary information (AEC 2009) and aerial views from Google Earth. A single AOI was assessed. In retrospect, the AOI could have been split into two or three AOIs, or one for each subwatershed drainage basin, but it would have been necessary to determine how much MC loading was deposited within each AOI. Firing records indicate which ranges are used for firing, but they do not delineate where munitions hit.

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 used to simplify calculation of the AOI surface area, which is a required model input. Sensitivity tests were run to determine how site dimensions affect soil and aquifer concentrations and are discussed later in this report.

A distance from the AOI center to each receptor groundwater well of interest must be specified. The nearest receptor well relative to the AOI is approximately 4,000 m downgradient, based on maps in the Phase I ORAP report (EA, Inc. 2006). One well location of 4,000 m was thus considered in the analysis. 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 resulted in the highest well MC concentrations, as predicted by the MEPAS aquifer model. Other well locations at greater depth or off-the-plume centerline can be considered, however.

The MEPAS aquifer model cannot address sinking plumes associated with fluid-density differences. Additionally, this model cannot address heterogeneities in porous media and associated heterogeneous flow and transport fields. Therefore, theoretical maximum plume constituent concentrations are always located at the water-table surface and along the plume centerline where the mass flux from the vadose zone enters the groundwater.

A representative water body was required to assess surface water and sediment impacts. 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 runof-the-stream lake. The length of the lake appears to be 1500 m with an approximate width of 50 m, resulting in a surface area of 75,000 m<sup>2</sup>. The mean depth was assumed to be 1 m, and the average annual flow through the lake was assumed to be 47,304,000 m<sup>3</sup>/year. This flow rate was based on an assumed average flow velocity of 0.1 ft/s. Given these lake dimensions and flow, the average residence time of water in the lake is 0.0016 years, or a little over half a day. Surface-water flow-through rates can also be estimated from the catchment basin area that drains into the surface waters. Thus, 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. Groundwater discharges, however, can contribute to lake inflow. Procedures for calculating runoff depth are presented in the "Hydrologic Characteristics" Section below.

#### Soil characteristics

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

Sandy-loam soil texture has a dry-soil bulk density of 1.48 g/cm³, a porosity of 44%, a field capacity of 17.5%, and a saturated hydraulic conductivity of 1.12 m/day. These values are from Tables B1 and B2 of the report by Dortch et al. (2009), except for hydraulic conductivity, which was from WSS. The soil water content is approximately equal to the field capacity on an average annual basis. WSS was used to obtain the soil-surface organic matter content, which was 1.2%. This organic matter content translates into a fraction of organic carbon of approximately 0.007. Soil pH was approximately 5.5.

#### **Hydrologic characteristics**

The Tier 1 soil model requires long-term average annual rates for rainfall, infiltration, and soil erosion, and the long-term average number of rain events per year. Before explaining estimation of these hydrologic variables used in this POC application, implemented TREECS procedures for calculating them must be reviewed. These procedures have been broadly defined previously by Dortch et al. (2009), but more explanation is warranted. Computations for the Ft. A.P. Hill application will be explained following a description of the calculation procedures.

When performing hydrologic computations, the first task is to determine the AOI, as discussed above. Within the AOI, land cover and type, soil texture (as described in the previous section), and land-surface slope must first be known. The Soil Conservation Service (SCS) curve number (CN), the Universal Soil Loss Equation (USLE) crop/land use management factor (C), and soil erodibility factor (K) can be estimated using standard tables. If the AOI is heterogeneous in terms of watershed properties such as cover and type, it may be advantageous to estimate a composite CN.

<sup>1</sup> http://websoilsurvey.nrcs.usda.gov/app/WebSoilSurvey.aspx.

-

As with any hydrologic analysis, a complete precipitation record over time is required. For this and other similar analyses, a minimum of 20 years of daily rainfall records must be acquired in order to accurately compute annual water balances and erosion amounts. In addition, a record of monthly air temperatures over time is required for computing potential evapotranspiration (PET).

#### Average annual runoff

Once the composite CN has been computed and the rainfall period of record has been assembled, the antecedent moisture content (AMC) needs to be computed for each day to modify the CN. The sequence of these computations is shown in Figure 2. The symbol I in Figure 2 is a day counter, and n is the number of days in a year.

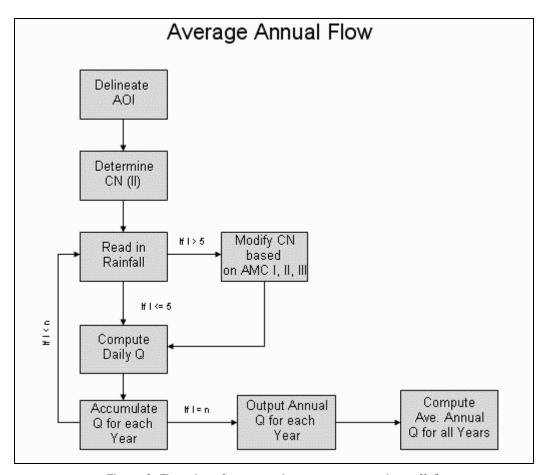


Figure 2. Flow chart for computing average annual runoff Q.

The AMC index is computed based upon rules in Table 4. When the AMC index is determined, the appropriate CN can be computed. If the AMC index is II, no computation needs to be performed; otherwise the CN needs to be adjusted to account for dry or wet soil conditions as follows:

$$CN_{I} = \frac{CN_{II}}{2.3 - 0.013CN_{II}} \tag{1}$$

$$CN_{III} = \frac{CN_{II}}{0.43 + 0.0057CN_{II}} \tag{2}$$

AMC Dormant Season Growing Season

I (Dry) Less than 1.3 Less than 3.6

II (Average) 1.3 to 2.8 3.6 to 5.3

III (Wet) More than 2.8 More than 5.3

Table 4. Seasonal rainfall limits for three levels of AMC.

After determining the modified CN, the daily runoff depth Q (inches) is computed as follows:

$$Q = \frac{(P_d - I_a)^2}{P_d - I_a + S} \tag{3}$$

where:

 $P_d$  = daily precipitation depth (in.)

 $I_a$ = initial abstraction (in.), which is the sum of the initial soil moisture loss (ISM), infiltration, and ET

S =potential retention (in.)

and where:

$$I_a = 0.2S \tag{4}$$

$$S = \frac{1000}{CN} - 10 \tag{5}$$

For runoff,  $I_a$  can be estimated from Equation 4. For infiltration, however, ISM and ET, which partly comprise  $I_a$ , must be determined. From previous experience, ISM loss can be estimated based upon the AMC category as shown in Table 5.

Antecedent Moisture Condition (AMC)	Daily Initial Soil Moisture Loss (ISM) (inches)
I (Dry)	0.02
II (Average)	0.01
III (Wet)	0.00

Table 5. ISM as related to AMC.

ISM is assumed to contribute directly to infiltration of water into the soil. The remaining initial abstractions are partitioned (Figure 3) between actual infiltration and evapotranspiration.

Daily computations will continue throughout the period of record. Total annual runoff will be computed for each year, and the period of record average of each year's annual runoff will be computed in order to reduce bias of extreme dry or extreme wet years.

#### Average annual infiltration

In order to compute infiltration, monthly average runoff and monthly average PET (cm) need to be estimated. The logic for computing infiltration is shown in Figure 3, where n is the total number of months in the record in this case.

The monthly average flow is actually the monthly average runoff-depth  $Q_m$  converted to centimeters and is a by product of computing the annual runoff depth of the previous section. The maximum monthly infiltration  $q_{wmm}$  (cm) is the monthly average precipitation  $P_m$  (cm) less  $Q_m$  and monthly ISM, and it must be corrected for PET to yield the monthly average infiltration  $q_{wm}$  (cm).

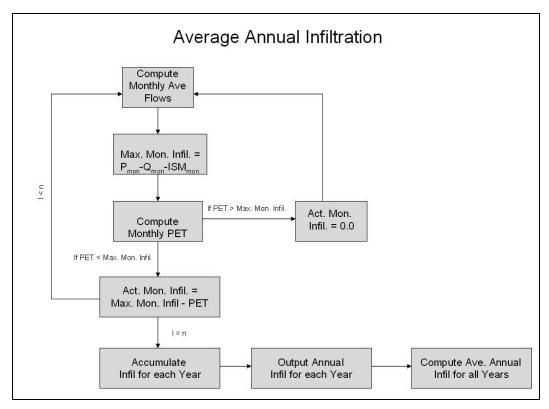


Figure 3. Flow chart for computing average annual infiltration.

Using the Thornewaite method, PET is computed as follows:

$$PET(0) = 1.6 \left(\frac{10T}{J}\right)^{c} \tag{6}$$

where:

T = mean monthly air temperature (°C)

J = sum of 12-monthly values of heat index (I) for each year (January through December)

and where:

$$I = \left(\frac{T}{5}\right)^{1.514} \tag{7}$$

The exponent *c* is computed from:

$$c = 0.000000675J^3 - 0.0000771J^2 + 0.01792J + 0.49239$$
 (8)

The monthly average *PET* (cm) for the known latitude is computed from:

$$PET = K \times PET(0) \tag{9}$$

The variable *K* is a constant for each month of the year and varies with latitude as shown in Table 6.

Latitude	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	1.0	1.07	1.14	1.17	1.16	1.11	1.03	0.96	0.89	0.85
20°N	0.92	0.96	1.0	1.05	1.09	1.11	1.10	1.07	1.02	0.98	0.93	0.91
10°N	0.97	0.98	1.0	1.03	1.05	1.06	1.05	1.04	1.02	0.99	0.97	0.96
Oo	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
10°S	1.05	1.04	1.02	0.99	0.97	0.96	0.97	0.98	1.0	1.03	1.05	1.06
20°S	1.10	1.07	1.02	0.98	0.93	0.91	0.92	0.96	1.0	1.05	1.09	1.11
30°S	1.16	1.11	1.03	0.96	0.89	0.85	0.87	0.93	1.0	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

Table 6. Constant K in the Thornewaite method.

If the monthly average PET is greater than  $Q_m$ , then  $q_{wm}$  is set to zero. If  $Q_m$  is greater than PET, then  $q_{wm}$  equals  $q_{wmm}$  minus PET. Once the monthly average runoff and PET are computed, annual infiltration depth is calculated for each year of the period of record. The period of record average annual infiltration depth is computed in order to reduce bias of extreme wet or dry years.

#### **Average annual erosion**

Average annual erosion is computed using the USLE according to:

$$A = RKLSCP (10)$$

where:

A = average annual soil loss due to sheet and rill erosion (tons/acre-year)

R = rainfall factor

K =soil-erodibility factor

L = slope-length factor

S = slope-gradient factor

C =crop-management factor

P =erosion-control practice factor

For firing range analyses, *P* should usually be set to 1.0. Other factors are discussed in Appendix B of the report by Dortch et al. (2009).

The annual soil loss actually delivered or exported from the AOI outlet can be less than the soil erosion rate computed by Equation 10 because of trapping within the AOI. Thus, the value of *A* computed by Equation 10 can be multiplied by the sediment delivery ratio (SDR) to correct the erosion rate. The SDR is computed (Julien 1995) from:

$$SDR = 0.31 A_t^{-0.3} \tag{11}$$

where  $A_t$  is the AOI area in square miles.

The soil erosion rate, A X SDR, has units of tons/acre-year, which must be converted to soil erosion rate E, which has units of m/year. This conversion can be calculated by dividing the product by soil dry-bulk density  $\rho_b$  (g/cm³) and applying appropriate conversion units. The complete conversion equation is as follows:

$$E(m/yr) = \frac{A(T/acre-yr) x SDR x 2000(lb/T) x 454(g/lb) x 10^{-6} (m^3/cm^3) x 10.76(ft^2/m^2)}{43,560(ft^2/acre) g fm/^3)}$$

$$E(m/yr) = \frac{2.24E - 4}{\rho_b} A SDR \tag{12}$$

#### **Calculated values for POC application**

Daily precipitation data from the Washington D.C. National Airport for the period 1970 – 1995 were assembled and input to a hydrologic computer program written in C programming language to perform computations described in previous sections. The processed data for the 25-year period resulted in an average annual precipitation of 39.05 in./year (0.992 m/year). The average daily rainfall for all daily rainfall events for the 25-year period was 0.343 in., and there was an average of 114 rainfall events per year for the 25-year period.

According to WSS, soil for the AOI falls in hydrologic soil group B. The land-cover type was considered as grassland with a relative poor hydrologic condition. From the SCS table of CNs for other agricultural lands (Table B5, Dortch et al. 2009), the CN for group B (poor grassland) is 79. Using daily precipitation values and a CN of 79 resulted in an average-event (daily) runoff depth of 0.023 in. for the 25-year period. The average annual runoff depth for the 25-year period is 2.64 in./year (0.067 m/year).

Daily average air temperatures from the same period and station (1970-1995 for Washington D.C. National Airport) were acquired and input to the hydrologic computer program. Mean monthly air temperatures were computed for each month of the 25-year period and used to compute mean monthly PET at 0 degrees latitude for each month. Using the site latitude of 38.3 degrees N and data from Table 6, the site meanmonthly PET was computed for each month. The average annual PET for the 25-year period is 30.09 in./year (0.764 m/year).

Using mean monthly computed precipitation, runoff, and PET, the monthly infiltration rate was computed. These monthly values were accumulated for each year and averaged for the 25-year period, yielding an average annual infiltration rate of 6.32 in./year (0.161 m/year). The average annual precipitation minus the average annuals for PET, runoff, and infiltration results in zero difference or a perfect water balance.

Erosion flux was computed using Equation 10. The *R* factor was set to 225 based on the U.S. map of *R* in Figure B1 of the report by Dortch et al. (2009). The *K* factor of 0.24 was based on WSS. The *LS* factor was set to 10 based upon Figure B2 in Dortch et al. (2009), using a slope length of 2,000 ft and a slope gradient of 14% for the site. Gradient was based on WSS-reported slopes for the AOI. Slope length was the maximum for

Figure B2 and is greater than the  $L_f$  dimension of the AOI. The C factor was set to 0.1 based upon Table B8 of Dortch et al. (2009), using no appreciable canopy and 40% grass cover. As stated previously, P should be set to 1.0 for firing ranges. Using these factors, the USLE-annual soil loss due to erosion was computed to be 54 tons/acre-year. Using Equation 12 and  $\rho_b$  = 1.48 g/cm³, the erosion rate was 0.00817 m/year. The SDR for this computation was conservatively set to 1.0, although the SDR was computed to be 0.2 from Equation 11 using the AOI area of 4.16 square miles. From a plot (Julien 1995) of the data used to develop Equation 11, the value of SDR can range from approximately 0.1 to approximately 0.7 for an area of 4 square miles.

#### **Fate-and-transport parameters**

Various fate-and-transport parameters had to be estimated and specified for Tier-1 models. Specification of these parameters for each model is discussed in this section.

#### Soil model

The soil model has four fate-and-transport-related parameters: soil-water distribution (or partition) coefficient,  $K_d$  for soil (L/kg); soil detachability due to rainfall, a (kg/L); soil-exchange layer thickness,  $d_e$  (m), associated with rainfall ejection of pore water; and the constituent solubility in water (mg/L). Estimations of values used for each of these parameters are discussed below.

For organic constituents,  $K_d$  (soil) can be estimated (Streile et al. 1996) from soil texture, fraction by weight of organic matter in soil, and the organic carbon-to-water partition coefficient  $K_{oc}$ , as follows:

$$K_d = 0.0001 K_{oc} (57.735 OM + 2.0 clay + 0.4 silt + .005 sand)$$
 (13)

where OM, clay, silt, and sand are the percent by weight of organic matter, clay, silt, and sand, respectively. If  $K_{oc}$  is not known, it can be estimated from  $K_{oc} = 0.617 \; K_{ow}$ . If OM is not known, it can be estimated from  $OM = 175 \; f_{oc}$ , where  $f_{oc}$  is the fraction by weight of organic carbon in soil. Soil composition must be known, or at least a texture classification such as sandy loam must be known, and the composition can be determined from Table B1 of Dortch et al. (2009).  $K_{oc}$  values suggested by the FRAMES (Framework for Risk Analysis in Multimedia Environmental Systems)

constituent database in ARAMS<sup>TM</sup> are 13.2 and 30.9 L/kg, respectively, for RDX and TNT. Placing these values, as well as soil composition, into Equation 13 results in  $K_d$  (soil) values of 0.13 and 0.31 L/kg for RDX and TNT, respectively. Perchlorate is highly soluble, highly stable, and highly mobile in water. The  $K_{oc}$  for potassium perchlorate is approximately 4E-8 L/kg (from Risk Assessment Information System [RAIS], <a href="http://rais.oml.gov/index.shtml">http://rais.oml.gov/index.shtml</a>). The resulting  $K_d$  (soil) from Equation 13 is 4E-10 L/kg.

Obtaining  $K_d$  (soil) values for metals is much more problematic because local aqueous chemistry can affect the value. The MEPAS aquifer model, however, has a table for soil  $K_d$  for metals, and the values suggested were 597 and 92 L/kg for lead and copper, respectively. Thus, these values were used for the soil model.

Rainfall ejection parameters,  $d_e$  and a, are not easily measured, and typical values reported by Gao et al. (2004), and in other literature, must be used. Both parameters are probably affected by soil texture, land use and cover, and perhaps soil chemistry. Typical values for a and  $d_e$ , as reported by Gao et al. (2004), are on the order of 0.4 kg/L and 0.005 m, respectively.

Solubility is a chemically specific property but can also be related to soilwater chemistry for metals. Solubility values for most constituents can be obtained from constituent databases (Army Range, FRAMES, and RAIS) in ARAMS and will also be in TREECS. Database solubility values for organic chemicals are fairly reliable, but this is not the case for metals, which are dependent on soil-water chemistry. Solubility values used for the analysis in mg/L were: RDX = 59.7; TNT = 130;  $KClO_4 = 20,800$ ; lead = 50,000; and copper = 24,400. The solubility values of RDX, TNT, and KClO<sub>4</sub> were obtained from the RAIS database, and values for the two metals were taken from the Army Range constituent database. These metal-solubility values are much higher than those that occur in natural conditions, but high values were used to provide worst-case, conservative results. Additionally, computed soil pore-water concentrations were well below any expected lower metal solubility values found. As long as soil pore-water concentrations are below solubility, the value for solubility has no effect on Tier 1 results.

#### **Aquifer model**

The three fate-and-transport parameters required by the aquifer model include dispersivities [x,y, and z directions] (m), the Darcy velocity, and aquifer thickness (m). The dispersivities, which were computed by the model, were set at 400, 132, and 1 m for the longitudinal, transverse, and vertical directions, respectively, based on a well located 4,000 m downgradient from the center of the AOI. The well location was assumed to be at the water table vertically (zero depth below water table) and along the groundwater plume centerline laterally (zero lateral distance) to provide conservative results as computed by the MEPAS aquifer model. Thickness of the aguifer was set at 15.2 m, based upon information in the Phase I ORAP report for Ft. A.P. Hill (EA, Inc. 2006), which agrees with data from WSS. Darcy velocity was set at 0.16 m/day, based on the product of saturated hydraulic conductivity of 112 cm/day of the site (see "Soil Characteristics") and the site's average ground-surface slope or gradient of 0.145, as determined from WSS. The ground-surface gradient was used rather than the water-table gradient because of lack of information on the latter.

The aquifer model in Tier 1 TREECS uses a  $K_{\rm d}$  of 1.0 for all constituents to accelerate the solutions to steady state. At steady state with no decay, aquifer concentrations are independent of  $K_{\rm d}$ . Other input values are required by the MEPAS aquifer model, but these were specified according to Table 4 of the report by Dortch et al. (2009) to be consistent with the Tier 1 approach.

#### Surface-water model

Various fate-and-transport parameters are required by the RECOVERY surface-water/sediment model used in Tier 1. The sediment-water distribution (partition) coefficient  $K_d$  (sediment) (L/kg), is required for deep and upper mixed-layer sediments and water-column suspended solids. RECOVERY calculates  $K_d$  (sediment) from the octonol-water distribution coefficient  $K_{ow}$  and  $f_{oc}$ , the fraction of organic carbon in the sediments, where  $K_d = .617 \ f_{oc} \ K_{ow}$ ;  $f_{oc}$  was set to 0.01 in this application.

The  $f_{oc}$  values for deep sediments, mixed-sediment layer, and water-column suspended solids are all set to the same input value for the Tier-1 version of RECOVERY. With  $K_{ow}$  values of 7.41 for RDX, 39.8 for TNT, and 6.6E-8 L/kg for potassium perchlorate, computed sediment  $K_d$  values are 0.046, 0.25, and 4.07E-10, respectively. RDX and TNT  $K_{ow}$  values are

from RAIS, whereas the *KClO*<sup>4</sup> value was obtained from an EPA fact sheet on perchlorate.

Metal  $K_d$  values are not calculated in RECOVERY because  $K_{ow}$  should be zero; thus, they must be specified. An internet search was performed for sediment lead and copper  $K_d$  values, and values of 4,000 and 600 L/kg, respectively, appeared to be appropriate. Sediment  $K_d$  values are usually much higher than those for soil because most sediments are anaerobic below a thin surficial layer where sulfate is reduce to sulfide in anaerobic sediments and metals precipitate with sulfide.  $K_d$  values for water-column solids and the benthic-mixed sediment layer can be different and should be lower than for deep sediment for metals. All three values were set equal for each metal for this application.

Mixed-layer sediment porosity was set to the default value of 0.7. Wind speed was set to the default value of 6 m/s, but this input is relatively unimportant for the two explosives because they are extremely slow to volatilize, given their low Henry's constant. The total suspended-solids (TSS) settling rate was set to the default value of 36 m/year, which is representative of fine particles approximately 1  $\mu$ m in diameter that are highly adsorptive of chemicals. Other input parameters for RECOVERY were set according to values stated in Table 9 of the report by Dortch et al. (2009) to be consistent with the Tier-1 approach.

Four chemical-specific physical/chemical properties are required by the RECOVERY model for fate-and-transport. These properties are shown in Table 7, along with values used. The definition for each variable in Table 7 is: molecular weight, MW (g-mole); diffusivity in water,  $D_w$  (cm<sup>2</sup>/sec); Henry's constant, H (atm-m<sup>3</sup>/g-mole), and octonol-water partition coefficient,  $K_{ow}$  (ml/ml). Values for MW, H, and  $K_{ow}$  came from the RAIS database, except for  $K_{ow}$  for  $KClO_4$ , which was obtained from the EPA fact sheet, as stated previously. Only the  $D_w$  value for TNT came from RAIS, whereas the D<sub>w</sub> field for the other constituents was blank in RAIS. Thus, the other  $D_w$  values were assumed to be 6E-6 as well. Values of the organic carbon-water partition coefficient  $K_{oc}$  are listed in RAIS for TNT and RDX but were not used in this application because the values seemed too high. The version of RECOVERY to be used in TREECS Tier 1 will provide the user with the option to use either  $K_{oc}$  or  $K_{ow}$ . The model requires  $K_{ow}$ . If  $K_{oc}$ is used, the model interface will convert it to  $K_{ow}$  by dividing the  $K_{oc}$  value by 0.617.

Table 7. Physical and chemical properties used in RECOVERY for modeled constituents.

Constituent	MW	D <sub>w</sub>	Н	Kow
RDX	222.12	6.0E-6	6.31E-8	7.41
TNT	227.13	6.36E-6	4.57E-7	39.8
KCIO <sub>4</sub>	138.55	6.0E-6	0	6.6E-8
Lead	207.2	6.0E-6	0	0
Copper	63.55	6.0E-6	0	0

## **Summary of model inputs**

Input values used for the soil model are summarized in Table 8. The sources of these values were discussed above. The MC-residue mass loadings are also an input and were discussed in Chapter 3.

Table 8. Summary of Tier 1 soil model input values.

Input Variable	Value	Units
Solubility RDX	59.7	mg/L
TNT	130	mg/L
Lead	50,000	mg/L
Copper	24,400	mg/L
KCIO4	20,800	mg/L
Volumetric soil moisture content	17.5	%
Soil dry-bulk density	1.48	g/cm³
Soil porosity	44	%
Soil-water partition coefficient RDX	0.13	L/kg
TNT	0.31	L/kg
Lead	597	L/kg
Copper	92	L/kg
KCIO <sub>4</sub>	4E-10	L/kg
AOI surface area	10,775,905	m²
AOI width	4,715	m
AOI length	2,285	m
Average annual precipitation rate	0.992	m/yr
Average number of rainfall days in a year	114	events/yr
Average annual water infiltration rate	0.161	m/yr
Average annual soil erosion rate	0.0082	m/yr
Soil detachability	0.4	Kg/L
Soil-exchange layer thickness	0.005	m

Tier 1 aquifer model inputs are summarized in Table 9. In addition to these inputs, AOI site dimensions and the average annual water infiltration flow rate of 1,729,834 m³/year were passed to the aquifer model from the soil model. The infiltration flow rate is the infiltration rate of 0.161 m/year multiplied by the AOI surface area of 10,775,905 m². Of note, the list of inputs described here is much shorter than standard MEPAS aquifer model inputs due to various simplifying assumptions for steady-state assessments as described by Dortch et al. (2009) for Tier 1 TREECS.

Table 9. Summary of Tier 1 MEPAS aquifer model input values.

Input Variable		Units
Darcy velocity	16	cm/day
Aquifer thickness	15.2	m
Longitudinal distance to well	4,000	m
Perpendicular distance from plume centerline to well	0	m
Vertical distance below water table of well intake	0	m
Longitudinal dispersivity (internally computed and set)	400	m
Transverse dispersivity (internally computed and set)	132	m
Vertical dispersivity (internally computed and set)	1	m

Tier 1 RECOVERY model inputs are summarized in Table 10. The list of inputs described here is much shorter than standard RECOVERY model inputs because of the various simplifying assumptions for steady-state assessments as described by Dortch et al. (2009) for Tier-1 TREECS. In addition to the inputs listed in Table 10, the chemical-specific properties listed in Table 7 must be provided to the RECOVERY model in Tier 1.

Table 10. Summary of Tier 1 RECOVERY surface-water model input values.

Input Variable	Value	Units
Partition coefficient Kd for water column		L/kg
RDX (computed from K <sub>ow</sub> =7.41)	0.046	
TNT (computed from K <sub>ow</sub> =39.8)	0.25	
Lead	4,000	
Copper	600	
KCIO <sub>4</sub> (computed from K <sub>ow</sub> =6.6E-8)	4.07E-10	
Partition coefficient K <sub>d</sub> for mixed-sediment layer		L/kg
RDX (computed from K <sub>ow</sub> =7.41)	0.046	
TNT (computed from Kow=39.8)	0.25	
Lead	4,000	
Copper	600	
KCIO <sub>4</sub> (computed from K <sub>ow</sub> =6.6E-8)	4.07E-10	
Partition coefficient K <sub>d</sub> for deep-sediment layers		L/kg
RDX (computed from K <sub>ow</sub> =7.41)	0.046	
TNT (computed from Kow=39.8)	0.25	
Lead	4,000	
Copper	600	
KCIO <sub>4</sub> (computed from K <sub>ow</sub> =6.6E-8)	4.07E-10	
Water surface area	75,000	m²
Mean water depth	1.0	m
Water flow-through rate	47,304,000	m³/yr
Mixed-sediment layer porosity	0.7	fraction
Mixed-sediment layer weight-fraction organic carbon in solids	0.01	fraction
Wind speed	6.0	m/sec
TSS settling rate	36	m/yr

# **5 Model Results**

Tier 1-soil, aquifer, and surface-water/sediment models were applied using input variables and parameters discussed in the previous chapter. The results of each model are discussed below.

#### Soil model

Soil concentrations and export fluxes computed by the Tier 1 soil model are presented in Table 11. Because the Tier 1 soil model is a steady-state model, these concentrations and fluxes do not change in time. For Tier 1, all soil concentrations are assumed to be in the aqueous phase (dissolved and adsorbed to soil) because steady state is assumed without dissolution and system losses (such as degradation and volatilization). Soil concentrations are probably unrealistically high, especially for metals, because of the steady-state assumption that ignores dissolution time (i.e., instantaneous and complete dissolution are assumed). Additionally, extreme heterogeneities in MC concentration can exist on firing ranges, but cannot be reflected by the present model.

Constituent	Soil concentration, mg/kg	Erosion flux, g/year	Rainfall-ejected runoff flux, g/year	Leaching flux, g/year
RDX	1.58E-3	206	4.00E3	1.10E4
TNT	1.01E-2	1311	1.88E4	4.06E4
Lead	369	4.81E7	7.86E5	1.07E6
Copper	184	2.40E7	2.53E6	3.46E6
KCIO <sub>4</sub>	4.07E-6	0.53	13.9	60

Table 11. Computed soil concentrations and export fluxes for Ft. A.P. Hill.

Export fluxes do not depend on area of the AOI, but soil concentrations do. Thus, for a smaller area, concentrations will be greater in a direct proportion; i.e., halving the area doubles the concentrations for the same loadings. However, if the AOI had been split into multiple AOIs, such as one for each SAFR or one for each sub-watershed, then loadings and areas would have been smaller. Whether concentrations would have been higher or lower, without actually distributing loads and making calculations, is unknown. Because export fluxes vary linearly and in direct proportion to

loadings, they would be halved if the AOI was divided into two AOI's, with each AOI receiving half of the loading.

The erosion-export flux is greater for constituents with the larger  $K_d$  (i.e., metals). As expected, rainfall-ejected runoff and leaching fluxes tend to be greater than erosion fluxes for constituents with smaller  $K_d$ . When comparing fluxes for RDX and TNT, as well as their respective  $K_d$  values, loading for TNT is much greater than loading for RDX, and export fluxes are directly and linearly proportional to loading.

Importantly, the assumption of steady state does not allow the Tier 1 model to consider time required for weathering and dissolution. At steady state, or at infinite time with a constant loading and input parameters, all solid-phase loading is available in the aqueous phase. This assumption provides a worst-case condition, with export flux yields that may be greater than reality, especially for metals that can have slow weathering and dissolution rates. The steady-state assumption is not unreasonable for HE constituents because they have much higher dissolution rates than metals, and their solubility is less dependent on ambient soil chemistry. Although results for the two metals are presented and discussed, an important recommendation is to use time-varying Tier 2 models, which include dissolution, for assessing metals.

# Receiving water models

The MEPAS aquifer model and RECOVERY surface-water and sediment model were applied using export fluxes computed from the soil model as input loadings. Each of these models is described by Dortch et al. (2009). Model output results for the Ft. A.P. Hill AOI are discussed below.

#### **Aquifer model**

Leaching fluxes in Table 11 were computed by the soil model and used as a boundary condition to the aquifer model to provide mass loading rates for each simulated constituent. At the location of the receptor well, computed aquifer concentrations versus time are plotted in Figures 4-8 for each of the five constituents. Results vary with time because the aquifer model is a time-varying model. Concentrations, however, do eventually reach a steady state because a constant import-flux loading was applied for 500 years. Thus, the peak steady-state concentrations eventually decrease

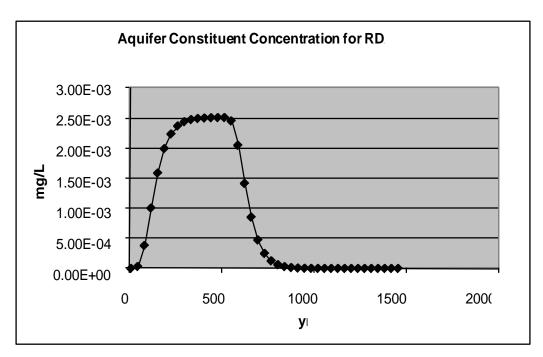


Figure 4. Computed RDX concentration versus time in groundwater at the location of the receptor well.

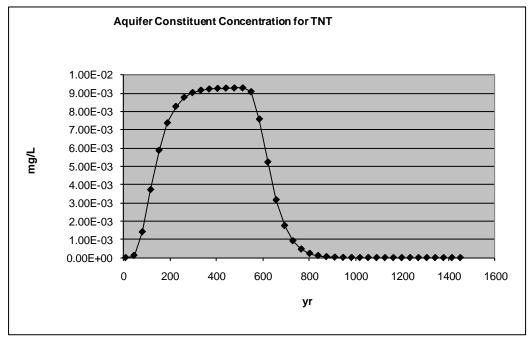


Figure 5. Computed TNT concentration versus time in groundwater at the location of the receptor well.

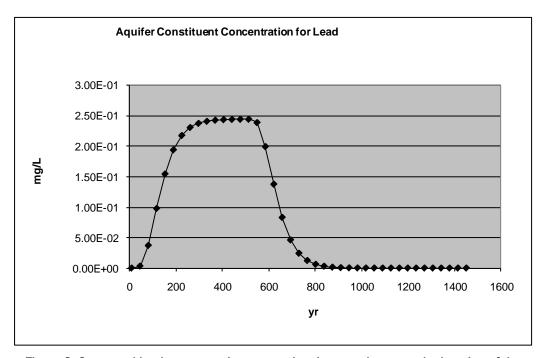


Figure 6. Computed lead concentration versus time in groundwater at the location of the receptor well.

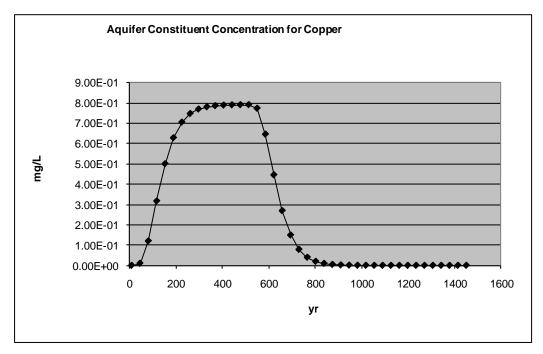


Figure 7. Computed copper concentration versus time in groundwater at the location of the receptor well.

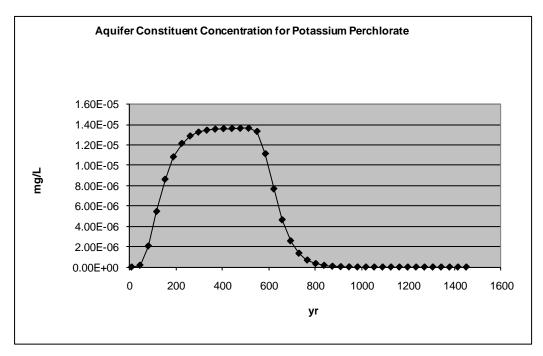


Figure 8. Computed KClO<sub>4</sub> concentration versus time in groundwater at the location of the receptor well

to zero after 500 years. The time to reach peak steady-state values is not important and should be ignored for Tier 1 because a default value of 1 L/kg was used for  $K_d$  in the aquifer model for all constituents to reduce input requirements needed for steady-state analysis and reduction of time to reach steady state. In reality, metal concentrations can take much longer to peak than shown in Figures 4-8, but explosives can peak sooner than depicted because their  $K_d$  values are typically less than 1.0. Tier 2 will be time varying, realistic  $K_d$  values will be used for the aquifer model, and time to reach peak will be important. Additionally, dissolution, which will also affect time responses, will be included.

Steady-state, peak constituent concentrations at the receptor well and drinking water protective health benchmarks for each constituent are shown in Table 12. Both HE constituents and lead exceed the protective benchmarks. As noted previously, use of Tier 1 to assess metals is probably inappropriate because of the length of time required for dissolution of metals, which is related to the potential for low solubility depending on soil chemistry. Increasing only the  $K_d$  values to values consistent with those used for the soil model resulted in thousands of years for the two metal concentrations to peak at the receptor well. Large metal retardation and associated attenuation of the 500-year loading resulted in peak concentrations, which were more than an order of magnitude smaller

Table 12. Computed aquifer receptor well peak constituent concentrations and drinking water protective benchmarks.

Constituent	Aquifer concentration at well, ppb	Protective benchmark, ppb
RDX	2.51	0.61
TNT	9.28	2.2
Lead	244	15
Copper	790	1500
KCIO <sub>4</sub>	0.014	15

than those computed with a  $K_d$  of one. Metals are not generally considered to be a problem for groundwater, as evidenced by detailed studies at Camp Edwards (Clausen et al. 2007), because of relatively high adsorption and low solubility. Modeling of lead at Camp Edwards, as cited and discussed by Clausen et al. (2007), indicated that transport of lead from soil to the groundwater table could take more than 1,000 years, even for favorable transport conditions such as high solubility and high loading concentrations.

Peak copper and  $KClO_4$  aquifer concentrations are below the protective benchmarks, although the copper concentration is quite high. Actual peak copper concentrations are expected to be much lower, for reasons discussed above for lead. Results for RDX and TNT raise a flag for potential concentrations that exceed health benchmarks in groundwater. Importantly, groundwater concentrations are directly proportional to MC-residue loading, and HE-MC residue loadings used in this application are based on the assumption of a 2% low-order rate with 50% yield. Thus, if the low-order rate was actually 0.5%, peak RDX concentration would be approximately the same as the protective benchmark of 0.61 ppb. Emphasis is placed on the highly-conservative assumption of no degradation, especially for TNT, which is known to degrade in soil.

Tier 1 is intended for screening, and results presented here indicate that HE constituents should be given further attention such as implementation of Tier-2 analysis. A Tier-2 analysis not only considers time-varying responses in soil and receiving media, but also time-varying loadings. If munitions use extends over a few decades, and the time response in groundwater occurs over several decades, peak groundwater concentrations can be lower than

those associated with the continuous, constant loadings of a steady-state analysis, as presented here. The Tier 1 analysis assumed that average annual loading, which was based on analysis of 7 years of range-use records, continues indefinitely at the same constant rate, or for 500 years for aquifer results presented here.

#### Surface-water/sediment model

The erosion and runoff fluxes in Table 11 were computed by the soil model and used as a boundary condition by the RECOVERY surface-water/sediment model for each simulated constituent. The computed-sediment (Figures 9 - 13) and water- (Figures 14 - 18) total (particulate and dissolved) concentrations versus time for the receptor water body (White Lake) are plotted for each of the five constituents. The results vary with time because the RECOVERY model is a time-varying model. Concentrations, however, do reach a steady-state concentration because a constant import-flux loading was applied for the 100-year period used in the model. For water, concentrations reach steady state almost immediately.

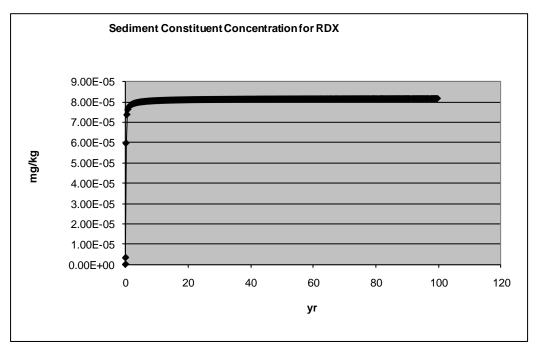


Figure 9. Computed sediment total concentration of RDX versus time for White Lake.

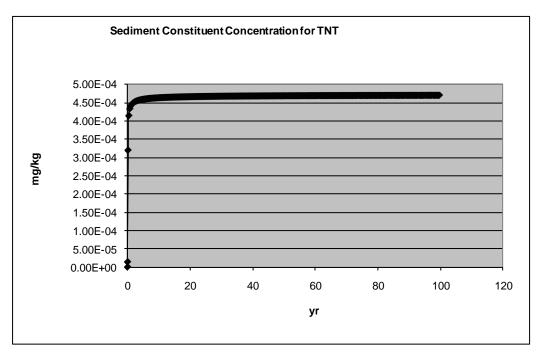


Figure 10. Computed sediment total concentration of TNT versus time for White Lake.

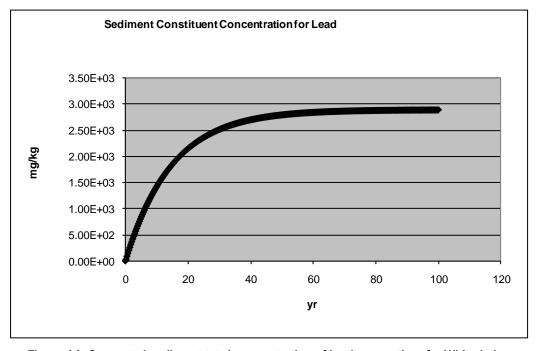


Figure 11. Computed sediment total concentration of lead versus time for White Lake.

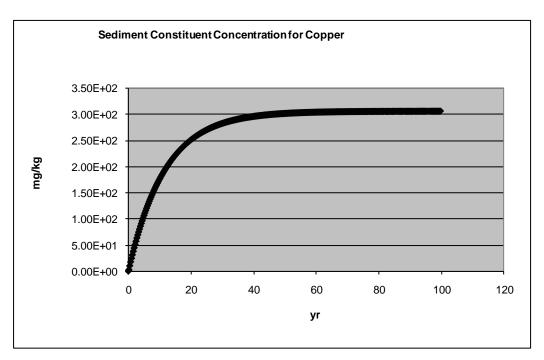


Figure 12. Computed sediment total concentration of copper versus time for White Lake.

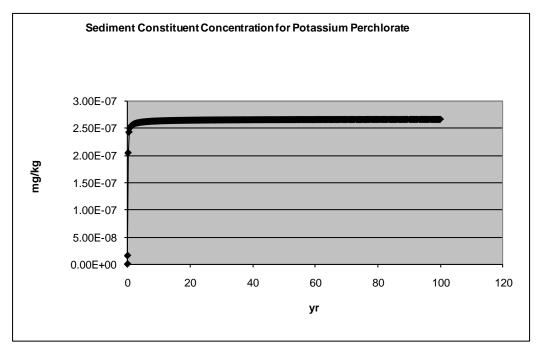


Figure 13. Computed sediment total concentration of KClO<sub>4</sub> versus time for White Lake.

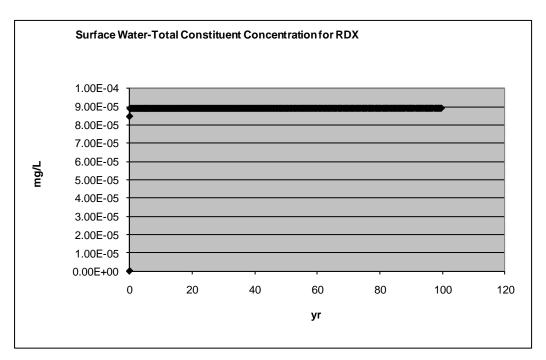


Figure 14. Computed water total concentration of RDX versus time for White Lake.

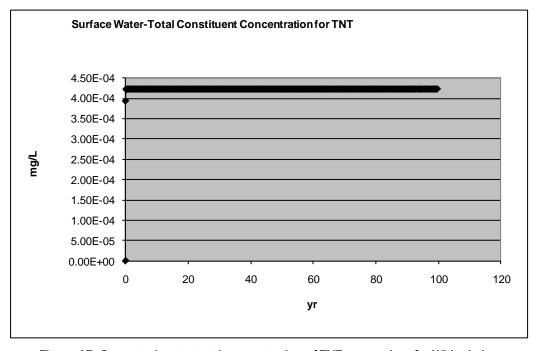


Figure 15. Computed water total concentration of TNT versus time for White Lake.

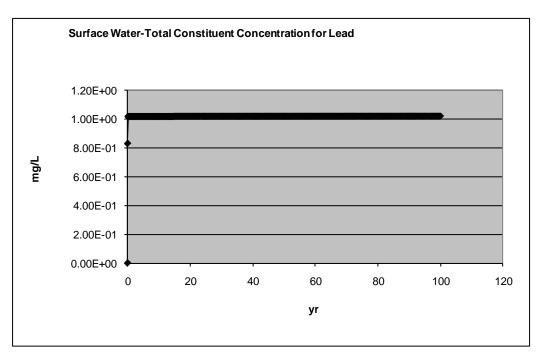


Figure 16. Computed water total concentration of lead versus time for White Lake.

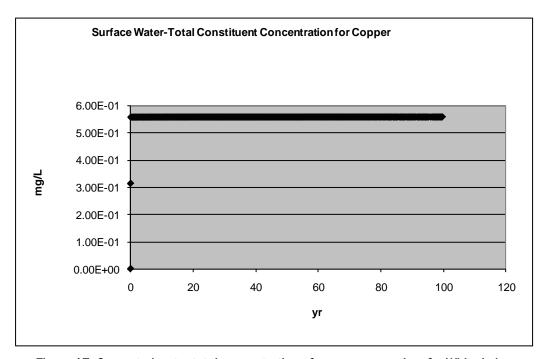


Figure 17. Computed water total concentration of copper versus time for White Lake.

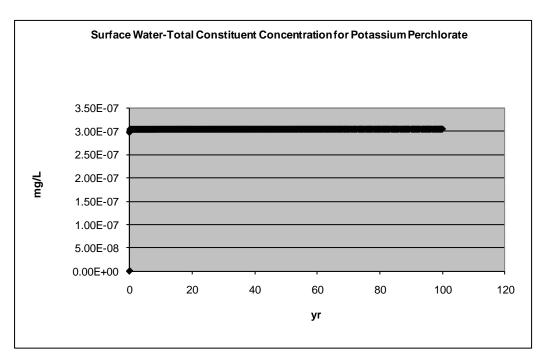


Figure 18. Computed water total concentration of KCIO<sub>4</sub> versus time for White Lake.

Computed peak water and sediment concentrations for White Lake and ecologically protective health benchmarks are presented in Table 13. These peak values correspond to the steady-state values plotted in Figures 9 - 18. Following this application, information was acquired indicating that ecological health benchmarks are established for dissolved instead of total water concentrations and the human health benchmarks use total concentration. Computed steady-state dissolved water concentrations were slightly lower than the total concentrations shown in Table 13. However, the dissolved MC concentrations are still far above protective ecological benchmarks for metals and far below protective ecological benchmarks for explosives and perchlorate. Although the results are not shown in Table 13, the only human health benchmark exceeded for surface water was for lead, which had a water concentration of 1.0 mg/L compared to a human health benchmark of 0.015 mg/L.

Again, the predicted metal concentrations can greatly exceed real expectations because of the long time periods required for occurrence of dissolution and low solubility. However, these projected concentrations signal that more detailed study and Tier 2 analysis are warranted for metals in surface water/sediment. Sediment concentrations for metals are much higher than those in the water column because of the relative high metal  $K_d$  values. Metals are much more likely to be a concern for surface-

water sediments than for groundwater. Metal contamination can be managed at SAFRs by practices such as metal removal from target area berms and water collection troughs at the base of berms, with distribution to collection areas for treatment/removal.

Table 13. Computed White Lake peak-constituent concentrations and
ecologically protective health benchmarks.

Constituent	Sediment concentration, ppb	Sediment- protective benchmark, ppb	Water concentration, ppb	Water- protective benchmark, ppb
RDX	0.082	26	0.089	190
TNT	0.47	184	0.42	90
Lead	2,880,000	47,000	1,020	2.5
Copper	305,000	34,000	559	9.0
KCIO <sub>4</sub>	2.67E-4	NA	3.05E-4	9300

Sediment-protective health benchmarks for RDX and TNT shown in Table 13 were obtained for a sediment organic carbon of 2%. Those benchmarks would be half of those in Table 13 if a sediment organic carbon of 1% was used. Lower sediment benchmarks, however, are still much greater than the predicted sediment concentrations for the explosives.

As noted in Chapter 4, the SDR for soil erosion was set to 1.0 rather than the computed value of 0.2. If the lower value is used, mass flux to ground-water and rainfall-induced runoff increases, whereas soil erosion mass flux decreases. The result is that aquifer concentrations for RDX, TNT, and perchlorate increase very slightly, whereas the concentrations for lead more than quadruple, and copper concentrations increase by a factor of approximately 2.8. The sediment and surface-water concentrations for the five MC constituents decrease from approximately 1% to 23%. Metal concentrations in sediment and surface water, however, still exceed health benchmarks. The only conclusion that changes regarding health benchmarks is that copper exceeds the aquifer benchmark, whereas copper was slightly below the benchmark with SDR equal to 1.0.

## **6 Additional Testing**

Additional testing included sensitivity runs of Tier 1 models and testing rainfall ejection and runoff calculations to verify their performance against measured laboratory data.

## **Sensitivity testing**

Sensitivity testing was conducted for input parameters for each of the three models (soil, aquifer, and surface water). Testing was limited to only those parameters considered to be the most uncertain or that could prove difficult for acquisition of an input estimate. Basic soil properties such as porosity and dry-bulk density were not evaluated because such properties can be readily determined from soil texture. Hydrology inputs, including average annual rainfall, infiltration, number of rainfall events, and erosion were not evaluated because these inputs are basic site characterizations that must be determined and can be estimated from the TREECS Hydrogeo-characteristics Toolkit (HGCT). These inputs are known to have a direct impact on site export, and they would be varied somewhat during an assessment to provide a better understanding of their importance and help bracket the results. Chemical properties were not evaluated because they are available from databases and are less uncertain.  $K_d$  values computed from  $K_{oc}$  or  $K_{ow}$  were not evaluated for the same reasons.

#### Soil-model inputs

The most uncertain input variables for the soil model include: solubility of metals; site area; partition coefficient for metals; soil detachability; and soil exchange layer thickness. Each of these was varied individually to assess effects and sensitivity of results. MC-residue loading is a sensitive input, but model responses are linear and directly proportional to the loading.

Solubility of lead was reduced from 50,000 to 10 mg/L, and models were run. No output results for lead changed for any of the three models (soil, aquifer, and surface water) because computed soil pore-water concentrations for lead did not exceed solubility, even for 10 mg/L. With solubility lowered to a value of 0.1 mg/L, which is below the computed pore-water concentration of 0.62 mg/L, aquifer concentrations decreased to the

solubility, and surface-water and sediment concentrations decreased just slightly because of less rainfall ejection/runoff.

AOI dimensions were cut in half to a width of 2,358 m and a length of 1,143 m, and this decreased the AOI area by a factor of four. As stated previously, this reduction will increase soil concentrations accordingly; i.e., by a factor of four in this case. Export fluxes from the AOI did not change. Additionally, surface-water and sediment concentrations did not change. An approximate 50% increase occurred in computed aquifer concentrations. AOI dimensions can affect computed aquifer concentrations when the receptor well is relatively close to the AOI. Additionally, the AOI area affects the infiltration flow rate (m³/year), and this flow rate affects source-boundary conditions in the aquifer model. These boundary conditions can ultimately affect receptor aquifer concentrations.

The soil-water partition (distribution) coefficient for lead was decreased from 597 to 200 L/kg. This reduction had the effect of decreasing the soil concentration of lead from 369 to 344 mg/kg. The leaching export flux nearly tripled with an increase from 1.07E6 g/year to 2.97E6 g/year. As expected, the rainfall-extracted runoff flux also increased and nearly tripled. Erosion-export flux decreased approximately only 8% because the computed erosion flux includes both adsorbed particulate and pore-water concentrations within the eroded soil layer. Computed aquifer concentrations increased in the same proportion (nearly tripled) as the leaching export flux. Computed sediment-and-water concentrations for lead decreased approximately 4%. Thus, aquifer concentrations are the most sensitive to changes in soil  $K_{\rm d}$ .

Rainfall detachability for soil was doubled from 0.4 to 0.8 kg/L. This change decreased soil concentrations slightly (reduced 1.6% for lead to 21% for TNT). Leaching-export fluxes decreased in the same manner and in approximately the same amount. The erosion-export fluxes also decreased in a similar manner and by similar amounts. Rainfall-extracted runoff fluxes increased substantially, with increases varying from 44% for non-metals to 97% for lead. Similar to leaching-export fluxes, aquifer concentrations decreased 1.2% for lead and 20% for TNT. Sediment concentrations increased only slightly for metals (e.g., 1% for copper) but substantially for other constituents (e.g., 40% for TNT). Surface-water concentrations increased in a similar manner.

The soil-exchange layer thickness for rainfall-ejected runoff was doubled from 0.005 to 0.01 m, which decreased soil concentrations slightly (reduced nearly 0% for metals to 2% for non-metals). Leaching and erosion-export fluxes decreased in the same manner and by nearly the same amount. Rainfall-ejected runoff fluxes increased by a greater amount, with increases varying from 9% for perchlorate to nearly 0% for metals. Aquifer concentrations decreased slightly in the same manner as leaching-export fluxes; i.e., 5% for perchlorate to nearly 0% for metals. Sediment concentrations did not increase for metals but increased somewhat for other constituents such as perchlorate (9%). Surface-water concentrations increased in a similar manner and in approximately the same amounts.

#### **Aquifer-model inputs**

The most uncertain inputs for the Tier 1 aquifer model included Darcy velocity, aquifer thickness, and the three dispersivities. The first two inputs were varied for sensitivity, but the dispersivities were not varied because they are estimated by the model. These parameters can substantially affect computed concentrations at well locations.

Darcy velocity was increased an order of magnitude to 160 cm/day. A tenfold increase in this parameter decreased aquifer concentrations by tenfold. Increasing Darcy velocity has the effect of diluting the loading flux to groundwater. Decreasing it has the opposite effect.

Doubling aquifer thickness to 30.5 m decreased aquifer concentrations by 50%. A decrease in aquifer thickness below the original value of 15.24 m to 10 m increased aquifer concentrations by approximately 50%. Increasing the thickness to 100 m had the effect of decreasing concentrations by about 84%. Further increases in thickness have a diminishing effect. For example, thicknesses of 500 and 1,000 m decrease aquifer concentrations by 86% from the original value.

#### Surface-water model inputs

Tier 1, surface-model inputs consist of the following, with the exception of chemically specific properties: partition coefficients for water, mixed-sediment layer, and deep sediment layers; water-surface area; mean water depth; water flow-through rate; mixed-layer sediment porosity; mixed sediment-fraction organic carbon ( $f_{oc}$ ); wind speed; and TSS settling rate.

In most cases, sensitivity test results for the surface water model are provided only for copper.

Increasing only the deep-sediment partition coefficient by a factor of 10 had almost no effect on computed mixed-layer and surface-water concentrations. The surficial sediment-mixed layer is important because it is usually biologically active. An increase by a factor of 10 in the mixed-layer sediment partition coefficient (alone) increased mixed-layer sediment concentrations by approximately 38%, whereas surface-water concentrations did not change at all. Similarly, decreasing the mixed-layer sediment-partition coefficient decreased mixed-layer sediment concentrations. Decreasing the water-column partition coefficient by tenfold decreased the mixed-layer sediment concentration approximately 67%, with unnoticeable changes in surface water. Increasing the water-column partition coefficient by tenfold increased mixed-layer sediment concentrations more than fourfold, with slight decreases (1.6%) for only copper in water-column concentrations.

Doubling the lake surface area to 150,000 m² resulted in a doubling of lake volume and water-retention time, but the effects on sediment and surface-water concentrations were unnoticeable at steady state. Doubling the lake mean depth to 2 m had exactly the same effect as doubling the surface area. Halving the water flow-through rate, however, resulted in doubling computed sediment and surface-water concentrations. At steady state without degradation and volatilization, the lake surface area and depth have little to no effect on concentrations. Flow-through rate does impact concentrations because it has a diluting effect on lake loadings and is a major determinant of resulting lake concentrations.

Changing mixed-sediment layer porosity from 0.7 to 0.5, and then to 0.9, had almost no effect on sediment and surface-water results. A default value of 0.7 was used for the Tier-1 RECOVERY model. Doubling the  $f_{oc}$  to 0.02 for the mixed-sediment layer had no effect on results for copper and lead because their  $K_d$  values do not depend on  $f_{oc}$ . Doubling the  $f_{oc}$  also had very little effect on other constituents because of their relatively low  $K_{ow}$  values. Even for constituents with high  $K_{ow}$  values, a doubling of the mixed-layer  $f_{oc}$  had an almost undetectable effect on computed concentrations. But a tenfold increase had the same effect as increasing the mixed-layer partition coefficient by tenfold; this resulted in an increase in mixed-layer sediment concentrations but not in surface-water concentrations. A

default value of  $f_{oc}$  = 0.01 should be used in the Tier-1 RECOVERY model-input interface, but the user should have the flexibility to change this value.

Doubling wind speed only affected constituents (RDX and TNT) with a non-zero value for Henry's constant. Because TNT has the highest Henry's constant value, it was affected the most. TNT-sediment and water concentrations were decreased less than 1%. The default value for the Tier 1 model is 6 m/s.

Increasing the TSS settling rate by tenfold to 360 m/year had relatively minor effects on computed sediment and surface-water concentrations. Overall, concentrations for these media decreased slightly, with the greatest change for lead, which experienced a 12% decrease. The decrease in concentrations is because of burial, which increases with accretion in settling rates and zero re-suspension; this is the Tier 1 assumption. The default value for the Tier 1 model is 36 m/year.

### **Sensitivity summary**

Sensitivity results presented above are summarized in Table 14 for each parameter, regarding relative, qualitative influence (weak, moderate, strong) on results from each model. Weak influence is defined as less than a 10% sensitivity effect. Moderate influence is defined as an effect between 10% and 100%. Strong influence is defined as an effect greater than 100%. The results in Table 14 are qualitative because level of sensitivity depends on amount of change in the input variable. The reported level of sensitivity is for amounts of change discussed in the sections above.

Because of impacts on aquifer and surface-water/sediment concentrations, Tier 1 input parameters that may not be readily obtained and should receive the greatest attention in determining input values include:

- Solubility in soil (primarily a concern for metals)
- Soil K<sub>d</sub> for metals
- Darcy velocity
- Water column K<sub>d</sub> for suspended solids in surface water
- Surface-water body-water flow-through rate

Table 14. Summary of sensitivity results for more uncertain input parameters for each Tier-1 model.

Input parameter	Soil con.	Leaching flux	Erosion flux	Rainfall runoff flux	Aquifer con.	Sed. con.	Surface water con.
	•	:	Soil model	1	1	•	
Solubility	None	1	None	2	1	2	2
Site area	S	None	None	None	М	None	None
K <sub>d</sub> metals	W-M	S	W-M	S	S	W-M	W-M
Soil detach.	W	W	W	М	W-M	W-M	W-M
Exchange layer thickness	W	W	W	М	W	W	W
	Aquifer model						
Darcy vel.	None	None	None	None	S	None	None
Aquifer depth	None	None	None	None	М	None	None
	•	Surfa	ce-water m	nodel		•	
Deep sed K <sub>d</sub>	None	None	None	None	None	W	W
Mixed sed K <sub>d</sub>	None	None	None	None	None	M	W
Water col K <sub>d</sub>	None	None	None	None	None	M-S	W
Water surf area	None	None	None	None	None	None-W	None-W
Mean depth	None	None	None	None	None	None-W	None-W
Water flow- through rate	None	None	None	None	None	S	S
Mixed-sed poros.	None	None	None	None	None	None-W	None-W
Mixed-sed foc	None	None	None	None	None	None-W3	None-W3
Wind speed	None	None	None	None	None	W	W
TSS settling rate	None	None	None	None	None	W-M	W-M

W, M, S = weak, moderate, strong, respectively.

con. = concentration; sed = sediment; poros = porosity; vel = velocity; detach = detachment

<sup>1 =</sup> No effect unless solubility is less than computed pore-water concentration, then leaching flux and aquifer results are limited to solubility; but Tier 1 should not be used for these cases.

<sup>2 =</sup> No effect unless solubility is less than computed pore-water concentration; then runoff flux and surfacewater/sediment concentrations are slightly reduced, but Tier 1 should not be used for these cases.

<sup>3 =</sup> Moderate effects can be realized for dramatic changes in  $f_{\text{oc}}$  such as tenfold changes.

Solubility and soil  $K_d$  for metals are not important issues for Tier 1 because metals should be assessed with Tier 2 rather than Tier 1. The water-column  $K_d$  value for suspended solids should be approximately the same as sediment  $K_d$  values for non-metals. The RECOVERY model in Tier 1 includes a  $K_d$  estimator for constituents that have either a  $K_{ow}$  or  $K_{oc}$  property value. Thus, for Tier 1, the highest emphasis should be placed on estimating Darcy velocity and water flow-through rate of the surface-water body.

Because of impacts on receiving water, input parameters that should receive moderate attention in regard to determining input values include:

- AOI dimensions (length, width, area) for groundwater
- Aquifer depth or thickness for groundwater
- Surface water K<sub>d</sub> for mixed-sediment layer

## Rainfall ejection and runoff testing

Annual rainfall ejection of pore water and runoff export-flux formulations proposed by Dortch et al. (2009) were based on an extension of short-term, time-varying, event-based formulations developed by Gao et al. (2004). Thus, it was necessary to test extended, annualized formulations against observed results.

Annualized formulations were tested against laboratory data reported by Gao et al. (2004) for phosphorus transport with a rainfall rate of 7.4 cm/hr. Rainfall was applied in the laboratory in a chamber filled with a mixture of soil and water, with phosphorus dissolved in the water. Runoff water was collected over time, and the runoff concentration of phosphorus was measured. The measured phosphorus concentration in runoff water,  $C_w$ , versus time, as extracted from the paper by Gao et al. (2004), is shown in Figure 19. The experimental rainfall event lasted for approximately 6,000 s (1.67 hr). The time-averaged value of  $C_w$  in Figure 19 is 34.2 mg/L. The surface area of the test chamber was 45 cm<sup>2</sup>. Given area, rainfall rate, rainfall duration, and average concentration of runoff, the estimated rainfall-ejected export mass for the event was 0.019 g of phosphorus.

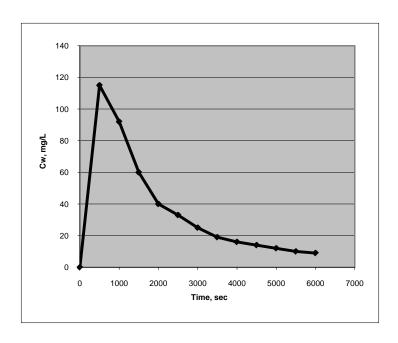


Figure 19. Runoff-phosphorus concentration versus time, extracted from Gao et al. (2004).

The rainfall ejection and runoff flux  $F_r$  (g/year) can be computed (Dortch et al. 2009) from:

$$F_r = Ad_e \left( 1 - e^{-\kappa} \right) C_{tt} N \tag{14}$$

where:

$$\kappa = \frac{a\varphi F_{dp}P}{\rho_b d_e N} \tag{15}$$

and where:

 $A = \text{surface area of AOI } (m^2)$ 

 $d_e$  = soil-exchange layer thickness (m)

 $C_{tt}$  = soil total concentration (particulate and dissolved) on a total soil volume basis (g/m<sup>3</sup>)

N = average number of rainfall events per year (year-1)

a = soil detachability (kg/L)

 $\varphi$  = soil porosity (fraction)

P = average annual rainfall rate (m/year)

 $\rho_b$  = soil dry-bulk density (kg/L)

$$F_{dp} = \frac{1}{\theta_w + \rho_b K_d} \tag{16}$$

For the rainfall saturated exchange layer,  $\theta_w$  (the soil-volumetric water content (fraction)), should be set equal to  $\varphi$  for calculation of the  $F_{dp}$  value used in Equation 15.

Values for the above equations were obtained from the experimental results reported by Gao et al. (2004), which are shown in Table 15. The value computed for  $F_{dp}$ , using parameters in Table 15, is 1.64. Because a single rain event was conducted, the modeling comparison was conducted for that single event, and thus N was set to 1. Rainfall during the event of 7.4 cm/hr, however, had to be converted to m/year in order to apply the above equations. A rainfall of 7.4 cm/hr for 1.67 hr is the same as 0.123 m/day. For a single rainfall event, or N=1 per year, the value of P is 0.123 m/year for Equation 15. If rainfall had occurred at a rate of 7.4 cm/hr for an entire day, then the annual rainfall for one event would be 1.78 m/year. Thus, both values are shown in Table 15; the reason for inclusion is explained below.

Table 15. Input parameters for the modeling the rainfall-ejection experiment.

Input parameter	Value	Units	
А	0.0045	m²	
а	0.4	Kg/L	
d <sub>e</sub>	0.0076	m	
Ctt	1103 or 1819	g/m³	
N	1	year-1	
Р	0.123	m/year for 1.67-hr rainfall	
	1.78	m/year for 24-hr rainfall	
Ф	0.37		
ρь	1.5	kg/L	
K <sub>d</sub>	0.16	L/kg	

The value of  $C_{tt}$  was computed from information in the paper by Gao et al. (2004). They reported that soil was pre-saturated with a water solution of phosphorus, with a concentration of 2.98 g/L. Knowing the volume of the soil matrix and its porosity, it was possible to calculate the water-solution

volume added to the soil, as well as the added mass of phosphorus. The total mass of added phosphorus divided by the soil-matrix volume resulted in the first value of  $1103 \text{ g/m}^3$  shown in Table 15. The statement regarding phosphorus concentration in the Gao paper could also have been interpreted to mean that the pore-water-phosphorus concentration was 2.98 g/L after equilibrium sorption. If this was the case, then  $C_{tt} = 2.98 \text{ x}$   $1000/F_{dp}$ , or  $C_{tt} = 1819 \text{ g/m}^3$ , which is the second value shown in Table 15. Both values were used to apply the model, but the first interpretation is presumed to be the authors' intent.

Using the first value of  $C_{tt}$ , the first P value, and other input parameters in Table 15, the computed value of  $F_r$  is 0.035 g/year or g/event. Using the second value of  $C_{tt}$  and the first P value, the computed  $F_r$  is 0.058 g/event. These two values of  $F_r$  are compared with the observed value of 0.019 g/event, as reported above. The computed and observed export masses are of the same order of magnitude, which is encouraging for use of the annualized rainfall-ejection formulations as proposed by Dortch et al. (2009).

Annualized formulations require N, which is the average number of rainfall days in a year. Thus, annualized formulations are based on daily rainfall records. The experimental runoff concentration appeared to asymptotically approach a value of approximately 6 mg/L over time. The experiment extended over 6,000 s (1.67 hr) as stated previously, but if it had continued for 24 hr or a full day, the average value of  $C_W$  would probably have been 8 mg/L rather than 34 mg/L, resulting in a daily export of 0.065 g. Using the second P value in Table 15, computed exports are 0.038 and 0.062 g for the two  $C_{tt}$  values, which compare more closely with the extrapolated observed daily export of 0.065 g. Regardless of whichever comparisons are made between computed and observed runoff export mass, the results tend to affirm use of annualized formulations for providing reasonable estimates for rainfall-ejected runoff.

## 7 Conclusions and Recommendations

The Tier 1 approach for TREECS is based on highly conservative, steady-state (time-invariant) assumptions where MC loadings to the firing range are constant over time, and receiving water media reach a constant MC concentration that can be compared with ecological and human-protective health benchmarks for screening-level evaluations. Furthermore, it is assumed that MC does not degrade or decay. This approach allows rapid assessments with use of limited data-input requirements. Tier 1 should prove useful during Phase II of ORAP. If a Tier 1 assessment indicates a potential concern, analysis should proceed to a Tier 2 assessment or other more in-depth site assessment. Results from a Tier 1 assessment can also be used to consider effects of different range usage strategies to ensure future protection of human and environmental health. Tier 1 models were applied to Ft. A.P. Hill for proof of concept. Lessons learned from this application are summarized below.

## **Munitions and MC loading**

Estimation of MC-residual loading is a critically important and relatively challenging process. Use of firing-range records to calculate loads can be tedious, although importing records into spreadsheets can greatly reduce the burden. If records do not exist, munitions-use assumptions must be made to estimate loadings. Projected concentrations in surface water and groundwater are linearly and directly proportional to the estimated loadings, which is the reason loadings are critically important. Assumptions regarding low-order detonation rates and percent yield affect estimates of MC-residue loading, and such values must be specified by the user. Fairly good guidance on dud and low-order rates is available (Concurrent Technologies Corporation 2004) for detonations, but only limited information is available on percent yield (Gerald et al. 2007). Such guidance should be made available to TREECS users.

In order to conduct estimates of MC-residue loading, the amount of MC-constituent mass in munitions delivered to the impact area must be known. This information can be obtained from MIDAS, but the process can be slow and tedious. A utility has been developed for automatically pulling this information into the TREECS application using only the DODIC or the National Stock Number (NSN). This utility requires a

special, processed subset database of MIDAS, developed by the Defense Ammunition Center (DAC). The MIDAS subset database is problematic because it only contains data for 164 DODIC values, whereas the full MIDAS database has data for over 9,000 munitions. Thus, many DODICs encountered in the Ft. A.P. Hill application had to be queried within MIDAS; this was a time-consuming process. More DODICs and their associated constituent masses need to be added to the MIDAS subset database to expedite the process of obtaining MC loadings.

A large number of DODICs were used at Ft. A.P. Hill. When estimating MC mass-residue loadings, consideration was given only to predominant and used DODICs, which were known to have HEs. Inclusion of all DODICs would have been a laborious and time-consuming task. Given uncertainty in low-order and yield rates, refinement of loadings for infrequently used munitions may not be worthwhile.

Better information is needed regarding emission factors for munitions that contain perchlorate. An emission factor of 1% was used in the application, but this value was a guess.

## **Delineation and application for AOI**

Firing ranges tend to be laid out like fans or spokes on a wheel, with a central-impact area at the center. Thus, many ranges may use only one or a few impact areas. For HEs, assessment of an AOI that consists of the total or major portion of an impact area makes good sense. Because individual craters resulting from HEs can be quite heterogeneous, determining AOI dimensions is difficult. Examination of maps does not generate sufficient data for delineating an AOI. Aerial photographs or satellite imagery should also be used to help with assessment of dimensions. Fortunately however, AOI dimensions have no effect on Tier 1 export fluxes.

SAFRs are more difficult to assess than HE impact areas because many ranges can be located in different areas throughout the installation. Grouping multiple HE- and SAFR-impact zones as a single AOI, if those zones drain into a common sub-watershed, and assessing export and receiving water for each sub-watershed is more meaningful. Only one receiving surface-water body and one aquifer for each sub-watershed or AOI should be assessed.

Because SAFRs are usually distributed throughout the installation and are more likely to drain into many different sub-watersheds, it may be prudent to assess each sub-watershed separately by combining loadings for SAFRs into an AOI for each sub-watershed.

Impact zones for SAFRs are usually small relative to the HE impact areas. Therefore, assigning an AOI to a sub-watershed is probably the best approach in these cases. However, HE impact areas are usually quite large. If a large impact area overlaps several sub-watersheds, the AOI could be split into multiple AOIs, with one for each sub-watershed. However, if this is done, estimation of the MC-residue loading for each AOI will also be necessary and could be highly uncertain. Distributing the loading equally among the AOIs may not be a good assumption. Given that the export of MC mass to surface water and groundwater is dependent on loading and not AOI area, assessing the large impact area as a single large AOI is more conservative.

For the current application presented, the AOI was assumed to be the entire, combined impact area, which actually included three impact areas. In retrospect, the AOI could have been split into two AOIs, one within the Smoots Run sub-watershed and one within the Beverly Run sub-watershed. When the impact area is subdivided by sub-watershed drainage basins, not only will the AOI dimension change, but the loadings for each AOI will change, as previously discussed. Receiving waters will be different such as Smoots Pond for Smoots Run and White Lake for Beverly Run. In these cases, erosion and runoff fluxes are exported to separate receiving surface-water bodies. Likewise, infiltration within separate sub-watersheds can result in separate aquifer plumes, different receptor wells, and different well locations relative to each AOI. Subdividing the AOI into two would have reduced the loadings and receiving water concentrations by half, assuming that loadings were split equally between the two AOIs. Therefore, treating the impact area as one AOI was more conservative.

For simplicity, ease of use, and clearer interpretation, it is recommended that Tier 1 and Tier 2 TREECS be developed only for single AOI applications. If an installation has multiple AOIs, each AOI will constitute a separate TREECS application. Additionally, each AOI should have no more than one aquifer and one surface-water body that receives loadings from the assessed AOI. Deviations would require the use of complex two-

dimensional, distributed watershed models coupled with two-dimensional or three-dimensional groundwater models.

## **Health impacts**

This POC application resulted in aquifer concentrations for HE and lead that exceeded protective health benchmarks for drinking water. Aquifer concentrations for copper were close to the benchmark, whereas perchlorate was far below. Tier 1 models and input assumptions provide results that are considered conservative, i.e., probably greater than expected to actually occur. Because predicted aquifer concentrations for HEs are on the same order of magnitude as and greater than the benchmark, application of a Tier 2 model should be considered for HE constituents.

Computed White Lake concentrations for HE constituents and perchlorate are far below the ecologically protective benchmarks for sediment and water. Thus, HE and perchlorate are not expected to be a concern for surface waters at this site. Metal concentrations, however, far exceed the surface-water and sediment benchmarks.

Predicted metal concentrations in surface water/sediment and ground-water can far exceed real expectations because of the long period of time required for dissolution and low solubility. The results here, however, indicate that a more detailed study and Tier 2 analysis are warranted for metals, especially in surface water. Sediment concentrations for metals are much higher than for the water column because of the relatively high metal  $K_d$  values. Additionally, metals are more likely to be a concern for surface-water sediments than for groundwater.

Tier 1 TREECS application results for metals should be viewed with caution because dissolution is not considered. Also, as pointed out in Chapter 3, the number of rounds fired per year may be off by a factor of seven because of a potential statement error in the ORAP Phase 1 report. Tier 1 can be applied for screening of potential metal concerns, but the results will probably be inflated towards high-media concentrations. Tier 2, with time-varying conditions and dissolution, will be much better suited for evaluating the fate of metals.

## Model inputs and sensitivity

If metals are considered within Tier 1, the value assumed for solubility could reduce groundwater concentrations if solubility is less than the computed soil pore-water concentrations. Rainfall-ejected runoff is also reduced if solubility is less than computed soil pore-water concentrations, but the impact on receiving-water/sediment concentrations is undetectable because most of the export flux to surface water for metals is due to soil erosion. When solubility limits soil pore-water concentrations, AOI area does affect export fluxes for infiltration and rainfall-ejected runoff. Thus, soil concentrations and fluxes should no longer be steady state. The Tier-1 soil model cannot consider these conditions, and the Tier 2 model should be used. If solubility limits have been reached in the Tier 1 model, the model will issue a warning to the user.

Most of the input parameters for applying Tier 1 models can be readily obtained. Less-easily attainable input parameters that should receive the greatest attention in regard to impacts on receiving water concentrations include:

- Solubility in soil for metals
- Soil K<sub>d</sub> for metals
- Darcy velocity
- Surface-water K<sub>d</sub> for water-column suspended solids
- Surface-water body water-flow through rate

The first two parameters, solubility and  $K_d$  for metals, will not require attention in the Tier 1 model if Tier 1 is not applied for metals. Furthermore, solubility is important only if computed soil pore-water concentrations exceed solubility. In such cases, soil concentrations and fluxes can change with time, and use of Tier 1 is inappropriate. Tier 2 is recommended. Darcy velocity and water-body water flow-through rate are very important parameters that can have strong influence over computed media concentrations due to dilution. Surface-water and sediment- $K_d$  values can be estimated for non-metals by the RECOVERY model if  $K_{ow}$  or  $K_{oc}$  properties are available.

Input parameters that should receive moderate attention in regard to impacts on receiving-water concentrations include AOI dimensions, aquifer depth, and  $K_d$  for the mixed-sediment layer. It is recommended that a default value of mixed-sediment layer  $f_{oc} = 0.01$  be implemented in

the Tier 1 RECOVERY model-input interface with flexibility for the user to change the value if desired. Default values of 0.4 kg/L and 0.005 m are also recommended for the soil-model parameters of soil detachability and exchange-layer thickness, which are used for rainfall ejection of pore water. The user will have the option to change these values. A default value for wind speed of 6 m/sec should also be implemented in the Tier 1 RECOVERY user interface.

It is recommended that the soil  $K_d$  estimator (Equation 13), based on soil texture, organic matter content, and  $K_{oc}$ , be incorporated into the soil-model user interface.

## **Additional pathways**

An additional transport pathway, which was not included in the Tier 1 soil model, is being considered for the Tier 2 soil model. This pathway is erosion and export of solid-phase (undissolved) constituent particles. This pathway was not included in the Tier 1 soil model because of the steady-state assumption, which makes all constituent, solid-phase mass loading instantly available in the aqueous phase. With inclusion of time in Tier 2 models, dissolution will be included, and solid and aqueous-phase mass will be tracked. Smaller solid-phase particles could possibly erode and be exported in runoff prior to dissolution.

Two additional potential pathways should be considered for Tier 1. These pathways include interflow of aqueous phase MC from soil to surface water and discharge of groundwater containing MC to surface water. Groundwater discharge is planned for Tier 2, but it can also potentially be added to Tier 1. However, this addition would come after the initial release of Tier 1 TREECS.

Interflow through the vadose zone or soil is a minor pathway in most cases but could be a potential pathway for surface soils having high hydraulic conductivity, with an impermeable or semi-impermeable layer at shallow soil depth, and thus create a perched-water table. Because TREECS Tier 1 and 2 models are based on average annual hydrology, interflow must be added through specification of the fraction of net annual infiltration (i.e., groundwater recharge) that is lost to interflow before reaching the aquifer water table. Interflow is being included in the Tier 2 soil model and can be added later to the Tier 1 soil model after the initial release. The fraction of

infiltration going to interflow will be based on the saturated hydraulic conductivity of the vadose.

### **General conclusions**

Overall, the Tier 1 TREECS models performed as planned and provided reasonable results given the steady-state assumption with no degradation. Tier 1 should be useful for determining cause for concern regarding concentrations of MC constituents in receiving waters. Thus, Tier 1 should prove to be a useful screening tool for ORAP Phase II and for similar firing-range management needs. Rather than Tier 1, however, Tier 2 is the preferred approach for better assessment of metals, which can have slow weathering and dissolution rates because of low solubility. Tier 2 will be time varying and will allow more accurate assessment of such needs.

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## REPORT DOCUMENTATION PAGE

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#### 13. SUPPLEMENTARY NOTES

#### 14. ABSTRACT

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 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 Army 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 will consist of screening-level methods that require minimal data input requirements and can be easily and quickly applied by environmental staff to assess the potential for migration into surface water and groundwater. Any predicted surface water and/or groundwater MC concentrations that exceed protective health benchmarks at receptor locations would require further action such as evaluation using TREECS Tier 2.

Highly conservative assumptions of steady-state (time-invariant) MC conditions and no MC degradation are used in the Tier 1 modeling approach. Thus, MC loadings to the range are constant over time, and fluxes to and concentrations within receiving water media reach a

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#### 14. ABSTRACT (Concluded)

constant MC concentration for comparison with protective ecological and human health benchmarks. Tier 1 includes an analytical soil model with computed leaching flux linked to a semi-analytical-numerical aquifer model. The computed runoff-erosion fluxes are linked to a numerical surface-water and sediment model. Tier 1 also includes a hydro-geochemical toolkit for estimating input parameters.

This report describes the proof-of-concept application of the prototype TREECS Tier-1 modeling approach and provides recommendations for final implementation and use of these methods.