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*Environmental Security Technology Certification Program (ESTCP)*

# **User Guidance for Application of TREECS™ and CTS for Environmental Risk Assessment of Contaminants on Department of Defense (DoD) Ranges**

Mark S. Dortch, Eric J. Weber, and Billy E. Johnson

June 2017

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Billy E. Johnson

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

Mark S. Dortch

*LimnoTech, Inc.  
501 Avis Drive  
Ann Arbor, MI 48108*

Eric J. Weber

*Exposure Methods and Measurements Division  
USEPA National Exposure Research Laboratory  
960 College Station Road  
Athens, GA 30605-2700*

Final report

Approved for public release; distribution is unlimited.

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

Under ESTCP Project ER-201435, Field Demonstration and Validation of TREECS™  
and CTS for the Risk Assessment of Contaminants on Department of Defense  
(DoD) Ranges

## Abstract

The Training Range Environmental Evaluation and Characterization System (TREECS™) was developed for the Army to forecast the fate of and risk from munitions constituents (MC), such as high explosives and metals, within and transported from firing/training ranges to surface water and groundwater. TREECS™ requires chemical-specific properties as part of the inputs. The Chemical Transformation Simulator (CTS) was developed by the U.S. Environmental Protection Agency (EPA) to provide physicochemical properties of complex organic chemicals. The CTS has capabilities for estimating chemical-specific properties in the absence of experimentally obtained properties; thus, CTS can help fill data gaps for properties, particularly for emerging MC that have limited experimental data. This report discusses the input requirements, sources of input data, and lessons learned from applying TREECS™ and CTS.

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## Preface

This study was funded by the Environmental Security Technology Certification Program (ESTCP) under the Environmental Restoration work topic area as ESTCP Project Number ER-201435, entitled Field Demonstration and Validation of TREECS™ and CTS for the Risk Assessment of Contaminants on DoD Ranges. Dr. Andrea Leeson was the Deputy Director of ESTCP and the Environmental Restoration Program Manager.

The work reported herein was conducted by Dr. Mark Dortch under contract to LimnoTech, Inc., which was under contract to the U.S. Army Engineer Research and Development Center (ERDC). Dr. Billy Johnson of the Water Quality and Contaminant Modeling Branch (WQCMB), Environmental Processes and Engineering Division (EPED), Environmental Laboratory (EL) of ERDC was the project leader and federal point-of-contact for this work. Dr. Eric Weber of the Exposure Methods & Measurements Division, National Exposure Research Laboratory, U.S. Environmental Protection Agency (EPA), was the technical point-of-contact for the Contaminant Transformation Simulator (CTS) that was developed by EPA and used as part of this project. Drs. Dortch, Weber, and Johnson coauthored this report.

The study was conducted under the general direction of: Dr. Dorothy Tillman, Chief, WQCMB; Mr. Warren Lorentz, Chief, EPED; and Dr. Elizabeth Ferguson who was Technical Director of Military Materials in the Environment. Dr. Jack E. Davis was Deputy Director, and Dr. Beth Fleming was Director of the EL.

COL Bryan S. Green was the Commander of ERDC and Dr. David W. Pittman was the Director of ERDC.

# Acronyms, Abbreviations, and Symbols

## Acronyms and Abbreviations

AIA	artillery impact area of the USMA
AOI	area of interest, such as HE impact area
ARCDB	Army Range Constituent Database within TREECS™
BMP(s)	best management practice(s)
CAS	Chemical Abstract Service registry number
CE	Chemical editor in CTS
CMS	Contaminant Model for Streams
CON	Certificate of Networthiness
Comp B	Composition B, a HE formulation containing RDX and TNT
CSM	Conceptual Site Model
CTS	Chemical Transformation Simulator
Demo	Demolition
DNAN	IM explosive component, 2,4-dinitroanisole
DoD	Department of Defense
EC	emerging contaminants or constituents
EFS	Environmental Fate Simulator, now referred to as CTS
EL	Environmental Laboratory
EPA	U.S. Environmental Protection Agency
EPI	Estimation Program Interface
EPED	Environmental Processes and Engineering Division
ERDC	Engineer Research and Development Center
ESTCP	Environmental Security Technology Certification Program
ET	Evapotranspiration
FRAMES	Framework for Risk Analysis in Multimedia Environmental Systems
GIS	Geographical Information System
HE	high explosives
HGCT	Hydro-Geo-Characteristics Toolkit within TREECS™
<i>HL</i>	degradation half-life, years
<i>HLC</i>	Henry's Law Constant, units of atm-m <sup>3</sup> /mol
HSDB	Hazardous Substances Data Bank
IM	insensitive munitions
MC	munitions constituents, such as the HE RDX
MCB	Marine Corps Base
MEPAS	Multimedia Environmental Pollutant Assessment System
MMR	Massachusetts Military Reservation
MUSLE	Modified Universal Soil Loss Equation used in HGCT for daily soil erosion estimates
<i>MW</i>	Molecular weight, g/mol
NCDC	National Climatic Data Center, now called NCEI

NCEI	National Centers for Environmental Information of the National Oceanic and Atmospheric Administration
NTO	IM explosive component, 3-nitro-1,2,4-triazol-5-one
NQ	IM explosive component, nitroguanidine
ORAP	Army's Operational Range Assessment Program
PALs	Protection action limits
PCP	Physico-Chemical Properties Calculator in CTS
PC	Personal Computer
p-chem	Physicochemical
RAIS	Risk Assessment Information System
RDX	Royal Demolition Explosive, a high explosive, hexahydro-1,3,5-trinitro-1,3,5-triazine
RFMSS	Range Facilities Management Support System for maintaining range firing records
RPS	Reaction Pathway Simulator in CTS
SAFRs	Small arms firing ranges
SCS	Soil Conservation Service that development the runoff curve number method
SPARC	SPARC Performs Automated Reasoning in Chemistry, a physicochemical properties estimation program in CTS
S/U	Sensitivity and uncertainty analysis within TREECS™
TEST	Toxicity Estimation Software Tool, a physicochemical properties estimation program in CTS
TNT	HE Trinitrotoluene
TREECS™	Training Range Environmental Evaluation and Characterization System
TSS	total suspended solids
UDM	User Defined Module in TREECS™ Advanced Tier 2 for specifying known fluxes or concentrations
UI(s)	user interface(s) for entering and viewing model inputs
USDA	U.S. Department of Agriculture
USLE	Universal Soil Loss Equation used for annual soil erosion estimates in HGCT
USMA	U.S. Military Academy, West Point, NY
UXO	Unexploded ordnance
WQCMB	Water Quality and Contaminant Modeling Branch
WSS	Web Soil Survey, USDA Web site for retrieving soil properties
ZIA	Zulu impact area of Camp Pendleton
0-D	Zero-dimensional in space
1-D	One-dimensional in space

## Symbols

$C_s$	water solubility limit, mg/L
$d$	solid phase MC residue initial particle size, $\mu\text{m}$
$D_a$	diffusion coefficient of vapor phase in air, $\text{m}^2/\text{day}$

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$D_w$	diffusion coefficient of dissolved phase in water, m <sup>2</sup> /day
$K_d$	sorption distribution coefficient for partitioning an MC between soil particles and water, L/kg
$K_{oc}$	organic carbon normalized soil–water sorption partition coefficient, L/kg
$K_{ow}$	octanol–water sorption partition coefficient, mL/mL
$K_v$	volatilization rate, m/yr
$\rho_s$	solid phase mass density, g/cm <sup>3</sup>

# 1 Introduction

## 1.1 Background

The Training Range Environmental Evaluation and Characterization System (TREECS™) was developed for the Army to forecast the fate of and risk from munitions constituents (MC), such as high explosives (HE) and metals, within and transported from firing/training ranges to surface water and groundwater. TREECS™ requires chemical-specific properties as part of the inputs. The Chemical Transformation Simulator (CTS), previously called the Environmental Fate Simulator (EFS), was developed by the U.S. Environmental Protection Agency (EPA) to provide physicochemical properties of complex organic chemicals. CTS has capabilities for estimating chemical-specific properties in the absence of experimentally obtained properties; thus, CTS can help fill data gaps for properties, particularly for emerging munitions constituents or emerging contaminants (EC) that have limited experimental data.

The Environmental Security Technology Certification Program (ESTCP) Project ER-201435 provided the resources to validate the use of TREECS™ with CTS for predicting MC concentrations in receiving waters down-gradient of training/firing ranges and to demonstrate their utility for forecasting the fate of MC and EC within and off-site of Department of Defense (DoD) installations. The utility of TREECS™ for evaluating best management practices (BMPs) was also demonstrated during this ESTCP project. The present report documents the lessons learned and guidance for applying TREECS™ and CTS as related primarily to the chemical-specific inputs. The details of the studies that lead to some of the guidance in this report are documented in three other reports, cited as Dortch (2015), Dortch et al. (2017), and Dortch and Johnson (2017). The overall benefit of this work is to help transition these tools to the appropriate user community so that they can be used to help ensure range compliance and sustainability into the future.

## 1.2 Objectives

The objectives of this report are to document the lessons learned and guidance for applying TREECS™ and CTS for assessing the environmental risk of contaminants on DoD training and firing ranges. The emphasis of

this guidance is on application, such as specifying chemical-specific inputs, rather than how to apply the software. These aspects are covered in user manuals and software help tools.

### 1.3 Approach

As part of ESTCP Project ER-201435, TREECS™ and CTS were applied to three study sites that had observed concentrations of the HE RDX (Royal Demolition Explosive, hexahydro-1,3,5-trinitro-1,3,5-triazine) for validation and demonstration purposes. The three study sites were: Demolition (Demo) Area 2 of Camp Edwards, Massachusetts Military Reservation (MMR), MA; the Artillery Impact Area (AIA) of the U.S. Military Academy (USMA), West Point, NY; and the Zulu Impact Area (ZIA) of Marine Corps Base (MCB) Camp Pendleton, CA. In addition to RDX, EC found in new insensitive munitions (IM) that are less sensitive to heat and shock were also modeled hypothetically at the three sites. Additionally, laboratory studies involving IM and fate of their EC components as reported by Dontsova et al. (2014) were also modeled to gain a better understanding of appropriate input parameters. The results of the modeling studies for the three field sites and laboratory investigations are reported by Dortch et al. (2017).

Two of the field sites, Demo Area 2 of MMR and the AIA of USMA, were used for further study of the components of the IM IMX-101. Surface soil, vadose zone, and groundwater were modeled for Demo Area 2 of MMR. Surface soil and surface water (Popolopen Brook) were modeled for the AIA at West Point. Thus, these two sites provide both types of receiving water (groundwater and surface water) that can exist down-gradient of firing ranges. These applications were used to evaluate the sensitivity of uncertain input parameters, and those results are documented by Dortch and Johnson (2017). Similarly, sensitivity of uncertain inputs for RDX at Demo Area 2 of MMR was conducted as reported by Dortch (2015) as part of this ESTCP project.

The present report is a culmination of guidance stemming from results documented in the three reports cited as Dortch (2015), Dortch et al. (2017), and Dortch and Johnson (2017), as well as experiences from other studies as cited herein. This report provides a general overview of input requirements for applying TREECS™ and CTS, where details can be found in the other cited reports. However, chemical-specific input parameters are given greater attention in this report since the purpose of CTS use with TREECS™ is to help provide information for such inputs.

## 2 Key Features and Input Requirements of TREECS™

It is important to first have an understanding of the key features of TREECS™ and CTS and a general understanding of the input requirements for use prior to user guidance discussions. Thus, the key features and general input requirements for use of TREECS™, as well as potential sources of information for establishing input values, are presented in this chapter. The next chapter provides similar information for CTS.

### 2.1 Key features

TREECS™ is designed for client-based installation on personal computers (PCs). The user, or PC system manager, downloads an install package from the Web site (<https://treecs.el.erdcdren.mil/>). PC administrator privileges are required to install the system on the user's PC. Instructions for installation are provided on the Web site with the install package. TREECS™ does not use any linkages to the Internet; therefore, it is totally PC contained and client based. TREECS™ does have a Certificate of Networthiness (CON) issued by the Army; thus, it is approved for installation on Army and other DoD computers via reciprocity.

The main feature of TREECS™ is that it computes contaminant concentrations over spatial locations and over time as a result of contaminant mass introduced (i.e., loaded) into an area of interest (AOI), which is generally a land surface, such as a firing range impact area. The computed contaminant concentrations at specific locations can then be compared within TREECS™ against protective action limits (PALs) that are highly protective (conservative values) of ecological and/or human health. Mass balance-based mathematical models with numerical solution methods involving various boundary conditions are used to perform the computations. Thus, the application of TREECS™ requires that the user have some professional familiarity with mathematical contaminant fate and transport modeling.

The fate and transport models within TREECS™ are models of reduced form. Reduced form primarily refers to the use of limited spatial dimensions, which reduces model complexity, reduces input data

requirements, and enables faster model setup and execution. As an example, the model for the surface soil of the AOI, or the source area for contamination, is zero dimensional (0-D), (i.e., fully mixed, with uniform concentrations throughout the AOI soil volume). There are two surface water models in TREECS™; one model, RECOVERY (Ruiz and Gerald 2001), has a fully mixed (0-D) water column that is well suited for small standing water bodies, such as small lakes and ponds; the other model, Contaminant Model for Streams (CMS) (Fant and Dortch 2007), has a one-dimensional (1-D) water column that is better suited for streams and rivers with the represented spatial dimension along the stream flow direction, with uniform concentrations across the stream width and depth. Assuming property uniformity is another means of reducing model form. Models of reduced form can provide insightful information rapidly with first-order accuracy. However, the primary limitation of such models is that they may not be able to capture the effects of complex site features, and in such cases, a more comprehensive model can be required.

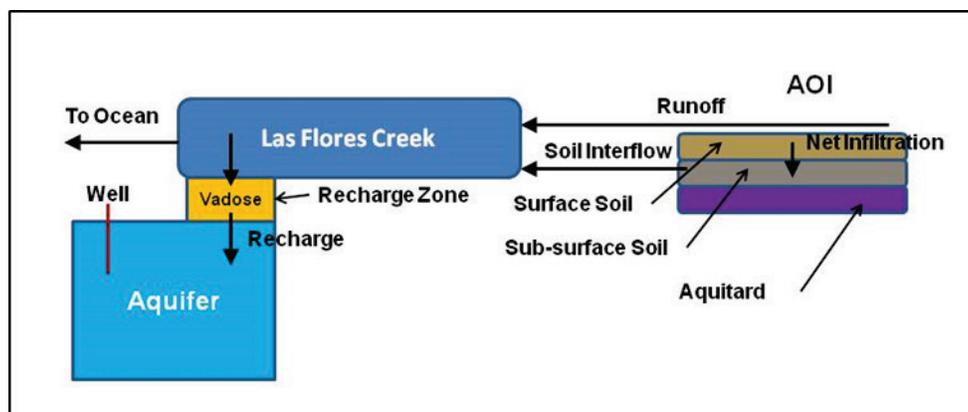
## 2.2 General application process

The first step in applying TREECS™ is to define the contaminant source area, or AOI, the target receptors and their exposure points, and the potential transport pathways from the AOI to each receptor. There can be human and ecological receptors. The type of receptor does not impact the application of the fate and transport models, rather the receptor type is used to determine the media PALs that are protective of receptor health. The receptor exposure points are the locations within an environmental medium where the receptor comes in contact with the medium. For example, specific locations within a stream can be designated as ecological receptor exposure points, and a groundwater well used for human drinking water can be a receptor exposure point. This information is then used to develop a conceptual site model (CSM) for how to represent the study site and to produce the required exposure concentrations for comparison with the PALs. An example of a CSM is shown in Figure 1 for the TREECS™ application at MCB Camp Pendleton (Dortch et al. 2017).

TREECS™ setup follows development of the CSM. Models are selected and inputs are developed and provided to the models during setup. Model setup is by far the largest part of the entire TREECS™ application process due to the input development step explained later below. Geographical Information System (GIS) data may exist for the study site, and such data can be pulled into TREECS™ and used to improve the site understanding

as well as to aid in establishing model inputs. TREECS™ application at Fort Leonard Wood, MO, used GIS fairly extensively to aid in setup, and the details for how the GIS data were set up and used is provided by Dortch et al. (2013).

Figure 1. CSM for modeling Zulu Impact Area and receiving waters, MCB Camp Pendleton, CA.



Model setup involves three processes, model selection, input data development, and input data entry. TREECS™ has standard templates for model selection involving surface water and groundwater pathways and exposure media. The user can select whether surface water, groundwater, or both are involved as pathways and exposure media. The template for surface water invokes the AOI soil model with its output linked to surface water. The surface water body can be represented by either the RECOVERY model or the CMS model. The template for groundwater invokes the AOI soil model with its output linked to a vadose zone model and the vadose zone model output linked to an aquifer model. The Multimedia Environmental Pollutant Assessment System (MEPAS) (Buck et al. 1995; Whelan et al. 1996) is used for the vadose and aquifer models. The standard templates are adequate for most applications, and they simplify and expedite model selection and linkage, allowing the user to proceed directly to input entry. For those applications that are more involved, such as the CSM shown in Figure 2 for an application at Fort Jackson, SC, the Advanced Tier 2 option in TREECS™ should be invoked. The user must then select and link each model as shown in Figure 3 for the Fort Jackson application.

Figure 2. CSM for Gills Creek watershed modeling, Fort Jackson, SC.

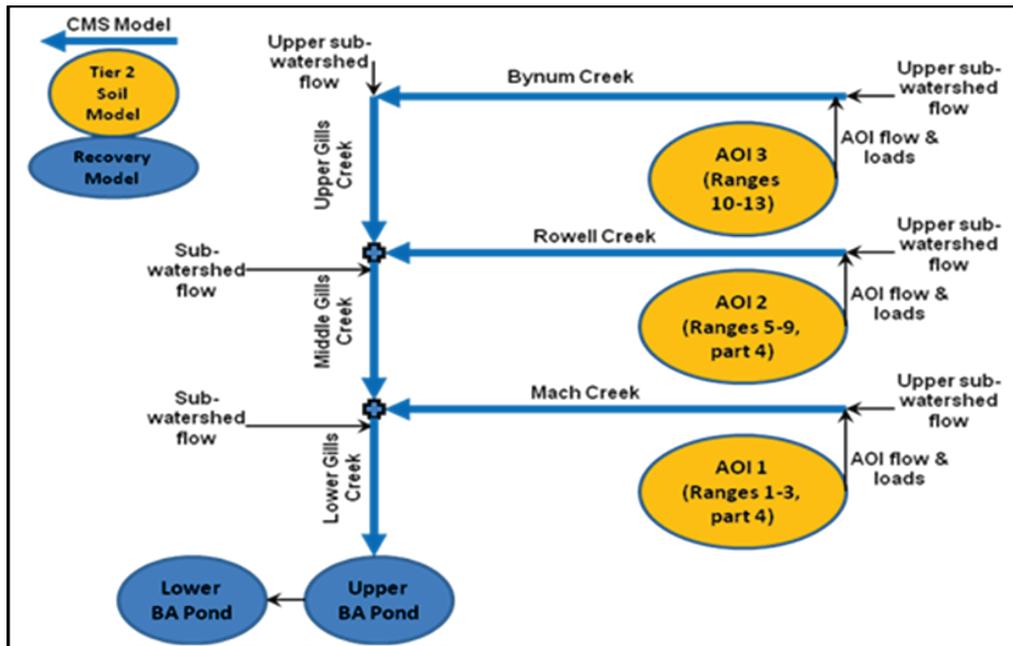
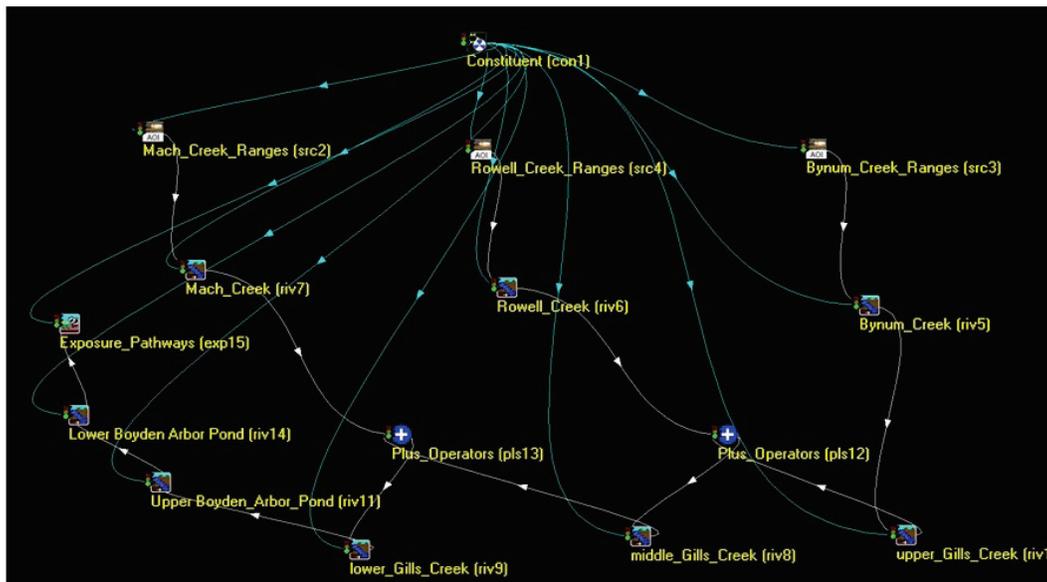


Figure 3. CSM for Gills Creek watershed modeling, Fort Jackson, SC.



Model input data entry requires little time, but development of the input data can be more time consuming. Data for development of inputs is usually readily available, but often some analysis is required to process the data for accurate use in the model. Input data development is by far the most time consuming step in TREECS™ set up. The input data requirements and how the input data are developed are described next. GIS data are excluded in the description since such data are not required, rather it can improve the quality of input data.

## 2.3 General input requirements

The first input tab-screen in the user interface (UI) consists of the installation or site name, a brief description of the installation or site, and a brief description of the AOI at the site. The user can be as brief or detailed as desired for these descriptions.

The second input tab-screen in the UI is *Tier Analysis Selection* and is used to specify the level of analysis, whether Tier I, Tier II, or Advanced Tier II. Tier II is used for most analyses. Tier I assumes steady-state conditions where contaminant loadings have occurred at a constant rate for a very long time, which results in steady-state media concentrations. Tier I also assumes that there is no degradation of contaminants. Thus, Tier I provides highly conservative, worst case, maximum concentrations. Model input requirements for Tier I are considerably less than those for Tier II. If a Tier I application indicates that computed receiving media concentrations are less than the protective health benchmarks, there should be no reason to proceed to a Tier II analysis. Otherwise, a Tier II analysis is warranted. Computed media concentrations should be less for Tier II compared with Tier I since there can be degradation and natural attenuating factors with Tier II. Tier II requires more inputs, so it takes longer to set up. As stated previously, advanced Tier II is for those applications that have more complex pathways. The applicable media (surface water, groundwater, or both) must be checked when using Tier I and Tier II so that the appropriate model connection templates are invoked.

The third input tab-screen is *Site Conditions* and contains two sub-tab-screens. The first sub-tab-screen is *Constituent Selection* and is used to select the constituent database to be used, with options for Framework for Risk Analysis in Multimedia Environmental Systems (FRAMES), Army Range, Risk Assessment Information System (RAIS), or User Defined constituent databases. Only one database can be selected. After selecting a database, the user can then select from a list of database constituents (i.e., chemicals) the constituents that are to be included in the modeling. The Army Range Constituent Database (ARCDB) was developed specifically to include constituents more commonly found on DoD training/firing ranges. Additionally, there are often multiple values for less certain physico-chemical properties within the ARCDB for each constituent. Upon selection of a constituent from the ARCDB, the constituent physicochemical properties screen is displayed and the user must select which value to use

for each property. This is where CTS information can be beneficial, especially for those property values that are less certain or even missing.

The second sub-tab-screen on the *Site Conditions* tab is *Operational Inputs* where information is entered to define the constituent mass loading rates into the AOI. The type of loading is selected first with options for impact zone, firing point, or general soil source zone. Impact zones are used for duded artillery impact AOIs and impact berms of small arms firing ranges (SAFRs). Firing points are used for positions used to fire artillery, rockets, and other projectiles that require energetic accelerants and where firing emissions residue can accumulate. The general soil source zone is for any AOI that has a known constituent mass loading rate.

For an impact zone, the user must select which munitions are fired. For each munition and for each time point (year), the user must specify the number of rounds fired, the percent of duds, the percent of low order detonations, the percent of low order yield, the percent of sympathetic duds (i.e., duds that are exploded by detonation of another round), the percent of yield for sympathetic duds, and the percent of high order yield. Yield refers to the percent of total HE in the round that is totally expended or exploded. The Munitions Mass Loading Module computes the mass loading rate to the AOI for each constituent for each year based on the munitions content. Munitions content is available from the Munitions Database within TREECS™. The computed AOI time-varying loading rates for each constituent can be viewed from the *Operational Inputs* screen.

For a firing point, the user must specify the number of rounds fired each year for each of the selected munitions. Emission factors (grams/item fired) must also be specified for each munition, or the percent unexpended energetic material for each munition can be specified and emission factors are calculated based on amount of material in the munition from the TREECS™ munitions database.

Most installations now maintain records of types and numbers of items fired on training/firing ranges. The Range Facilities Management Support System (RFMSS) can be used to provide such records. This information can be used with the Munitions Mass Loading Module within TREECS™ to estimate MC residue mass deposition rates on ranges.

Input for the general soil source zone is simply pairs of time (years) and loading rate (grams/year). All time varying inputs require at least two time points. Any input is assumed to be constant over time until the next input time point is encountered. Thus, inputs are stepped over time, not linearly interpolated.

The fourth input tab-screen is *Target Health Benchmarks*. The user can use the default DoD benchmarks or a user-defined benchmark database. Only two inputs are required, the fraction of sediment total organic carbon and water hardness if metals are included as munitions constituents of concern.

The remaining TREECS™ inputs are model-specific for each type of fate and transport model. If Tier I or Tier II options are selected, there is an *Inputs* tab-screen. There are buttons on this screen to launch UIs for the AOI soil model, vadose zone model, groundwater aquifer model, and surface water and sediments model. Active buttons depend on which pathways were selected on the *Tier Analysis Selection* screen. When the button is clicked for a model type, the UI for that model launches, and there are a series of input screens specific to that model.

If the Advanced Tier II option is selected, there is an *Advanced Tier II Modeling* tab-screen rather than the *Inputs* tab-screen. This tab allows the user to launch FRAMES (Whelan et al. 1997) <http://mepas.pnnl.gov/FramesV1/index.stm>. FRAMES is an object-oriented model linkage system with an example shown in Figure 3. Various models can be linked together in various ways within FRAMES. The UI for each model is launched by right-clicking the model icon object. The details of how to use FRAMES or how to use each model UI is not covered here since all information can be found in the TREECS™ user manual (Gerald et al. 2012) and model UI and FRAMES *Help* screens. However, the general types of inputs and how they are developed for the fate/transport models are discussed in the next section below.

## 2.4 Fate/transport model inputs

TREECS™ fate/transport model inputs can be described generally as fitting into the following categories:

- Site media characteristics
- Meteorology
- Hydrology

- Fate/transport parameters
- Solution and output control parameters
- Chemical-specific physicochemical properties
- Initial conditions
- Boundary conditions

Each of the above categories is discussed in general terms below for the TREECS™ fate/transport models. These discussions are presented for Tier 2 and advanced Tier 2 modeling since Tier 1 modeling is simpler, and Tier 1 input requirements can be inferred from the Tier 2/advanced Tier 2 requirements. TREECS™ contains the following fate/transport models in Tier 2/advanced Tier 2: Tier 2 soil model for AOI surface soil; MEPAS vadose and aquifer models for groundwater; RECOVERY model for standing surface water (e.g., ponds and lakes); and the CMS for surface water streams.

The sources and rationale for the model inputs are presented in detail by Dortch et al. (2017) for three demonstration-validation site applications. These three applications can be used as a guide for establishing inputs for other study sites.

#### **2.4.1 Site media characteristics**

Input requirements for site media characteristics vary widely depending on the type of model. For the soil model, these inputs include AOI geometric information and surficial soil properties, including AOI length and width, AOI surface area, AOI active surface soil thickness, average annual soil temperature, volumetric soil moisture content, soil dry bulk density, and soil porosity. The AOI active surface soil thickness can also be considered a solution control parameter as discussed again later.

For surface water models, site characteristics include water body geometry, such as stream top width and mean depth or surface area and mean depth, location of receptor downstream of contaminant entry for CMS, mixed benthic sediment thickness, benthic sediment porosity, sediment particle specific gravity, dry benthic sediment bulk density, mean annual temperature of water, mean annual wind speed, average total suspended solids (TSS) concentration, fraction of organic carbon in TSS, and fraction of organic carbon in benthic sediment solids. Additionally, two of the three following long-term average rates related to sedimentation must be entered: TSS settling, benthic sediment burial, and benthic sediment resuspension.

The benthic sediment thickness can also be considered a solution control parameter as discussed again in Section 2.4.5.

For vadose and groundwater models, site characteristics include: soil or media properties, including texture (percentage of sand, silt, clay, and organic matter) or soil class (such as loam), pH, dry bulk density, and porosity; field capacity; saturated hydraulic conductivity; vadose zone and aquifer thicknesses; effective porosity; and location of receptor wells relative to the AOI.

Site media characteristics can usually be obtained from Operational Range Assessment Program (ORAP) reports or other study site reports for Army installations, or similar reports for the other services of DoD. Information that is not available from installation study site reports can usually be obtained from the World Wide Web. For example, Web Soil Survey (WSS<sup>1</sup>), which was developed for World Wide Web applications by the Natural Resources Conservation Service of the U.S. Department of Agriculture (USDA), can often be used to obtain AOI soil characteristics as well as vadose zone information. Google Earth™ can be used to obtain a wealth of geometric information, such as ground elevations, AOI delineation and dimensions, water body dimensions, watershed delineation, and watershed area and slope. There is also a tool within TREECS™ called the Hydro-Geo-Characteristics Toolkit (HGCT) that can be used to assist in developing inputs, including soil properties, hydrology, erosion, and Darcy velocity. Some model inputs can be set to recommended values to provide meaningful results when certain site-specific information is not available. Examples of such inputs include mixed benthic sediment thickness, benthic sediment porosity, sediment particle specific gravity, dry benthic sediment bulk density, and fraction of organic carbon in sediments.

#### **2.4.2 Meteorology**

Meteorology primarily affects hydrology in TREECS™. TREECS™ has the option of using either average annual or daily varying hydrology. Most TREECS™ applications use average annual hydrology. Meteorology requirements for average annual hydrology include daily precipitation and minimum and maximum daily air temperatures, which should be obtained for a meteorological station near the study site. These meteorological data can be freely downloaded on the World Wide Web from the National

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

Oceanic and Atmospheric Administration's National Centers for Environmental Information (NCEI), previously the National Climatic Data Center (NCDC). These data should cover a fairly long time period, such as 20 years or more, and should be as complete as possible. If there are data gaps for short durations, those should be filled via interpolation or other synthetic means, such as using data from other stations in the region. Then a daily precipitation file and a daily mean and maximum air temperature file should be built for the period of record. Daily mean air temperature can be estimated from the average of the daily minimum and maximum air temperatures. The two files are then used by the TREECS™ hydrology model in HGCT to develop average annual values for precipitation, rainfall, runoff, evapotranspiration (ET), net infiltration (after runoff and ET losses), number of rain days, soil volumetric moisture (water) content, air temperature, and soil temperature. These values are then automatically transferred as inputs to the soil model. The hydrology model uses the Soil Conservation Service (SCS) curve number method to compute runoff. The curve number can be estimated in HGCT with information on land use/cover type and amount of cover.

If the daily hydrology option is used, hourly precipitation data are used rather than daily precipitation. Otherwise, the other input requirements are the same as for average annual hydrology. Discussions of the processing and use of meteorological and hydrological data in TREECS™ can be found in several reports (Dortch 2012a; Dortch et al. 2012; Dortch et al. 2013; Dortch 2014; Johnson and Dortch 2014; Dortch et al. 2017).

Long-term average wind speed (length/time) is also required for both surface water models. Wind speed information can be obtained from the National Renewable Energy Laboratory (<http://www.nrel.gov/gis/wind.html>).

### **2.4.3 Hydrology**

The contaminant fate models in TREECS™ solve only the contaminant fate processes and resulting contaminant mass and concentrations; they do not solve for any hydraulic, hydrodynamic, or hydrologic variables. Rather, these are inputs which result in contaminant transport. Hydrology here refers to inputs relating to water movement. The discussion in Section 2.4.2 for meteorology relates directly to hydrology.

The hydrology inputs for the soil model include either average annual or daily (depending on option selected) values for precipitation, rainfall,

runoff, net infiltration, and soil volumetric water content, and average number of rain days (events) per year for average annual hydrology. Additionally, the number of hours of rainfall each day is required for daily hydrology. All of these inputs are output produced by the hydrology model within HGCT and can be automatically transferred to the soil model input file. Soil properties are also used in the hydrology model in HGCT to compute these hydrologic outputs.

Soil erosion rate is also required by the soil model. Erosion rate is computed by the Universal Soil Loss Equation (USLE) (USDA SCS 1983) for average annual hydrology and by the Modified Universal Soil Loss Equation (MUSLE) (Williams 1975) for daily hydrology. There is an erosion rate estimator tool in HGCT for both average annual and daily hydrology. This tool requires information on land use/cover type, land cover amount, ground slope, and soil properties. There are help files accessible within HGCT to assist in setting input parameters for the hydrology model, USLE, and MUSLE.

The vadose and aquifer models in TREECS™ use only average annual hydrology, which consists of the average annual values of net infiltration from soil to vadose zone and aquifer Darcy flow velocity in the horizontal plane from the location below the source zone to the receptor wells. The use of average annual hydrology in these two models is not usually a problem since groundwater movement is normally very slow and fairly well represented by long-term, average flow conditions. The net infiltration rate used by the vadose model is the average of those used by the soil model for the entire simulation period when the daily hydrology option is selected.

As explained previously, two surface water models are presently available within TREECS™, RECOVERY and CMS. RECOVERY uses only average annual hydrology. The user must specify the average annual water flow rate (cubic meters per year) through the water body for that model. For sites where observed flow records are not available, this flow rate can be estimated by multiplying the surface area of the watershed draining into the water body by the average annual runoff rate for the watershed. If the watershed is similar to the AOI, the value determined for AOI runoff rate can be used. Otherwise, the same approach used for the AOI can be used in HGCT for the watershed to determine its runoff rate. Google Earth

Pro™ has been used to delineate watersheds and their surface area. Also, most installations have GIS files that include watershed delineations.

The CMS model requires two types of stream flow input, stream flow at point of (contaminant) entry on the *Hydraulic Parameters* screen of the UI and contaminant loading water flow rate on the *Loading Data* screen of the UI. The stream flow rate at point of entry, also referred to as background stream flow rate, is the average annual stream flow rate excluding any loading flow rate. The discussion in the above paragraphs applies to setting this flow rate.

The loading water flow rate in the CMS is the water flow from an upstream source that is contaminated, such as the AOI or some other source, or possibly another stream reach. If standard Tier 2 is used, the loading flow comes from the AOI Tier 2 soil model. The AOI flow can be either average annual or daily (depending on the option selected in the AOI Tier 2 soil model), and the flow is provided to the CMS automatically by the AOI soil model. If advance Tier 2 is used, there are several possible sources for the loading flow, including the AOI Tier 2 soil model, another CMS model representing another stream reach that flows into the present CMS stream reach, or specified flows/loadings as provided by the User Defined Module (UDM). As before, loading flows from an AOI can be either annual average or daily. Loading flows from another CMS are the same as the upstream CMS output flows, which can vary over time. Loading flow rates can be specified at any time points the user chooses within the UDM. In all cases, the upstream module automatically provides the loading flow rates to the CMS. Loading flows can be viewed as time series in the *Loading Data* screen of the CMS UI. Given that the loading flows are provided by an upstream module, the only hydrologic input the user must determine and specify for CMS is the background stream flow rate.

#### **2.4.4 Fate and transport parameters**

Fate and transport parameters required by the Tier 2 soil model include soil – pore water adsorption partitioning distribution coefficient ( $K_d$ , L/kg), degradation half-life ( $HL$ , years) for aqueous dissolved and adsorbed phases, solid phase MC residue initial particle diameter ( $d$ , micrometers), and volatilization rate ( $K_v$ , meters/year) of aqueous phase from soil. The volatilization rate can be computed within the soil model UI using soil properties and the chemical-specific diffusion coefficient in air, which can be estimated from molecular weight if a value is not available within the

selected constituent database. There is guidance within the Help screens for estimating input values for  $d$ . Therefore, the primary need is for estimating input values for  $K_d$  and  $HL$ . There is a  $K_d$  estimator tool within the soil model UI, and there is also information in *Help* screens. However, estimating  $K_d$  values can still be problematic given the wide variation in values and the effects of local soil chemistry. Chemical-specific abiotic and biotic factors can affect constituent degradation, resulting in a major challenge to provide reliable values for  $HL$ . As a result,  $K_d$  and  $HL$  values are usually quite uncertain and require some attention within an application.

There are three other fate/transport parameters required by the Tier 2 soil model, the soil exchange layer thickness (meters) and the soil detachability (kilograms/liter) for rainfall extracted pore water export, and the diffusion layer thickness (meters) for volatilization. Default values of 0.005, 0.4 and 0.4, respectively, have always been used for these three parameters.

Similar to the soil model, the vadose and aquifer models share the same difficulties associated with input values for  $K_d$  and  $HL$ . There is also a  $K_d$  value estimator within the vadose and aquifer model UIs, similar to the one in the soil model. The transport parameter dispersivity (length units) must also be specified for each spatial dimension (vertical for vadose model and all three dimensions for aquifer model). Dispersivity is used to calculate dispersion for transport. There are general Help guidelines and estimator tools within the model UIs for setting dispersivity.

Both surface water models require fate parameter inputs for partitioning between water and sediments ( $K_d$  values). Partitioning values are required for water column TSS and for benthic sediments. Values for  $K_d$  can be calculated for organic constituents or specified within the model UIs. The surface water models use degradation rate rather than  $HL$ . First-order degradation rates (per time) are required for dissolved and particulate constituents in the water column and sediment bed. The particulate degradation rates are often set to zero, and usually the water column and surficial sediment pore-water dissolved constituent rates are set to the same value that may not be zero. The deep benthic sediment pore-water dissolved constituent rate should be set to a higher value for some organic chemicals due to anaerobic reduction since deep sediments are usually anoxic.

The surface water models also require a volatilization rate (length/time) for water-dissolved organic constituents, which can be calculated within the

model UIs. A mass transfer velocity (length/time) is required for diffusion of dissolved constituents across the sediment-water interface associated with the exchange of sediment pore-water and water column. This velocity can be calculated within the model UIs using other input data.

The CMS model requires a longitudinal (along the stream flow axis) dispersion coefficient (length<sup>2</sup>/time), which is roughly 1 m<sup>2</sup>/sec for streams, but results are relatively insensitive to the value specified. The RECOVERY model allows the user to include enhanced diffusion due to bioturbation between the surficial benthic sediment layer and the top layers of the deep benthic sediments. This option is often not used, but if it is used, it requires specifying the enhanced diffusion coefficient (cm<sup>2</sup>/sec), the ambient water-sediment temperature (°C), and the enhanced mixing depth (cm).

None of the above fate/transport parameters present any particular estimation difficulties with the exception of the *HL* or degradation rate values. Estimating those for organic constituents can be challenging. For inorganic constituents, such as metals, degradation is usually assumed to not occur. Thus, for inorganic constituents, the *HL* should be set to a very large value, such as 1E20 years, or the degradation rate should be set to zero. In practice, organic chemicals are often assumed not to degrade, which results in highly conservative, worst case predictions. Such assumptions can result in overly protective measures or actions. Improved estimates of natural degradation rates in environmental media, particularly groundwater, are needed to provide more accurate predictions for decision makers so they can recommend more reasonable measures or actions.

#### **2.4.5 Solution and output control parameters**

For the most part, these input parameters are set according to the user's discretion and simulation needs. The Tier 2 soil model requires the time length of simulation (years), the minimum time step (years) to be used in making calculations and the time step type (either constant or adaptive). The length of simulation depends on the simulation needs, such as how far back or forward into the future the simulation should extend. When using average annual hydrology, it is common for a simulation time length to be decades or even centuries long. Simulation time length is usually much shorter (e.g., less than 10 years) when daily hydrology is used. The default minimum time step is 0.001 years. However, the time step should be set smaller, such as 0.0001 years, when using daily hydrology. If the step type is set to constant, the time value that is entered is used for the simulation

duration. If step type is set to adaptive, the soil model computes and uses the maximum allowable step required to maintain numerical accuracy and stability. It is prudent to make several simulations varying both the time step size and type to see how results are affected and to settle on values that don't appreciably alter results.

The soil model also requires the AOI active surface soil layer thickness, which has a default value of 0.4 m. This input parameter was also mentioned under inputs for *Media Characteristics*. Computed soil constituent concentrations are inversely related to the active soil layer thickness. However, for steady-state applications, receiving water (surface water and groundwater) concentrations are insensitive to the active layer thickness. Receiving water concentrations are affected by the active layer thickness for transient conditions. This input parameter is discussed again in the section on *Sensitivity and Uncertainty of Inputs* in Chapter 5.

The vadose and aquifer models have only one solution and output control parameter, the simulation ending time, which is actually the length of the simulation (user specified time units). The default value for ending time is zero, allowing the model simulation to extend as long as necessary to capture the entire rise and fall of the mass flux (for vadose model) or constituent groundwater concentration (for the aquifer model) time series. Thus, the default value of zero is normally used. However, for some special cases, such as when greater time resolution is required during a certain time frame, it may be necessary to set an ending time value. This parameter can be accessed under the *Options/Advanced* menu of the UI.

The CMS model requires four solution and output control parameters: computational segment control, time step size, total simulation time, and depth (thickness) of mixed benthic sediment layer. The mixed benthic sediment layer thickness was also mentioned under inputs for *Media Characteristics*. The computational segment control can be set by either specifying the number of computational segments or the length of each computational segment. If the number of segments is specified, then the length of each segment is computed by dividing the distance to the usage location (another input which is the length of the entire modeled reach) by the number of segments. The segment size is set by user discretion, but there should be enough segments to capture any gradients in stream concentrations (which is on the order of 20 to 30 segments). The time step is also set by user discretion. The time step should be varied and set small

enough so that further reduction does not change results substantially. Generally, for simulations extending over decades, time steps should be on the order of 0.1 to 0.25 years when using average annual hydrology. Time steps of a day or less should be used when using daily hydrology. The total simulation time depends on the needs of the study. For average annual hydrology, total simulation time may be decades and longer. For daily hydrology, it is generally less than 10 years. The mixed benthic sediment layer thickness is the zone at the top of the sediment bed where properties are fairly uniform due to mixing. A value between 0.1 m to 0.2 is typically used for this parameter. Water column concentrations are insensitive to variations in this parameter, but sediment concentrations are inversely proportional to it for time-varying constituent loadings into the stream; thus, doubling and halving the value approximately halves and doubles the computed benthic sediment constituent concentration. For long-term and constant stream loadings, sediment concentrations will eventually reach steady-state, and the steady-state sediment concentration is insensitive to the size of the mixed benthic sediment layer thickness.

The RECOVERY model has some of the same solution and output control parameters as the CMS. It requires the total period of simulation (years) like the CMS. It also requires the mixed sediment layer thickness (meters) like the CMS, but it additionally requires the total sediment thickness to be modeled since RECOVERY models the benthic sediments with multiple 1.0-cm thick layers below the mixed layer to predict the fate of contaminants in deep sediments. A value of 1.0 m is typically used for the total sediment thickness (referred to as contaminated sediment depth in the model UI). Like the CMS, the mixed layer thickness affects mixed layer constituent concentrations for time-varying stream loadings but not for long-term constant stream loadings after sediments have reached steady-state conditions.

RECOVERY does not require a time step size since the time step is auto-calculated throughout the simulation to maintain numerical accuracy and stability. There are three output control parameters, the number of time steps between print intervals for water column and mixed sediment layer output concentrations, the number of time steps between print intervals for deep sediment concentration profile output, and the number of layers of deep sediment to include in the sediment concentration profile output. These three parameters should be set to provide reasonable output definition without creating excessively large output files.

#### 2.4.6 Chemical-specific physicochemical properties

Physicochemical properties for each modeled constituent are supplied by the constituent database in TREECS™ selected by the user. If a property value is missing from the database, the user is required to enter a value. CTS can be used to help provide missing property values.

Chemical-specific physicochemical properties required by the Tier 2 soil model include: water solubility limit,  $C_s$  (mg/L); Henry's Law Constant (HLC) (atm-m<sup>3</sup>/mol); molecular weight, MW (g/mol); solid phase mass density of chemical to undergo dissolution,  $\rho_s$  (g/cm<sup>3</sup>); diffusion coefficient of vapor phase in air,  $D_a$  (m<sup>2</sup>/day); and the organic carbon – water sorption partitioning distribution coefficient,  $K_{oc}$  (mL/g or L/kg), for organic constituents. The first four properties are usually available within each constituent database. However, it is cautioned that the weathered form of the solid phase constituent should be carefully considered when setting  $\rho_s$  used for dissolution. For organic chemicals, it is acceptable to use the pure solid phase constituent density. However, for metals, it is preferable to use the density of the weathered constituent that will dissolve, such as hydrocerussite for lead, which has a density of approximately 6.6 g/cm<sup>3</sup> rather than 11.3 for pure metallic lead. In some cases, the diffusion coefficient in air may be missing from the database. For those cases, the soil model UI automatically computes a value for the air diffusion coefficient based on the constituent's molecular weight. If a value for  $K_{oc}$  is not available from the constituent database for an organic constituent, it can be estimated from the Property Estimation Utility within the Site Conditions/Constituent Selection/Currently Selected Constituents/Info screen of TREECS™. This utility requires a value for the octanol – water sorption partitioning distribution coefficient,  $K_{ow}$  (mL/mL), which is usually available within each constituent database. The value for  $K_{oc}$  is used to estimate the soil partitioning coefficient,  $K_d$ .

The vadose and aquifer models only require the water solubility and  $K_{oc}$ , which is used to compute  $K_d$  for organic chemicals. As explained above,  $K_{oc}$  can be estimated from  $K_{ow}$ .

The two surface water models require the following chemical-specific physicochemical properties: MW; HLC;  $K_{ow}$ , which is used to compute  $K_d$  values for organic chemicals; and the diffusion coefficient of water-dissolved phase in water (i.e., diffusivity in water),  $D_w$  (length<sup>2</sup>/time).

The chemical-specific physicochemical properties required for a TREECS™ application are summarized in Table 1. The constituent *HL* values or degradation rates were discussed as fate parameter inputs, but they could also be considered a physicochemical property since they are chemical-specific. Similarly, *K<sub>d</sub>* values were discussed as fate/transport parameters, but they too could be considered as chemical-specific properties since they can often be estimated from a chemical specific property, such as *K<sub>ow</sub>* and/or *K<sub>oc</sub>*. Regardless of whether *HL* and *K<sub>d</sub>* values are categorized as fate/transport or physicochemical properties, estimating input values for them requires special, and sometimes substantial, attention.

**Table 1. Chemical-specific physicochemical properties required for TREECS™ application.**

Property	Property symbol	Units
Molecular weight	MW	g/mol
Henry's Law Constant	HLC	atm-m <sup>3</sup> /mol
Water solubility	C <sub>s</sub>	mg/L
Solid phase density	ρ <sub>s</sub>	g/cm <sup>3</sup>
Diffusivity in water	D <sub>w</sub>	Length <sup>2</sup> /time, e.g., cm <sup>2</sup> /sec
Diffusivity in air	D <sub>a</sub>	Length <sup>2</sup> /time, e.g., cm <sup>2</sup> /sec
octanol – water sorption partitioning distribution coefficient	K <sub>ow</sub>	mL/mL
Organic carbon – water sorption partitioning distribution coefficient	K <sub>oc</sub>	g/mL or kg/L

#### 2.4.7 Initial conditions

In the case of fate/transport models, initial conditions usually refer to initial constituent concentrations at the beginning of the simulation in each modeled media, such as soil, water, and sediments. The Tier 2 soil model and both surface water models require initial concentrations in soil and surface water/sediments, respectively. The CMS assumes initial concentrations for the water column are zero (requiring no input by the user) since stream initial water concentrations are expected to be fairly rapidly flushed. The vadose and aquifer models do not require initial conditions since they assume no contamination at time zero. Initial concentrations can be set to zero for most application. However, there can be special cases where the initial concentrations may be either known or previously predicted, and future fate must be simulated based on these initial concentrations.

### 2.4.8 Boundary conditions

All fate/transport models require boundary conditions, which are also referred to as loadings. Loadings are constituent mass that enter the modeled domain within a time period (i.e., mass/time), and loadings with TREECS™ can vary over time. For a range AOI represented by the soil model, loadings are the MC residue mass deposition rate (mass/time) into the AOI. As discussed previously, MC loadings can be estimated with the TREECS™ Munitions Mass Loading Module. For the vadose model, loadings usually arrive via leaching from the AOI surface soil, which are automatically transferred from soil model output to the vadose model. An exception to this is the application for MCB Camp Pendleton (Dortch et al. 2017), where alluvial recharge from Las Flores Creek provided vadose zone loadings via the UDM. For the aquifer model, loadings are usually provided automatically from vadose model output (i.e., mass flux through the vadose zone enters at the water table of the aquifer). There could be exceptions where there is a known, user-specified mass loading into an aquifer, in which case the UDM would be used. Similarly, mass loadings for the surface water models are usually automatically transferred from output of an upstream model, such as runoff and erosion from the AOI soil model or an upstream stream model representing an upstream reach or branch in a stream system. Exceptions require use of the UDM for user-specified loadings.

Both surface water models also allow for an additional external mass loading of constituent that is constant over time, in addition to the time-varying loadings delivered by an upstream module. This loading is specified by the user in units of kilograms/year in RECOVERY. For CMS, a constant background concentration, which is the concentration entering at the upstream head of the modeled reach, is specified by the user in water concentration units (mass/volume). A loading is manifested by multiplication of the background concentration by the constant background (point of entry) water flow rate that is also entered by the user.

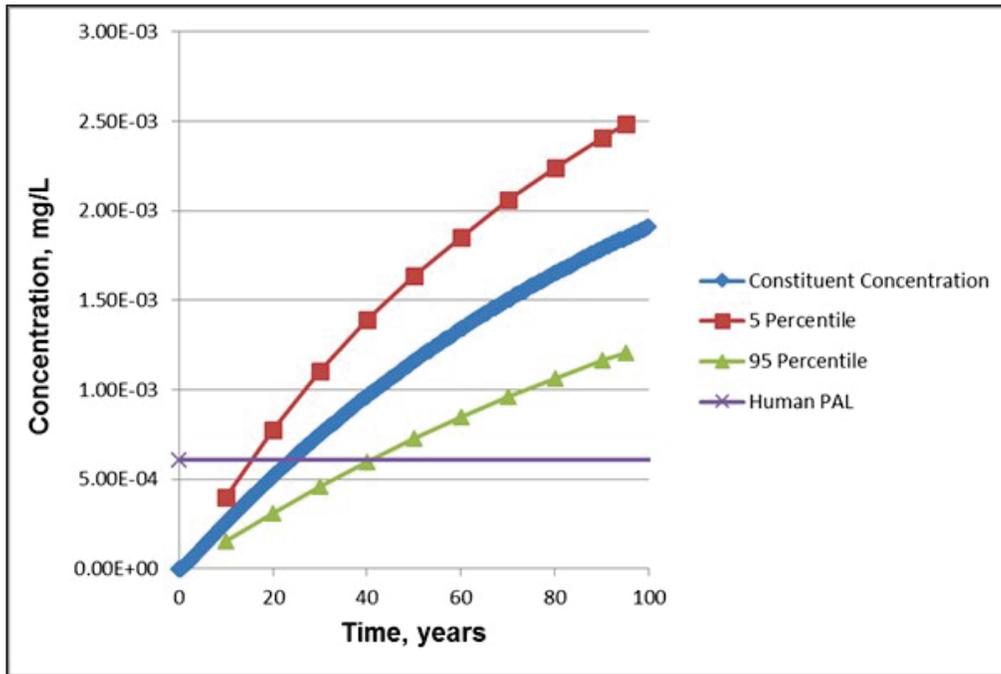
## 2.5 Output

TREECS™ provides two basic types of output, graphical and textual. The graphical output is provided mostly via Excel® files, but there are some model-specific, legacy graphics packages as well for RECOVERY and the CMS. The Tier 2 soil model has a text viewer in addition to graphical viewers.

There are output viewers for each type of model, soil, vadose zone, aquifer, surface water, and UDM. The viewers for each model can produce graphical plots (using Excel®) of concentrations versus time, mass flux versus time, and probability of exceedance (based on time) for concentration and mass flux. There is an exception for the vadose viewers. Those viewers provide only mass flux since the vadose model does not produce concentrations.

Most of the output analysis focuses on graphs of concentration versus time for receiving media where there are potential receptors. The protective health benchmarks, or PALs, can also be placed on each graphical plot. There are also output viewers for sensitivity and uncertainty (S/U) analysis. TREECS™ contains an S/U module that is based on Monte Carlo simulation with Latin Hypercube sampling of random and uncertain inputs. The user can select the inputs that are uncertain, provide statistical information for the uncertain inputs, and run Monte Carlo analysis to assess the effects of the uncertainty on results, as well as the sensitivity of each uncertain input. Output viewers from the S/U module include cumulative distribution functions, histograms, partial R sensitivity results, cumulative and exceedance probabilities, and sample variable versus time with confidence bands. An example is shown in Figure 4 of graphical output for constituent concentration versus time in a stream with uncertainty confidence bands and human PAL.

Figure 4. Example of constituent concentration plot for a stream with uncertainty 95% confidence bands and human PAL



## **3 Key Features and Input Requirements of CTS**

### **3.1 Key features**

CTS is Web-based, thus, to use it, a user must access the CTS public domain Web site, which will be provided when the review of the  $\beta$ -version has been completed during 2017. CTS can provide physicochemical properties of complex organic chemicals for both the parent chemical and predicted transformation products. CTS has capabilities for estimating properties in the absence of experimentally obtained properties; thus, CTS can help fill data gaps for properties, particularly for emerging contaminants with limited experimental data.

The CTS currently consists of three major components: (1) Chemical Editor that allows for the entry of the chemical of interest through either provision of the common name, smiles string notation, Chemical Abstract Service (CAS) registry number, or chemical structure; (2) Physicochemical Properties Calculators, which through access to SPARC (SPARC Performs Automated Reasoning in Chemistry), EPI (Estimation Program Interface) Suite, TEST (Toxicity Estimation Software Tool), and ChemAxon's plug-in calculators provide the necessary physicochemical properties required for predicting environmental concentrations; and (3) Reaction Pathway Simulator, which is based on description of the environmental conditions (e.g., anaerobic vs. aerobic) and provides the major transformation products based on the execution of reaction libraries for abiotic reduction, hydrolysis, aerobic biotransformation, and mammalian metabolism. Information from CTS can provide the constituent properties necessary for modeling contaminant fate in TREECS™.

### **3.2 Application process**

The first step in applying the CTS is the selection of one of three available work flows described below. Each workflow invokes the CTS modules required to provide the data requested by the user. For each of the workflows, the Chemical Editor is the first module to appear when the option for submitting a single chemical is selected.

1. **Calculate Chemical Speciation Workflow:** Invokes the Chemical Editor (CE) Module which provides the user options for chemical entry and calculates the speciation for the chemical of interest. This workflow provides the user the option of calculating the ionization constants, the tautomer distribution and the possible isomers for the chemical of interest.
2. **Calculate Physico-Chemical Properties Workflow:** The User inputs chemical information through the CE and then invokes the Physico-Chemical Properties Calculator (PCP) Module. The PCP Module then calls upon four stand-alone widely recognized calculators (EPI Suite, SPARC, ChemAxon, and TEST), all of which calculate physicochemical (p-chem) properties by mutually exclusive methods. The user can select the p-chem properties of interest and the calculators to execute for the calculation of the selected properties. The user also has the option of selecting the option Measured, which will provide existing measured data for the chemical of interest that is stored in the chemical properties database associated with EPI Suite.
3. **Generate Transformation Products Workflow:** The User inputs chemical information through the CE and then invokes the Reaction Pathway Simulator (RPS) Module to generate transformation products through the execution of reaction libraries based on user-specified conditions. The user is then given the option to invoke the PCP Module for the calculation of p-chem properties for one or more product chemicals.

The CE allows for the entry of the chemical of interest through either provision of the common name, smiles string notation, CAS registry number, or chemical structure. Because the CE retains the information provided by the user, it is possible to move from one workflow to another without having to reenter the chemical information.

### 3.3 Input requirements

The input requirements will vary depending on the workflow chosen by the user. Accordingly, the input requirements will be described for each of the workflows.

### 3.4 Calculate chemical speciation workflow

Selection of the *Calculate Chemical Speciation Workflow* provides a page illustrating the workflow overview. The user is provided with the option to submit a single chemical for processing, or click on the Batch tab to submit a batch run with multiple chemicals. As stated previously, for each of the

workflows, the CE is the first module to appear when the option for submitting a single chemical is selected.

The user can select any combination of the calculators and can use the provided default values or change the default values to user preferred values. The following parameters can be adjusted:

- Calculate Ionization Constants
  - Number of decimals: Number of decimal places calculated for acidic and basic  $pK_a$  values
  - pH lower limit: Specifies the lower end of the pH range for which the micro-species will be generated
  - pH upper limit: Specifies the upper end of the pH range for which the micro-species will be generated
  - Generate major micro-species at pH: Generates the major micro-species at the specified pH
  - pH step size: Specifies the pH step size for the X-Axis of the plot illustrating the distribution of the micro-species as a function of pH
- Calculate Dominant Tautomer Distribution
  - Maximum number of structures: Specifies the maximum number of structures that will be generated
  - At pH: Specifies the pH at which the dominant tautomer distribution will be calculated
- Calculate Stereoisomers
  - Maximum number of structures: Specifies the maximum number of structures that will be generated

The results from each calculator are illustrated in within CTS and can be captured in pdf files.

### 3.5 Calculate physico-chemical properties workflow

Selection of the *Calculate Physico-Chemical Properties Workflow* provides a window illustrating the workflow overview. The user is provided with the option to submit a single chemical for processing, or click on the Batch tab to submit a batch run. As with each of the workflows, the Chemical Editor is the first module to appear when the option for submitting a single chemical is selected. The *Physico-Chemical Properties Workflow* inputs screen is then used to select the p-chem properties and p-chem calculators of

interest. After selection of the reaction libraries and reaction options have been made, the user should click the submit key to generate the p-chem properties.

### 3.6 Generate transformation products workflow

Selection of the *Generate Transformation Products Workflow* provides a window illustrating the workflow overview. The user is provided with the option to submit a single chemical for processing, or click on the Batch tab to submit a batch run. As with each of the workflows, the CE is the first module to appear when the option for submitting a single chemical is selected.

The first required input is the selection of the reaction libraries based on the transformation pathways of interest. Three reaction libraries, including abiotic hydrolysis, abiotic reduction, and Phase 1 mammalian metabolism, are available in the  $\alpha$ -version of the CTS. Three options are available for the selection of the reaction libraries:

- Reaction System Conditions
- Office of Chemical Safety and Pollution Prevention Harmonized Test Guidelines
- User Selected

For example, selection of the Reaction System Conditions provides two options for reaction systems (i.e., Environmental or Mammalian). Selection of the Environmental Reaction System provides the option to select respiration type: Aerobic or Anaerobic. Based on the selection of these options, a window with the available reactions libraries for the reaction system condition and respiration type will appear. After selection of the reaction libraries and the option for the number of generations of transformation products has been set, the transformation products generated based on the execution of the selected transformation libraries are illustrated on the screen and are available in pdf or Excel® files. By selecting any of the transformation products, the user can return to the *Calculate Physico-Chemical Properties Workflow* to generate the p-chem properties for the transformation products of interest.

## 4 Establishing Physicochemical Properties and Related Inputs

### 4.1 General considerations

Chemical-specific physicochemical properties required for TREECS™ application are listed in Table 1. Molecular formula can also be included in this list. The ARCDB is one of three constituent property databases available within TREECS™. The ARCDB contains values for each of the properties in Table 1, with the exception of  $K_{oc}$ , for over 200 constituents commonly found on ranges. There are values of  $K_{oc}$  for some chemicals, but values are missing for many. However, as mentioned previously, there is a tool in TREECS™ for estimating  $K_{oc}$  from  $K_{ow}$ . Of course, there are no values in ARCDB of some properties that are not appropriate for metals, such as  $C_s$ ,  $HLC$ ,  $K_{ow}$ , and  $K_{oc}$ . In many cases, there are multiple values of the chemical-specific properties in ARCDB from different sources, and the user must select which value to use. The source of the value as well as how it was obtained, such as experimental, calculated, etc., is displayed to help the user in making a selection.

There can be cases where a specific chemical is not available within any of the TREECS™ three constituent databases, such as new ECs associated with IMs. For such cases, CTS can be used to provide estimates. Several ECs and their properties were recently added to the ARCDB. The CTS was used to help assign properties for those ECs (Dortch and Johnson 2017).

The properties that are usually considered well-known or readily obtained include molecular formula,  $MW$ , and  $\rho_s$ . The molecular diffusivities can be estimated with reasonable accuracy if not experimentally available using the method of Hayduk and Laudie (1974) for  $D_w$  and the method of Fuller et al. (1966) for  $D_a$ . Many of the diffusivity values in ARCDB were estimated using these calculation methods. Overall, quite reliable information can be obtained for four of the eight physicochemical properties listed in Table 1.

Values also can usually be estimated for the remaining four physicochemical properties if experimental values are not available, but there is generally less certainty in these estimated values. There are four physicochemical calculators in CTS that can be used for estimating values for the remaining

four properties,  $C_s$ ,  $HLC$ ,  $K_{ow}$ , and  $K_{oc}$ . These calculators were available as stand-alone properties estimator software prior to the development of CTS.

As stated previously, values for  $K_{ow}$ , and  $K_{oc}$  are needed for estimating respectively the sediment and soil partitioning coefficients for organic chemicals. However,  $K_{ow}$  and  $K_{oc}$  do not provide accurate estimates of partitioning coefficients for some organic chemicals, such as ionic organic chemicals where partitioning is affected more by pH than organic matter content. At this time, searching the scientific literature for  $K_d$  information is the only recourse for established values for such chemicals. Additionally, establishing  $K_d$  values for metals is particularly challenging given the dependence on local soil and sediment chemistry. There is guidance in TREECS™ Help menus, as well as a tool for soils in the model UIs, for estimating  $K_d$  values for metals.

A similar challenge exists for estimating the solubility of metals since not only does local soil chemistry affect solubility but also the weathered metal products affect it. For these reasons, there are no solubility values ( $C_s$ ) for metals in any of the constituent databases. There is a tool in TREECS™ for estimating solubility of lead and copper, and there are several publications in which estimating solubility of metals found on ranges is discussed (Dortch et al. 2011b; Dortch 2012b).

Although degradation rate, or  $HL$ , is classified as a fate parameter input, it also could be considered a physicochemical property. The degradation rate (or  $HL$ ) of organic chemicals is the most sensitive and uncertain of all the model inputs affecting the prediction of constituent fate. These inputs are chemical-specific and can be affected by local chemistry, soil and sediment characteristics, and micro-biology. For these reasons, the worst case assumption is often made that there is no degradation. However, such a highly conservative assumption does not provide a sound basis for considering the benefits of natural attenuation. The CTS does not provide estimates for degradation rates or  $HL$  values. As with  $K_d$  values for some organic constituents, searching the scientific literature is the best approach for obtaining estimates for degradation rates or  $HL$  values. This approach was used to estimate  $K_d$  and  $HL$  values for IM ECs as discussed by Dortch et al. 2017 and Dortch and Johnson (2017). There has been progress in the field of computational chemistry in recent years for estimating complex properties, such as degradation rate, but such techniques have not matured enough yet for wide acceptance.

## 4.2 Experience with using CTS for estimating physicochemical properties

The CTS was used to estimate the properties  $C_s$ ,  $HLC$ ,  $K_{ow}$ , and  $K_{oc}$  for four MC found in IMs: RDX; 2,4-dinitroanisole (DNAN); 3-nitro-1,2,4-triazol-5-one (NTO); and nitroguanidine (NQ). Three of the four MC, DNAN, NTO, and NQ are considered EC. The CAS registry number, the molecular formula, and the molecular weight of the four MC are shown in Table 2.

Table 2. Four MC found within IMs.

MC	CAS registry number	Molecular formula	Molecular weight
RDX	121-82-4	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	222.12
DNAN	119-27-7	C <sub>7</sub> H <sub>6</sub> N <sub>2</sub> O <sub>5</sub>	198.13
NTO	932-64-9	C <sub>2</sub> H <sub>2</sub> N <sub>4</sub> O <sub>3</sub>	130.06
NQ	556-88-7	CH <sub>4</sub> N <sub>4</sub> O <sub>2</sub>	104.07

Attempts were made to use all four calculators in CTS for each MC and each property; although, in some cases certain calculators did not provide estimates as noted in the results below. The results from each calculator for each MC are shown in Table 3 through Table 6 for the properties  $C_s$ ,  $HLC$ ,  $K_{ow}$ , and  $K_{oc}$ , respectively. Also shown in these tables are values available from ARCDDB and used in TREECS™ modeling (Dortch et al. 2017; Dortch and Johnson 2017). The ARCDDB values used in TREECS™ modeling are considered to be the most appropriate to use based on multiple considerations. A blank in the tables below indicates no value available.

The ChemAxon value from CTS for solubility of DNAN is close to the measured values shown in Table 3. However, the other estimated values retrieved from CTS for solubility of the other three MC are quite different from the measured or recommended ARCDDB values. These results suggest that estimated  $C_s$  values of MC from CTS should be used with caution at this time.

Table 3. Values for physicochemical property  $C_s$ , mg/L.

MC	Chem-Axon	EPI Suite	TEST	SPARC	Measured available in CTS	ARCDB	ARCDB source
RDX	236	8,890	3.99E9	194	59.7	59.8	Measured <sup>1</sup>
DNAN	268	632		1,240	155	276	Measured <sup>2</sup> at 25 deg C
NTO	888	39,400		399		16,600	Interpolated from measured <sup>3</sup>
NQ	25,900	1.00E+06		22,300	4,400	2,600	Measured <sup>4</sup>

<sup>1</sup>Yalkowsky et al. 2010 at 25 deg C; there is a TREECS™ tool to correct RDX solubility for local temperature.

<sup>2</sup>Boddu et al. 2008.

<sup>3</sup>Spear et al. 1989.

<sup>4</sup>Haag et al. 1990.

Table 4. Values for physicochemical property  $HLC$ , atm-m<sup>3</sup>/mol.

MC	Chem-Axon	EPI Suite	TEST	SPARC	Measured available in CTS	ARCDB	ARCDB source
RDX		6.32E-8		5.06E-15	2.01E-11	6.32E-8	EPI Suite bond method
DNAN		3.01E-7		2.69E-7		3.01E-07	EPI Suite group method
NTO		4.07E-13		3.23E-11		4.07E-13	EPI Suite bond method
NQ		4.49E-12		6.89E-10		4.49E-12	EPI Suite bond method

Table 5. Values for physicochemical property  $K_{ow}$ , mL/mL.

MC	Chem-Axon	EPI Suite	TEST	SPARC	Measured available in CTS	ARCDB	ARCDB source
RDX	1.95E-06 KLOP <sup>a</sup> 2.40E-06 VG <sup>b</sup> 4.68E-06 PHYS <sup>c</sup>	4.79			2.45	6.31	7.41 Measured <sup>1</sup>
DNAN	54.95 KLOP 50.12 VG 44.67 PHYS	51.29			165.96		43.6 Measured <sup>2</sup>
NTO	0.095 KLOP 26.9 VG 0.24 PHYS	0.028			0.033		2.34 Measured <sup>2</sup>
NQ	0.0017 KLOP 0.0032 VG 0.0051 PHYS	0.019			0.068	0.16	0.13 HSDB <sup>3</sup>

<sup>a</sup> log P data is used from <https://www.chemaxon.com/marvin-archive/5.9.3/marvin/help/calculations/partitioning.html#ref2>.

<sup>b</sup> Viswanadhan and Ghose method is used, <https://www.chemaxon.com/marvin-archive/5.9.3/marvin/help/calculations/partitioning.html#ref1>.

<sup>c</sup> log P data is used from PHYSPROP© database, <http://esc.syrres.com/fatepointer/search.asp>.

<sup>1</sup>Sangster 1993

<sup>2</sup>Sokkalingam et al. 2008

<sup>3</sup>Hazardous Substances Data Bank (HSDB), <https://toxnet.nlm.nih.gov>

Table 6. Values for physicochemical property  $K_{oc}$ , L/kg.

MC	Chem-Axon	EPI Suite	TEST	SPARC	Measured available in CTS	ARCDB	ARCDB source
RDX		89.1				*	
DNAN		229.9				158.5	Estimated <sup>1</sup>
NTO		12.1				125.9	Estimated <sup>1</sup>
NQ		20.6				12	Estimated <sup>2</sup>

\* No value for RDX in ARCDB, but a range of 42–167 has been reported by Hazardous Substances Data Bank (HSDB), <https://toxnet.nlm.nih.gov>.

<sup>1</sup> Chakka et al. 2010.

<sup>2</sup> Hazardous Substances Data Bank (HSDB), <https://toxnet.nlm.nih.gov>.

The  $HLC$  values in ARCDB were obtained from EPI Suite; thus, those values agree with the EPI Suite values retrieved from CTS as shown in Table 4. The SPARC value retrieved from CTS for  $HLC$  of DNAN is close to the EPI Suite value, but the SPARC values of  $HLC$  for the other three MC are substantially different from the EPI Suite values. Prior experience suggests that EPI Suite can provide reasonable estimates for  $HLC$ . The accuracy of  $HLC$  for the four MC is not critical since these four MC have very low volatility.

Examination of Table 5 indicates mixed results for estimating  $K_{ow}$  values with CTS. ChemAxon provided an estimate for  $K_{ow}$  of DNAN that agrees fairly well with the measured value in ARCDB. The EPI Suite estimates for  $K_{ow}$  of RDX and DNAN agree fairly well with measured values. The SPARC estimate of  $K_{ow}$  for RDX, DNAN, and NQ are the same order of magnitude as measured values. These results suggest that reasonable values of  $K_{ow}$  can be estimated with CTS, but good judgement should be exercised in selecting the appropriate value to use. However, the value for  $K_{ow}$  is irrelevant for ionized chemicals, such as NTO, for which sorption partitioning is affected more by pH than organic matter and  $K_{ow}$ .

Examination of Table 6 indicates that EPI Suite within CTS provided  $K_{oc}$  values for the MC that agree fairly well (with the exception of NTO) with values in ARCDB, which were based on estimates. As noted above, NTO is not expected to correlate well with organic carbon. Detailed discussions of soil and sediment  $K_d$  estimates for these MC are provided by Dortch et al. (2017) and Dortch and Johnson (2017).

The CTS was still in beta testing mode and undergoing revisions at the time this report was prepared. Thus, some estimates for property values could change from those shown in this report.

## **5 Lessons Learned from Applying TREECS™**

### **5.1 General exposure risks of range MC**

The lessons learned from applying TREECS™ as presented herein pertain to Army firing range applications. The MC most often found on firing ranges are HE associated with dudded artillery impact areas, as well as ordnance demolition areas, and metals associated with SAFRs. HE constituents, such as RDX, are more mobile than metals at SAFRs, such as lead, due to higher water-solubility and lower sorption partitioning. The higher sorption partitioning of metals greatly retards their leaching to groundwater; thus, metals are much less likely to cause groundwater exposure risks than HE. However, firing range metals can be exported to surface water via erosion of soils containing adsorbed metals. Long-term metal exposure risks in surface water can be greater than that of HE because of the much higher adsorption of metals to sediments, thus increasing sediment retention times. HE exposure risks in surface water are usually transient, occurring only during and immediately following rainfall-runoff events on ranges. Additionally, the relatively low sorption partitioning of HE to sediments greatly lowers risks for long-term exposure in surface water. Therefore, metals can present more exposure risk than HE for surface water, and HE tend to present more exposure risk than metals for groundwater. Applications of TREECS™ to firing ranges with pathways to surface water and groundwater demonstrate quite well the above exposure risk trends (Dortch et al. 2011b; Dortch 2012a; Dortch et al. 2013; Dortch 2016; Dortch et al. 2017).

### **5.2 Average Annual versus Daily Hydrology**

As noted in section 5.1, surface water concentrations of HE can be quite transient. As discussed by Dortch et al. (2017), an analysis of rainfall data and observed RDX concentrations for two surface water sites (Popolopen Brook, USMA, and Las Flores Creek, Camp Pendleton) showed that the detection of RDX concentrations in streams is dependent on the occurrence of substantial rainfall just prior to or during stream sampling. RDX concentrations were below detection in Popolopen Brook and Las Flores Creek when there had not been substantial rainfall a day or two prior to sampling. RDX concentrations were above detection when there had been recent rainfall. Given the low sorption partitioning of RDX, its capacity to

dissolve, and its slow degradation rate, RDX moves from range soils to streams when it rains, and it travels out of the stream system quickly, dropping below detection not long after rainfall-runoff has ceased.

The TREECS™ models for Popolopen Brook and Las Flores Creek used average annual hydrology (Dortch et al. 2017). When average annual hydrology is used, TREECS™ predicts stream concentrations that would exist for the average annual rainfall per rainfall day, which is calculated from the average annual rainfall depth divided by the average number of significant rainfall days per year. A significant rainfall day is roughly determined by rainfall rates greater than 0.1 inch per day. Dortch et al. (2017) found a correspondence in ratios for rainfall and stream concentrations. Specifically, the ratio of the sampling date rainfall to the average annual rainfall per rainfall day was computed for each observed stream concentration of RDX. The ratio of observed stream RDX concentration to predicted stream concentration (using average annual hydrology) was also computed. A comparison of the two ratios showed remarkable agreement, thus supporting the concept that TREECS™ applied with average annual hydrology predicts stream concentrations associated with average annual rainfall per rainfall day (i.e., the average storm).

The use of the daily hydrology option in TREECS™ should allow closer agreement between model and observed stream concentrations, which vary widely from below detection during dry periods to measureable concentration spikes during periods of rainfall. However, use of the daily hydrology option can result in much longer model execution times for the CMS, which hinders making long-term (e.g., 100-year) simulations, especially when including Monte Carlo uncertainty analysis.

TREECS™ applications for SAFRs and a receiving stream (Dortch 2014) showed highly transient (i.e., widely fluctuating) water column concentrations for lead and RDX in the surface water stream when using daily hydrology. However, the sediment concentrations of lead did not fluctuate nearly as much as the sediment concentrations of RDX due to much higher sediment retention (or sediment *memory*) associated with the much higher sorption partitioning of lead. The study by Dortch (2014) provides a detailed comparison of using average annual versus daily hydrology and the trade-offs of each. Overall, average annual hydrology is acceptable and should be used unless daily fluctuations in surface water stream concentrations are required for relatively short time frames (e.g., a year or less).

The daily hydrology option should not be used for groundwater receptors. The MEPAS vadose and aquifer models can use only average annual flows, so applying daily hydrology for soil is of little value for groundwater. Furthermore, the use of average annual hydrology provides conservatively higher groundwater concentrations than daily hydrology (Dortch 2014). Also, the RECOVERY model, which is typically used for standing surface water bodies, such as ponds or lakes, presently uses only average annual water flow rate. The use of daily hydrology for the soil model will result in daily constituent loadings to the RECOVERY model for surface water, but the fate of the constituents within the water body is the result of average annual water flow rate through the water body. Water flow rate affects constituent residence time within the water body, thus affecting concentrations resulting from fate processes, such as degradation. To realize the full benefits of daily hydrology for surface water, the CMS should be used.

### **5.3 Sensitivity and uncertainty of inputs**

TREECS™ inputs that draw the most attention during an application are those for which model output is particularly sensitive to input specification and are also not well known, or highly uncertain. Fortunately, most of the inputs can be fairly easily obtained or reasonably estimated. The discussion below focuses only on those inputs that have been found to be the most problematic to determine while also having a substantial effect on output results.

#### **5.3.1 Mass loading**

Often TREECS™ applications for firing ranges require starting the models in the past with imposed, uncertain firing rates (and sometimes uncertain items fired) and projecting AOI soil MC residue concentrations to present time, as well as into the future. This modeling approach is required when present-day AOI soil MC concentrations are not known and must be predicted. AOI soil MC concentrations are not usually known since there is too much danger of sampling ranges that have unexploded ordnance (UXO). Unfortunately, range firing rates, and even the types of items fired, may not be well known decades in the past. Model results are quite sensitive to these inputs since the types and number of items fired directly define the MC mass residue loading rates, and media concentrations are directly, linearly proportional to mass loading rate. Firing records from recent years and discussions with installation personnel have been used to estimate past firing items and rates.

### 5.3.2 Media Characteristics

Most media characteristics can be readily obtained or estimated with acceptable accuracy. Thus, these inputs have not presented much of a problem. However, two inputs, TSS concentration and TSS settling rate, have been found to be an exception for modeling metals in surface water. In the absence of data, these two inputs for the surface water models must be estimated or assumed. Surface water dissolved metal concentrations are sensitive to TSS concentration, and benthic sediment total metal concentrations are sensitive to TSS settling rate. This sensitivity is due to the high TSS  $K_d$  values of metals. Water column dissolved metal concentrations are inversely proportional to TSS concentration; and benthic sediment total metal concentrations are directly proportional to TSS settling rate. The proportionality is less than linear in both cases. TSS settling rate can be estimated if the TSS size is known or assumed. Metals mostly adsorb to fine sediments, such as clays and fine silt, resulting in settling rates on the order of 0.1 to 1.0 m/day.

### 5.3.3 Hydrology

Inputs pertaining to hydrology can usually be estimated quite well if measurements are not available. However, there have been exceptions. The three applications reported by Dortch et al. (2016 Draft) demonstrate such exceptions. For the application to Demo Area 2, MMR, the lateral distance of the receptor well relative to the centerline of the RDX groundwater plume was not exactly known. Computed receptor well concentrations were sensitive to relatively small changes in the lateral distance because of the close proximity of the well to the AOI source area.

For the application to the AIA, USMA, computed stream concentrations were sensitive to stream flow rate. A doubling of the flow rate approximately halved the stream RDX concentrations. The input value for average annual stream flow rate was estimated using the area of the Popolopen Brook watershed, which was difficult to estimate due to the very hilly terrain. All of the water infiltration through the surface soil was assumed to divert to stream flow via soil interflow due to bedrock below the surface soil. Model results are highly sensitive to the amount of interflow, and the amount of interflow can be highly uncertain for some sites.

For the application to ZIA, MCB Camp Pendleton, the water recharge rate from Las Flores Creek into the underlying aquifer was difficult to estimate.

Additionally, there was some discrepancy in reported aquifer Darcy flow velocities that created uncertainty. Computed aquifer RDX concentrations were sensitive to both of these variables.

For all three applications, hydrology issues required special attention, but all such issues were dealt with acceptably as reported by Dortch et al. (2017). Generally, hydrologic inputs are not problematic.

#### 5.3.4 Fate and transport parameters

There are three fate and transport parameters that create output sensitivity while having considerable uncertainty, and they are: degradation half-life (*HL*) or degradation rate; soil-water and soil-sediment sorption partitioning distribution coefficients,  $K_d$ ; and solid-phase MC residue initial particle size,  $d$ , which affects solid-phase MC dissolution rate into water.

Degradation rates (or *HL*) can greatly affect organic constituent concentrations in environmental media, particularly groundwater where constituent travel times to receptor wells can be quite long. The effects of degradation can be much less for surface water, especially in streams where travel times to receptors are generally short. Large standing water bodies have longer residence times, thus exhibiting greater influence of degradation on constituent concentrations. The effects of degradation in soil depend on the organic constituent soil  $K_d$  values, where the higher the  $K_d$  value for prolonging residence time, the greater the effect of degradation. The high importance of obtaining better estimates of *HL*, particularly in the vadose zone and groundwater, is discussed in detail by Dortch (2015) and Dortch and Johnson (2017).

Soil and sub-subsurface groundwater  $K_d$  values affect constituent retardation, where higher values result in longer transit times through these media. Retardation causes delay and attenuation of peak concentrations at receptor wells. Higher  $K_d$  values provide more time for media degradation. Estimating soil and sediment  $K_d$  values can be problematic for organic and inorganic constituents. Reliable estimates are particularly important for  $K_d$  values of metals partitioning to water column TSS and benthic sediments in surface waters as discussed by Dortch et al. (2017). Site-specific, concurrent measurements of TSS and total and dissolved metal concentrations in the water column can be used to determine  $K_d$  values for TSS; and measurements of sediment dry bulk density and sediment total and pore-water

dissolved metal concentrations can be used to determine sediment  $K_d$  values. There are tools and *Help* files in TREECS™ to help users establish appropriate  $K_d$  values for constituents. Estimates for  $K_d$  values for EC are discussed by Dortch et al. (2017) and Dortch and Johnson (2017).

Dortch and Johnson (2017) concluded that future research should focus predominantly on determining natural degradation rates of EC in surface soil, vadose zone (partially water-saturated groundwater), and water-saturated groundwater. Vadose zone and groundwater should receive higher priority than surface soil. It is expected that EC degradation rates are not only chemical-specific, but are also affected by site-specific media characteristics, thus complicating their estimation.

The time of arrival of MC in receiving water down-gradient of firing ranges is related to the dissolution rate into water of solid-phase MC residue in the AOI soil. The faster the dissolution rate, the sooner MC will arrive in off-range receiving water. The dissolution rate is inversely proportional to the MC residue initial particle size. Thus, the smaller the initial particle size ( $d$ ), the faster the dissolution due to a higher specific surface area. There is guidance within TREECS™ *Help* files for setting  $d$  for various types of HE residue and bullet fragments in SAFRs. It is a good idea to consider the effects of initial particle size on output results. There is more discussion of initial particle size in the section below on *Handling HE Formulations*.

### 5.3.5 Chemical-specific physicochemical properties

Most physicochemical properties are fairly well known or have been reasonably well estimated. In most cases, values are available within one or more of the three constituent databases within TREECS™. For constituents that are not in the TREECS™ databases, CTS can be used to estimate properties. Also, there are web-based sources that can provide values, such as those cited by Wagner (2003) (<http://www.acsu.buffalo.edu/~abwagner/PhysProp-STL-ArticleRev3.pdf>).

The dissolution rate is directly proportional to the MC solubility. The solubility of organic constituents is usually known fairly accurately. Pure metals are considered insoluble. However, metal weathered products can dissolve. Estimating the solubility of weathered metal products is complex with dependency on the product form and local soil chemistry. Some

guidance on solubility of lead, copper, zinc, antimony, and uranium 238 is provided by Dortch (2012b).

### 5.3.6 Solution control parameters

In general, most of the inputs that involve solution control have a minor impact on model results. However, there are several such inputs that merit discussion.

Model time step size can affect output results. The MEPAS vadose and groundwater models do not require a time step input by the user. However, the user can vary the ending time (TFINAL) for a simulation (this input is under *Options/Advanced* in the UI). The default value for this input is zero, which causes the model to run for as long as needed to capture the entire Gaussian-shaped output. If the user enters a value for TFINAL different from zero, the model will run for the length of time specified. This option is usually used when it is necessary to obtain more temporal detail of output for the early stages of a simulation. The RECOVERY surface water model does not require time step entry since it has auto-time-stepping. The soil model also has auto-time-stepping, but the user can over-ride that and provide a constant value for special cases. The CMS requires that the user enter a time step size. For many applications, the size of the time step will have a minimal effect on the solution due to the implicit solution procedure built into the model. However, the time step should be small enough to ensure adequate accuracy. The user should try several time steps to test if the results change or not. The largest time step that does not alter the solution results substantially should be used.

Values must be entered for the AOI active soil layer thickness and the active, mixed, surficial layer thickness of benthic sediments. A default value of 0.4 m is provided for the active soil layer thickness. A value of 0.1 m is typically used for the mixed surficial benthic sediment layer thickness. Constituent concentrations in soil are certainly affected (inversely proportional) by the soil layer thickness. Experience has shown that model results for groundwater concentrations are nearly insensitive to the soil layer thickness. However, surface water concentrations can be quite sensitive, depending on the constituent, whereas metals are far more sensitive than explosives for example. Halving the soil layer thickness has been found to approximately double the surface water and sediment concentrations of lead, whereas surface water and sediment concentrations

of RDX were only slightly affected. It is suspected that higher soil adsorption partitioning results in greater surface water sensitivity to the soil layer thickness.

Surface water and sediment concentrations are affected by the benthic, surficial, sediment layer thickness in varying amounts. For highly partitioning constituents, such as metals, benthic sediment concentrations are highly affected by the surficial sediment layer thickness; but for low partitioning constituents, such as explosives, sediment concentrations are weakly sensitive to the thickness. Water column concentrations are very weakly to slightly sensitive to the benthic sediment layer thickness for all types of constituents. It is recommended that the active soil layer thickness be varied within Monte Carlo uncertainty analysis so that output bounds due to that input can be determined. A range of 0.1 to 0.5 m with a mean of 0.3 m is suggested for the active soil layer thickness. Likewise, the benthic, surficial layer thickness in the surface water models should be varied to evaluate the effects on computed benthic sediment concentrations, particularly for highly adsorptive constituents, such as metals (e.g., lead). Typically, the surficial, mixed sediment layer thickness should vary between about 0.1 and 0.2 m.

#### **5.4 Handling HE formations**

Many HE are formulations containing multiple constituents. For example the IM IMX-101 has three EC components: 2, 4-dinitroanisole (DNAN); 3-nitro-1, 2, 4-triazol-5-one (NTO); and nitroguanidine (NQ). TREECS™ was developed to allow modeling of multiple independent constituents within the same application; thus, modeling the fate of IMX-101 at a site entails modeling the fate of DNAN, NTO, and NQ, which are assumed not to interact with each other. The constituent concentrations are usually low enough to warrant treating each constituent independently.

The one process that warrants special consideration of the interaction of multiple constituents in the same application is dissolution of solid phase HE formulations. The presence of multiple constituents in the HE formulation with each constituent having a different solubility can affect the dissolution rate of each component. HE formulations are often molten-cast where one component is liquefied and then solidified to embed the other components in crystalline form. For IMX-101, DNAN is the molten-cast matrix within which the smaller crystals of NTO and NQ reside. Of these three EC, DNAN has the lowest solubility. Thus, the DNAN matrix

surrounding the crystals of much higher solubility can retard the dissolution rate of the crystals, and vice versa, as the high solubility crystals dissolve, the specific surface area of the DNAN matrix increases, which later accelerates the DNAN dissolution.

TREECS™ models each constituent independently. The TREECS™ dissolution model resides within the Tier 2 soil model. Dissolution of each modeled constituent requires inputs for each constituent's solid phase density, water solubility limit, and initial particle size of the solid phase residue (Dortch et al. 2011a and Dortch et al. 2013). These three inputs are straightforward for a single pure HE constituent. However, there are questions as to what to use for each constituent's inputs when HE formulations are involved. Model-computed dissolution flux (mass/time) also depends on the precipitation rate and the initial constituent mass in the AOI soil.

The dissolution model within the TREECS™ Tier 2 soil model is not elaborate enough to account for the complex interaction of multiple constituents that can affect the dissolution of a formulation. However, experience has shown that the dissolution model can provide reasonably accurate dissolutions rates of components within formulations if the proper adjustments are made to the model inputs. Such adjustments for cases involving the three formulations, Tritonal, Composition (Comp) B, and IMX-101, are discussed below.

#### **5.4.1 Tritonal**

Comparisons of model-computed results (using the TREECS™ dissolution model) with experimental results of Tritonal dissolution (Taylor et al. 2009) are presented by Dortch et al. (2011a). Tritonal is 80 percent trinitrotoluene (TNT) and 20 percent aluminum, where TNT has a water solubility limit of 71 mg/L based on an estimation presented by Taylor et al. (2009) using the rainfall weighted average temperature for the year of the outdoor experiments. Aluminum can be assumed to have zero water solubility.

The constituent TNT in Tritonal was modeled using the Tritonal formulation particle's initial mass, solid mass density, and size (diameter assuming a spherical particle) as described by Dortch et al. (2011a). Thus, the water solubility limit of TNT was the only input that was varied in the dissolution model. Assuming the Tritonal particle solubility is the same as that of TNT (i.e., using TNT solubility of 71 mg/L in the model input)

resulted in a model-computed cumulative dissolved TNT mass that was double the measured amount over the observation time period of one year. Thus, the zero solubility of aluminum appears to retard the TNT dissolution in the experiments conducted by Taylor et al. (2009). Another model run was made assuming that the solubility limit of TNT within Tritonal was less than TNT solubility and in proportion to the 80:20 mixture of TNT and aluminum with a zero solubility for aluminum. This assumption resulted in a model input solubility of 56.8 mg/L for TNT. The computed cumulative TNT mass dissolved after one year for the lower solubility was still too high, about 80 percent higher than measured.

The solubility limit of TNT within Tritonal had to be reduced to 35 mg/L for the model-computed cumulative TNT dissolved mass to match the amount measured. Thus, the model input solubility of TNT had to be set to about half the true solubility of TNT. Although the mass of aluminum in Tritonal is only 20 percent of the total mass of Tritonal, the insoluble aluminum flakes have a greater dissolution-retarding effect than expected based on the proportion of aluminum mass alone.

#### **5.4.2 Comp B**

The results of a laboratory dissolution study of Comp B by Lever et al. (2005) were also used to evaluate the TREECS™ dissolution model as reported by Dortch et al (2011a). Water was dropped on individual particles of Comp B recovered from low-order detonations, and the dissolved masses of the Comp B components RDX and TNT were measured in the laboratory experiments. The TREECS™ dissolution model was applied for the conditions of particle 1 as presented by Lever et al. (2005), which had an estimated initial Comp B mass of 1.821 mg with a RDX/TNT mass ratio of about 1.74 (average for multiple Comp B particles). This mass ratio of RDX/TNT is higher than unexploded Comp B, which is about 60 and 40 percent RDX and TNT, respectively, with a mass ratio of about 1.5. The solid phase density of the Comp B particles was 1.65 g/cm<sup>3</sup> (Lever et al. 2005)

Using the mass ratio of RDX/TNT in Comp B of 1.74, the computed solubility limit of the Comp B mixture is 76.9 mg/L based on the solubility values of 130 and 46 mg/L for TNT and RDX, respectively, as recommended by Lever et al. (2005). As with Tritonal, the solid phase mass, density, and particle size of the Comp B particle was used as input as described by Dortch et al. (2011a). Using the mixture solubility of 76.9 mg/L, the TREECS™ dissolution model predicted that 1.74 mg of Comp B would be

dissolved in the laboratory observation period of 68 days with 1.1 mg of RDX and 0.63 mg of TNT dissolved compared to the laboratory measured values of 1.1 mg of RDX and 0.63 mg of TNT dissolved in 68 days, indicating excellent agreement between model and measured. The model-computed RDX and TNT dissolved masses are simply the computed Comp B dissolved mass times the respective mass fractions of each component. During later testing, it was found that using as input the initial mass of each component (RDX and TNT) in the Comp B particle resulted in the same results as using the initial Comp B mass.

If the solubility of the individual constituents are used, then the dissolved mass of RDX is under-predicted, and the mass of TNT is over-predicted. Therefore, it is better to use the solubility of the Comp B mixture. It is noted that the individual constituents (e.g., TNT and RDX) are modeled within TREECS™, not the formulations (e.g., Comp B). Thus, it is important to discuss how to implement the above finding as can be found in the section on *Dissolution Model Implementation Recommendations* presented below.

#### **5.4.3 IMX-101**

Appendix B of the final report for this ESTCP project (Dortch et al. 2017) that supported this report contains an analysis of model-computed IMX-101 component dissolution compared with laboratory studies involving dissolution of IMX-101 (Dontsova et al. 2014). The NTO and NQ components are crystalline particles imbedded within a molten-cast DNAN matrix. Given the much higher solubility of NTO and NQ compared to DNAN as well as their small crystal size (yielding greater specific surface area), NTO and NQ are expected to dissolve much faster than DNAN. However, the NTO and NQ crystals are imbedded within a DNAN matrix that dissolves much slower, thus potentially delaying the exposure of crystals' surface area to water.

The modeling of IMX-101 components was handled differently than the modeling of Tritonal and Comp B components, where formulation rather than component solubility was used. Since there are two type of crystalline particles (NTO and NQ) embedded within a molten-cast DNAN matrix, it was more straightforward to use the individual component initial mass, solid phase particle densities, and water solubility limits as inputs, and evaluate the appropriate initial particle size input for each component.

In order to match the measured laboratory results for IMX-101 as reported by Dontsova et al. (2014), it was necessary to use particle sizes for NTO and NQ that were greater than their crystalline particle size imbedded with IMX-101. Similarly, it was necessary to use a particle size for DNAN that was smaller than the estimated size of the IMX-101 particle. The mass-weighted average particle size of representative constituent particles was found to produce reasonably accurate results as explained by Dortch et al. (2017). The rationale for using the mass-weighted particle size is that the slower dissolving DNAN matrix surrounds the crystalline NTO and NQ particles, thus limiting the crystal surface area exposed to water and slowing their dissolution rate, which is characteristic of a larger particle. However, after some of the fast-dissolving crystals are gone, the exposed DNAN surface area increases, which corresponds to a smaller particle for DNAN. Particle size affects the specific surface area and its adjustment is the easiest and most logical way to more accurately portray dissolution of the molten-cast IMX-101 formulation with the present model.

## 5.5 Dissolution model implementation recommendations

The munitions database within TREECS™ contains information on the amount of constituent mass within various munitions types. Thus, for a given munitions identifier, the database provides the amount of mass for each HE component, such as TNT, RDX, etc., but it does not provide the amount of mass of the formulation, such as Comp B, nor does it show whether a formulation exists in the munitions. One can possibly deduce whether a formulation is in the munitions by examining the constituent proportions, such as 60% RDX and 40% TNT for Comp B. The presence of HE formulations is a determinant for whether to adjust inputs affecting dissolution.

The state variables (primary unknowns being solved) in TREECS™ applications are constituent (such as RDX) concentrations in various media over time. There are no explicit inputs or outputs associated with HE formulations. As stated previously, the only place where formulation information might be used is within the Tier 2 soil model inputs that affect dissolution of solid phase mass. These inputs include initial solid phase mass in the AOI, solid phase mass density, water solubility limit, and initial solid phase average particle size that must be entered for each modeled constituent.

The constituent concentrations are computed from the constituent masses starting with the initial constituent mass (i.e., individual component mass for a formulation). It was possible to use formulation mass when applying the stand-alone dissolution model for a single particle, but it is presently not possible to use formulation mass in a TREECS™ application without a major overhaul of TREECS™. Additionally, the constituent initial mass in the AOI is set to zero in most applications since applications are often started at the beginning of range use.

This leaves solid phase mass density, initial average particle size, and solubility as the remaining inputs that can be manipulated to more accurately represent dissolution of a formulation. Constituent (component) solid phase mass density and solubility are well known, and these properties can be computed for a formulation based on the fractions of each component in the formulation. Thus, the formulation mass density and solubility could be used as input for each constituent within the Tier 2 soil model UI. Modeling of Tritonal and Comp B can be handled this way, where the mass density of the formulation is used as input for both TNT and RDX, and the solubility of the formulation Comp B is used as input for TNT and RDX solubility. About half the solubility of TNT should be used for Tritonal. Application results should be fairly insensitive to variation in inputs for mass density of HE components and formulations since the range of mass density values is relatively small. Thus, for convenience, the user can use the component density that is automatically pulled from the constituent database into the soil model input field.

Initial average particle size of HE residue must be entered for each constituent, and this is a highly uncertain input. There are *Help* screens within TREECS™ to assist the user in setting the input values for HE residue particle size. *Help* screen particle size information is based on measured data for low-order detonations for artillery and mortar rounds. In general, HE low-order residue particles are on the order of 1 cm (10,000 μm). Computed dissolution rates are fairly sensitive to initial particle size since it, along with mass density, are used to compute specific surface area, which is used to compute dissolution flux. As computed mass dissolves over time, the computed average particle size shrinks, which in turn feeds back into the next update over time for specific surface area and dissolution flux. The estimated HE residue particle size should be used as input for the initial average particle size of TNT and RDX in Tritonal and Comp B.

The following is recommended to model the formulation IMX-101 in TREECS™ applications. The residue initial particle size should be estimated first using the *Help* screen information. This size will be used to represent the DNAN particle size, which is the molten-cast matrix of IMX-101. The NTO and NQ crystals can be assumed to be much smaller (information on crystal sizes can be obtained from the Army). Given the three component particle sizes and the fractions of each component in IMX-101, the mass-weighted average particle size can be calculated and used for initial average particle size input for each of the three components. The solid phase mass density and solubility for each individual component should be used as input as well.

### 5.5.1 Examining fate of emerging constituents

One of the benefits of TREECS™ is that it can be used cost-effectively to examine the fate of emerging (munitions) constituents, or EC, such as DNAN, NTO, NQ, etc. An example of such use is documented by Dortch and Johnson (2017) for IMX-101. The key lessons learned from those TREECS™ applications for IMX-101 are listed below.

- The biggest obstacles for modeling the fate of EC at any specific site are obtaining accurate estimates for site-media-specific constituent sorption partitioning distribution coefficients,  $K_d$ , and constituent degradation rates (or  $HL$ ).
- Computed surface water and groundwater EC concentrations are far more sensitive to estimates of media degradation rates than media  $K_d$  values.
- EC concentrations at aquifer receptor wells are highly sensitive to EC degradation rates in vadose zone and aquifer.
- EC concentrations for surface water receptors are moderately sensitive to EC degradation rates in surface water.
- The importance of more accurately estimating EC degradation rate increases as media transit time increases, and media transit time increases as media  $K_d$  values increase.
- Research should be conducted to determine natural degradation rates of EC in surface soil, vadose zone (partially water-saturated groundwater), and water-saturated groundwater. Vadose zone and groundwater should receive higher priority than surface soil given the usually much longer transit times in vadose and groundwater.

## 6 Conclusions

The CTS can be rather quickly and easily applied to provide physicochemical properties that are needed for TREECS™ application. There are multiple sources of estimates for physicochemical properties in CTS for each constituent. However, application experience has shown that some of the property estimates can be inaccurate; thus, the user must use some discretion when selecting property values.

Application experience has shown that TREECS™ can be set up and applied relatively quickly using data that is readily available for the most part. Although data for development of inputs is usually readily available, analysis is often required to process some of the data for appropriate use in the model. Input data development is by far the most time consuming step in TREECS™ set up. Data input requirements, as well as sources for these data, are discussed in this report.

Most of the TREECS™ inputs can be fairly easily obtained or reasonably estimated. Inputs that have been found to be the most problematic to determine or estimate while also having a major effect on output results include: mass loading rates in the source zone (e.g., HE MC residue loading in impact areas) for past operations; natural degradation rates of organic constituents, particularly in soil, vadose, and groundwater; and constituent  $K_d$  values in various media, particularly organic constituents in soil, vadose zone, and groundwater and metals in surface water and benthic sediments. Estimates of past MC mass loading rates on firing ranges are hindered by the lack of information on past firing rates and items fired. Given such information, the MC residue mass loading module in TREECS™ can be used to provide useful values. There are tools in TREECS™ to help users estimate  $K_d$  values for organic and metal constituents in various media, and site-specific measurements or observed data can be used to make estimates of  $K_d$  values. Presently however, there is nothing available within TREECS™ to help users set degradation rates or  $HL$  for organic constituents due to the paucity of such information in general. Future research is needed to extend the knowledge base of constituent degradation rates in various media. These rates are specific to the chemical and media characteristics.

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**REPORT DOCUMENTATION PAGE**Form Approved  
OMB No. 0704-0188

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<b>1. REPORT DATE (DD-MM-YYYY)</b> June 2017		<b>2. REPORT TYPE</b> Final report		<b>3. DATES COVERED (From - To)</b>	
<b>4. TITLE AND SUBTITLE</b> User Guidance for Application of TREECS™ and CTS for Environmental Risk Assessment of Contaminants on Department of Defense (DoD) Ranges				<b>5a. CONTRACT NUMBER</b>	
				<b>5b. GRANT NUMBER</b>	
				<b>5c. PROGRAM ELEMENT NUMBER</b>	
<b>6. AUTHOR(S)</b> Mark S. Dortch, Eric J. Weber, and Billy E. Johnson				<b>5d. PROJECT NUMBER</b> ER-201435	
				<b>5e. TASK NUMBER</b>	
				<b>5f. WORK UNIT NUMBER</b>	
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> U.S. Army Engineer Research and Development Center, Environmental Laboratory, 3909 Halls Ferry Road, Vicksburg, MS 39180-6199				<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b> ERDC/EL TR-17-8	
<b>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b> Environmental Security Technology Certification Program (ESTCP) 4800 Mark Center Drive, Suite 17D08, Alexandria, VA 22350-3605				<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b> ESTCP	
				<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b>	
<b>12. DISTRIBUTION / AVAILABILITY STATEMENT</b> Approved for public release; unlimited distribution.					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> The Training Range Environmental Evaluation and Characterization System (TREECS™) was developed for the Army to forecast the fate of and risk from munitions constituents (MC), such as high explosives and metals, within and transported from firing/training ranges to surface water and groundwater. TREECS™ requires chemical-specific properties as part of the inputs. The Chemical Transformation Simulator (CTS) was developed by the U.S. Environmental Protection Agency to provide physicochemical properties of complex organic chemicals. CTS has capabilities for estimating chemical-specific properties in the absence of experimentally obtained properties; thus, CTS can help fill data gaps for properties, particularly for emerging MC that have limited experimental data. This report discusses the input requirements, sources of input data, and lessons learned from applying TREECS™ and CTS.					
<b>15. SUBJECT TERMS</b> Fate/transport modeling		Chemical-specific physicochemical properties		Application guidance	
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>	<b>18. NUMBER OF PAGES</b>	<b>19a. NAME OF RESPONSIBLE PERSON</b>
<b>a. REPORT</b> UNCLASSIFIED	<b>b. ABSTRACT</b> UNCLASSIFIED	<b>c. THIS PAGE</b> UNCLASSIFIED		60	<b>19b. TELEPHONE NUMBER (include area code)</b>