



US Army Corps
of Engineers®

ERDC TN-EQT-06-1

October 2006

CTT&F: Distributed Sources Chemical Transport, Transformation and Fate Submodel

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PURPOSE: The distributed watershed Chemical Transport, Transformation and Fate (CTT&F) Sub-model was developed and documented by the Environmental Laboratory of the U.S. Army Engineer Research and Development Center to characterize spatial and temporal dynamics of chemicals from both point and non-point sources. The sub-model simulates multi-chemical transport and transformation processes across watershed systems. CTT&F has a modular, process-oriented structure so that it can be easily modified, extended, or even provide a library of contaminant transport and transformation processes from which the user can select a sub-set of processes suitable for a particular application. This technical note describes the CTT&F sub-model and its capabilities. As shown by its applications to military training ranges, CTT&F may be used in conjunction with distributed hydrologic and sediment transport models to quantify contaminant transport processes and certain chemical reactions in watershed systems. It can be used to study the environmental impacts of explosive compounds from military installations on surface water and groundwater quality. CTT&F can also be applied to other contamination problems for environmental assessment of the behavior of contaminants entering in watershed systems such as accidental spills of toxic chemicals, acid mine drainage and metals from mining areas, application of pesticides on the land surface, and the deposition of solid compounds from the atmosphere to land surface.

BACKGROUND: Many U.S. Department of the Army and other Department of Defense (DoD) installations contain soil, sediment, surface water, and groundwater environments contaminated with explosives (Brannon and Myers 1997). Explosive compounds and heavy metals can and often do enter the environment when munitions are produced, disposed, or used. According to the Center for Public Environmental Oversight (2002), when a conventional high-explosive munition detonates, it potentially releases a variety of chemical compounds and metals into the environment. Low-order detonations (in which the munition does not explode completely) seem to produce greater amounts of explosives contamination than high-order (complete) detonations, which fully combust the explosive compound. Many explosives and their degradation products persist in the environment for long periods of time (at least decades). Even when munitions detonate as designed, heavy metals including lead, cadmium, chromium, nickel, copper, and barium remain and can contaminate soil and water. Once released into the environment, contaminants generally are subjected to a large number of simultaneous physical, chemical, and biological processes, and are transported across the land surface to locations beyond the original point of release (Figure 1). During the course of these movements, recharge to groundwater and delivery to streams can have adverse water quality and ecological impacts. Furthermore, growth of the chemical industry has been accompanied by increasing concern over the effects of synthetic chemicals on the environment. Exposure assessment and risk management of chemical-

Report Documentation Page

Form Approved
OMB No. 0704-0188

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1. REPORT DATE OCT 2006		2. REPORT TYPE N/A		3. DATES COVERED -	
4. TITLE AND SUBTITLE CTT&F: Distributed Sources Chemical Transport, Transformation and Fate Submodel				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Engineer Research and Development Center Vicksburg, MS 39180				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES The original document contains color images.					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 7	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

contaminated soil, sediment, surface water, and groundwater require knowledge of the fate and effects of chemicals and their transformation products in the environment. To date, quantitative information on dynamic chemical concentration and the rates at which these processes occur has been limited. To increase knowledge in this area, distributed sources chemical transport, transformation and fate models are required, given that no single model adequately represents the effects of these contaminants on the watershed system.

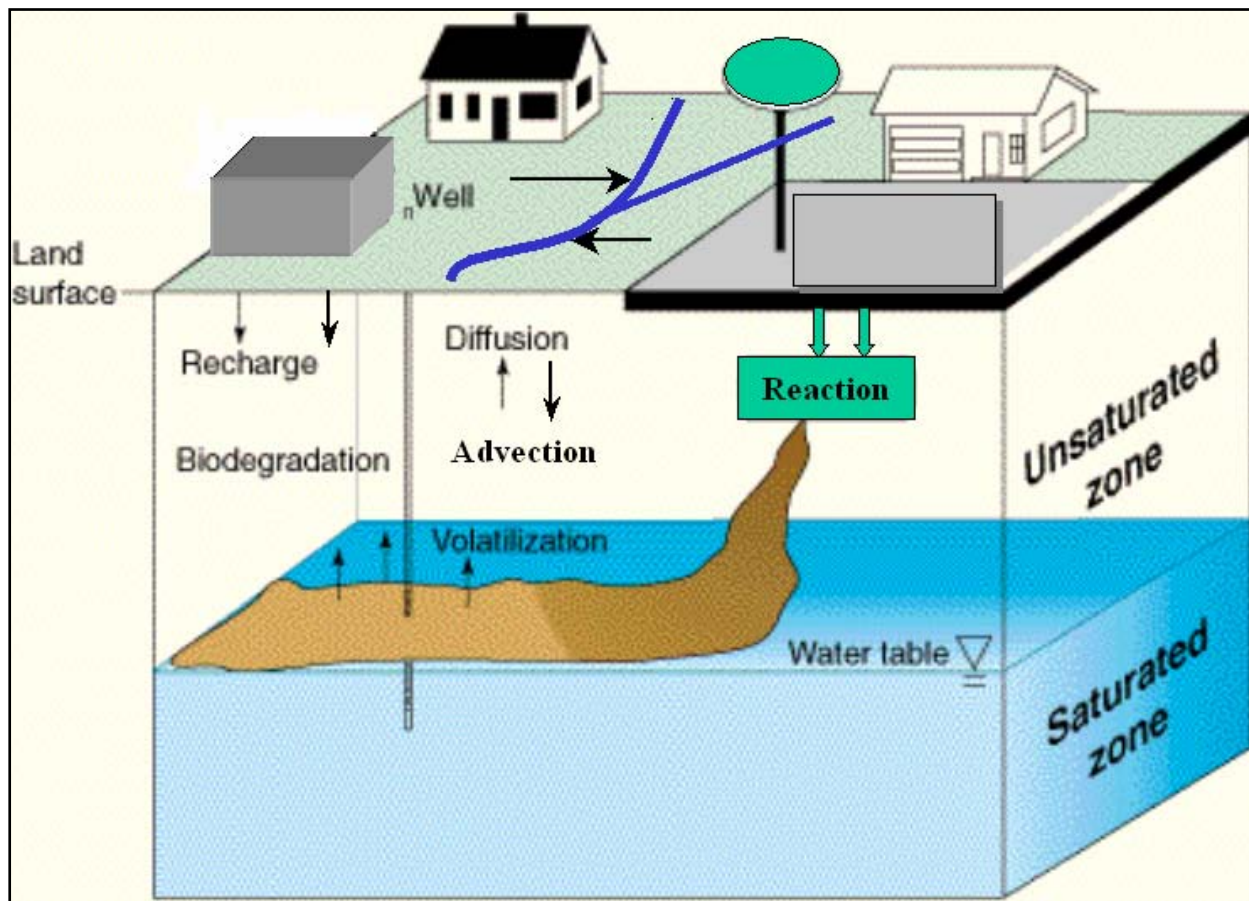


Figure 1. Conceptualization of the fate of chemicals in a watershed system.

CTT&F SUBMODEL DESCRIPTIONS

Model Functional Capabilities: CTT&F has been developed to link with a variety of physically based, spatially distributed watershed hydrologic models for characterizing chemical transport, transformation, and fate (Johnson and Zhang 2006). Initially, CTT&F will be linked with the Gridded Surface Subsurface Hydrologic Analysis (GSSHA) model. More details on the GSSHA model can be found in Downer and Ogden (2004). CTT&F's core is a set of process modules that link fundamental chemical properties to the hydrologic parameters that control the kinetics and transport in watershed systems. The sub-model relies on physical, rather than empirical, constructs for its core process descriptions wherever possible. Physical models are more robust predictors than are purely empirical models, which cannot safely be extended beyond the range of prior observations. CTT&F operates on a grid basis and allows analyses at any point within the watershed. Potential contaminants are routed through grids from the

watershed divide to the outlet. CTT&F coupling with distributed hydrologic and sediment transport models gives a quantitative basis in time and space for the fate of contaminants in the watershed including two-dimensional (2D) overland and one-dimensional (1D) channels. 1D transport and transformation of multi-chemicals in the unsaturated zone will also be provided through the linkage with GSSHA.

In CTT&F, the loadings, transport, and transformations of a contaminant are combined into differential equations by using the mass conservation law as an accounting principle. This law accounts for all contaminants entering and leaving a system as the algebraic sum of (1) external loadings, (2) transport processes exporting the contaminant out of the system, and (3) transformation processes within the system that degrade the contaminant. The fundamental equations of the sub-model describe the rate of change in chemical concentrations as a balance between increases due to loadings, and decreases due to the transport and transformation processes removing the chemical from the system.

CTT&F allows for the simultaneous treatment of multi-species of a chemical, each of which can occur in a dissolved (i.e., colloidal and filterable particulate) organic compounds (DOC)-complexed, sediment-sorbed, or separate solid form. The sub-model computes the fraction of the total concentration of a chemical. The sub-model thus completely accounts for differences in reactivity that depend on the form of the chemical, as a function of the spatial distribution of environmental parameters controlling chemical speciation. CTT&F allows for entry of external loadings of chemicals via point sources, non-point sources, dry fallout or aerial drift, and atmospheric wash-out. Any type of chemical load can be entered for any system sector, but the sub-model does not compute loadings. Loadings may be developed via projected or measured effluent fluxes, and distributed mass, by transfer from other source models, etc., but these computations must be executed externally to CTT&F.

CTT&F can be applied, however, to simulate transport of compounds in the aqueous phase associated with infiltration and surface runoff at the watershed scale. It can also be used to quantify transport of multi-chemicals and effects (rates) of a variety of biochemical processes of these chemicals in different media. By using the grid-based methodology, contaminant dynamics can be examined at any point within the watershed.

Model Framework: A chemical's fate with watersheds is governed by both hydrological and biochemical processes. Hydrologic processes include advection, diffusion or dispersion, infiltration, erosion (resuspension) and deposition. Biochemical processes determine the distribution of chemical mass among dissolved, bound, particulate, and solid phases and thereby affect the amount of mass available for hydrologic transport. Several biochemical processes can affect the transport and fate of chemicals in the watershed. Some chemicals undergo a complex set of reactions, while others behave in a more simplified manner. The sub-model developed allows for the simulation of a variety of processes that may affect chemicals. CTT&F is designed to provide a broad framework for the analysis of reactive contaminants within the context of hydrologic transport, which is applicable to many environmental problems and to allow the user to match the numerical complexity with the requirements of the problem. The chemicals may be independent or they may be linked with reaction yields, such as a parent compound-daughter product sequence.

When a chemical is released into a watershed, the entire array of transport and transformation processes begins at once to act on the chemical. The most efficient way to accommodate this parallel action of the processes is to combine them into a mathematical description of their total effect on the rate of change of chemical concentration in the system. Systems that include transport and transformation processes lead to partial differential equations, which must be solved by numerical methods, as in CTT&F, by using a finite-difference algorithm. The numerical techniques in one way or another break up the system, which is continuously varying in space and time, into a set of discrete elements. Spatial discrete elements in CTT&F are represented as “grids.” Continuous time is represented by fixing the system driving functions for a short interval, integrating over the interval, and then “updating” the forcing functions before evaluating the next time-step. At any given moment, the behavior of the chemical is a complicated function of both present and past inputs of the chemical and states of the system.

Solution of the CTT&F sub-model yields a general equation of the form:

$$C(x, y, t) = \left(\begin{array}{c} \text{Hydrologic} \\ \text{Transport} \end{array} \right) + \left(\begin{array}{c} \text{Chemical} \\ \text{Transformation} \end{array} \right) \quad (1)$$

where x, y is the location, t is time, and $C(x, y, t)$ is the chemical concentration at location x, y and time t .

This equation describes the spatial and temporal variation in chemical concentration as a function of several hydrologic and biochemical parameters. Given a description of hydrologic transport, the model may be used to investigate the underlying transformation processes. The hydrologic processes affect the transport of all waterborne chemicals. Biochemical reactions can be sources or sinks for each modeled chemical. The user can select either a first- or second-order kinetics model for these purposes. A single chemical can be rate-limiting or the reaction kinetics can be coupled; for example, the production rate of one chemical can be defined by the consumption rate of another. If the available kinetics models are not appropriate, users can substitute their own model directly into the model program. CTT&F is structured to permit easy substitution of transport and transformation subroutines into the overall package to form problem-specific modeling.

Model Key Transport and Transformation Processes: The processes that affect chemical transport and transformations in the watershed environment depend on the phase in which the chemicals are present and the environmental media. Processes considered for each phase are depicted in Figure 2, where the system is represented as two compartments: water column and sediment deposition. Key processes affecting chemical fate include: (1) chemical partitioning; (2) chemical transformation; (3) chemical transport through sediment and runoff; (4) chemical transport in stream channels; and (5) chemical transport in unsaturated soils. Not all processes affect chemical fate equally, each transport or transformation process accounts for only part of the total behavior of the contaminant. The relative importance of each process can be determined from the percentage of the total system loadings consumed by the process. The relative importance of the transformations indicate which process is dominant in the system, and thus in greatest need of accuracy and precision in its kinetic parameters. In principle, key processes can be

split up into the four areas in a watershed: surface runoff, transport in channels, transport in unsaturated soils, and transformation behavior of chemicals.

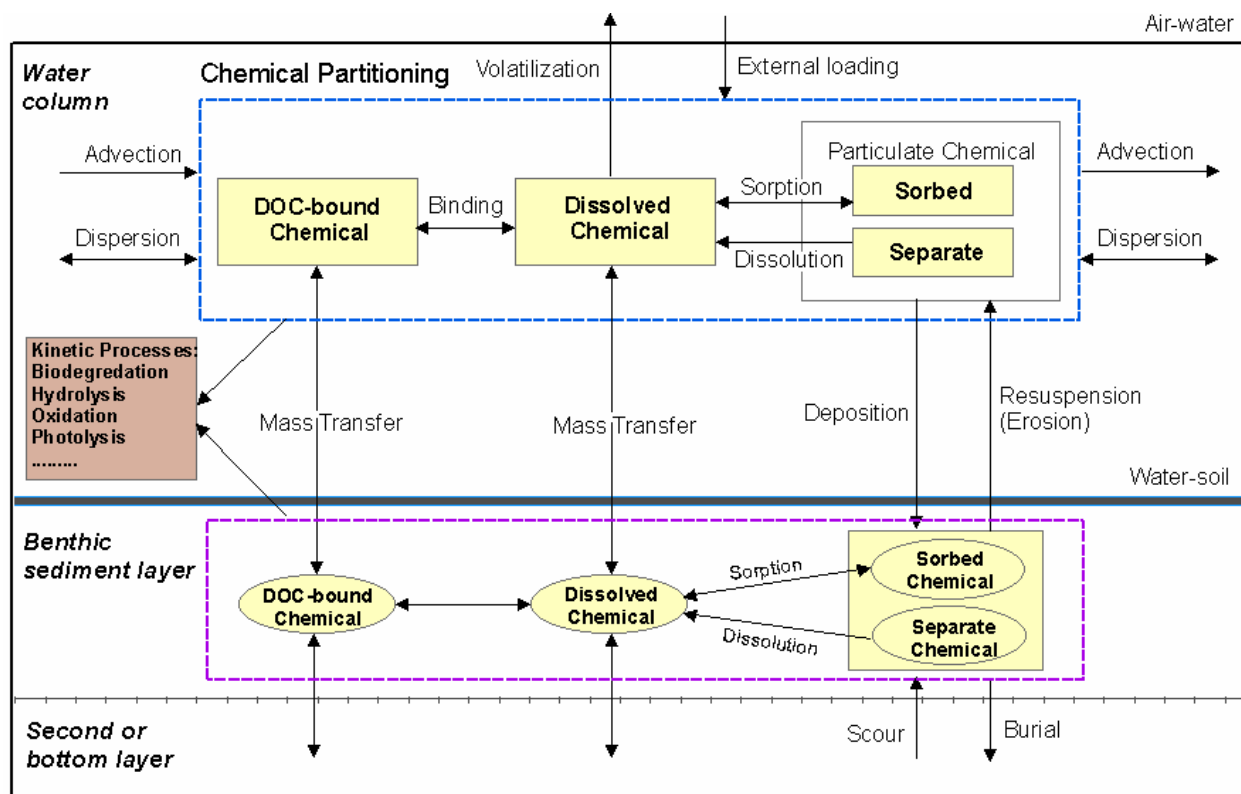


Figure 2. Chemical partitioning and key transport and transformation processes.

Equilibrium Partitioning Process: CTT&F accounts for equilibrium partitioning of mass among the particulate (sorbed) phase, the aqueous (dissolved) phase, and the DOC bound phase. The sub-model computes the distribution of the chemical among the three phases. The pure solid chemical is assumed to be a separate phase and is modeled as a reactive sediment particle. The equilibrium partitioning of chemicals between phases is described by the distribution coefficient, concentration and binding effectiveness of binding agents, and the concentration of particles or organic carbon. The equilibrium partition coefficient can be used to describe the fraction of the total chemical that is associated with each phase. In this fashion, the concentration of the chemical in the dissolved, bound, and particulate phases can be calculated from the total chemical concentration as follows:

$$C_d = f_d C_T, \quad C_b = f_b C_T, \quad C_p = \sum_{n=1}^N f_{pn} C_T \quad (2)$$

where C_d is dissolved phase concentration [M/L³], C_b is bound phase concentration [M/L³], C_p is particulate phase concentration [M/L³], C_T is total chemical concentration [M/L³], f_d is the fraction of the total chemical in the dissolved phase, f_b is the fraction of the total chemical in the bound phase, and f_{pn} is the fraction of the total chemical in the particulate phase associated with particle “ n .”

Governing equations for CTT&F are formulated in terms of chemical components. The total component concentration consists of dissolved, DOC bound, sediment sorbed, and solid phases.

Transformation Processes: Beyond partitioning and mass transport processes, the fate of chemicals is potentially influenced by a number of biochemical transformation processes that include, but are not limited to, biodegradation, hydrolysis, oxidation, photolysis, volatilization, and dissolution. These processes act to add or remove chemical mass. All processes may not be operative in all phases and environmental settings. For general simulation of elemental metals, volatilization, biodegradation, and photolysis do not occur. For RDX and other explosives, additional processes such as mineralization to CO₂ may also be important processes. Chemical transformation processes may be identified by analyzing field data that describe the spatial and (or) temporal distribution of contaminant concentration.

CTT&F computes the kinetics of domain chemical transformation processes. The input chemical data for the kinetics of transformations can be entered either as single-valued first or second-order rate constants, or as a pair of values defining the rate constant as a function of environmental temperatures. However, process descriptors for explosives are poorly developed because specific reaction mechanisms and their interrelations are poorly understood (McGrath 1995). CTT&F computes transformation of the chemical in the water column and in the bottom soils (sediments) of the watershed system as entirely separate functions. The following algorithms of transformation processes used in the sub-model were adapted, in part, from the WASP User's Guide (Ambrose et al. 1993) and IPX User's Guide (Velleux et al. 2001).

Biodegradation/decay of chemicals. Decay may be due to such processes as mineralization, detoxication, cometabolism, and microbial decay. CTT&F simulates biodegradation as a first-order decay process, which means that since the rate of loss of mass at any given time is directly proportional to the mass present at that time, the rate coefficients can be combined into a single decay coefficient.

$$\frac{\partial C_T}{dt} = k_{bio} C_T \quad (3)$$

where k_b is overall biodegradation rate [1/T].

Hydrolysis of chemicals. Hydrolysis, or reaction of the chemical with water, is known to be another pathway for degradation of chemicals. Hydrolysis is a reaction in which cleavage of a molecular bond of the chemical and formation of a new bond with either the hydrogen or the hydroxyl component of a water molecule occurs. Hydrolysis by specific acid, neutral, or base-catalyzed pathways is considered for the various species and phases of each chemical. The reactions are first order for the neutral chemical and second order for the acidic or basic forms of the chemical.

The total rate of hydrolysis transformation of a chemical is computed by CTT&F as the sum of three contributing processes.

$$k_{hyd} = \sum_j (k_{a_j} [H^+] + k_{n_j} + k_{b_j} [OH^-]) f_j \quad (4)$$

where k_{hyd} is the overall hydrolysis rate [1/T]; k_{aj} , k_{bj} are the specific acid catalyzed and base rate constants for the chemical in phase j, respectively [$L^3/M/T$]; k_{nj} is the neutral rate constant for the chemical in phase j [1/T]; and f_j is the fraction of the chemical in phase j.

Oxidation of chemicals. Oxidation in aquatic systems can be a consequence of interactions between free radicals and contaminants. Oxidation is modeled as a general second-order process for the various species and phases of each chemical. Oxidation reactions are computed from the chemical input data and the total environmental concentrations of reactive oxidizing species.

$$k_{oxi} = [RO_2] \sum_j k_{oj} f_j \quad (5)$$

where: k_{oxi} is the overall oxidation (or reduction) rate [1/T]; $[RO_2]$ is the molar concentration of oxidant [M/L^3]; and k_{oj} is the second-order oxidation rate constant for the chemical in phase j [$L^3/M/T$].

Photolysis (photodegradation) of chemicals. Photolysis is the transformation of a chemical due to absorption of light energy. The first-order rate coefficient for photolysis can be calculated from the absorption rate and the quantum yield for the chemical in each phase.

$$k_{phl} = \sum_j k_{aj} \phi_j f_j \quad (6)$$

where k_{phl} is the overall photolysis rate [1/T], k_{aj} is the specific sunlight absorption rate for the chemical in phase j [E/M/T], and ϕ_j is the reaction quantum yield for the chemical in phase j [M/E].

Dissolution of solid chemicals. Dissolution into water is a primary mechanism by which solid chemical contamination spreads. Once dissolved, the chemicals are available for other transport or transformation processes. The maximum aqueous concentration that the chemical can attain at a specific temperature if the water and solid phases remain in contact long enough is the solubility. Not only would inclusion of solid chemical aqueous dissolution rates improve modeling accuracy, but they have the potential of aiding the prediction of hazard persistence and assessment of remediation alternatives affected by the dissolution of solid chemicals. For explosive chemical compounds, dissolution rates have not been widely studied. In CTT&F, the first-order approximation of the dissolution process is used to describe the explosive dissolution rate (Cussler 1997):

$$\frac{\partial VC_c}{dt} = k_{dsl} \alpha [S - (f_d + f_b) C_T] \quad (7)$$

where k_{dsl} is the dissolution mass transfer coefficient [L/T], α is the area available for mass transfer between the solid and liquid [L^2], and S is the solubility of the chemical [M/L^3].

User-defined extra reaction of chemicals. An extra user-defined, second-order reaction for the various phases of each chemical is included. The second-order reaction allows the user to simulate the effect of processes not considered by the modeling system. The reaction depends

upon a rate constant and an environmental parameter which may be taken to represent, for example, some reducing or oxidizing agent.

$$k_{urd} = [E] \sum_j k_{ej} f_j \quad (8)$$

where k_{urd} is the net user-defined reaction rate constant [1/T], $[E]$ is the intensity of environmental property driving the reaction, and k_{ej} is the second-order rate constant for the chemical in phase j , $[E]^{-1}T^{-1}$.

Transformations and daughter products. The chemicals simulated by the model may be independent, or they may be linked with reaction yields, such as a parent compound-daughter product sequence. Linked transformations may be implemented by simulating two or three chemicals and by specifying appropriate yield coefficients for each process.

$$J_{kji} = \sum_j \sum_k k_{kj} C_j Y_{kji} \quad (9)$$

where J_{kji} is the production of chemical “i” from chemical “j” undergoing reaction “k” [M/L³/T]; K_{kj} is the effective rate coefficient for chemical “j” reaction “k” [1/T]; and Y_{kji} is the yield coefficients for production of chemical “i” from chemical “j” undergoing reaction “k” [M/M].

Transport Processes in Overland Flow: Several processes that govern the transport of chemicals in the overland plane are considered in the model, in which advection, dispersion, infiltration, erosion and deposition are the dominant hydrologic transport mechanisms (Figure 3). Consideration of these important mechanisms leads to the 2D advection-dispersion equation. Within the CTT&F sub-model, additional terms are added to the advection-dispersion equation to account for the effects of the upper soil layer and point source. The exchange of chemical mass between the overland flow and the upper soil layer is modeled as a first-order mass transfer process.

Advection of chemicals. Advective transport is the process by which chemicals are transported by flowing water at its mean velocity. Advective flow transports all chemical phases downstream with the water. The chemical advective flux is calculated based on the flow velocity.

Dispersion of chemicals. Dispersion causes mixing and dilution between regions of high concentrations and regions of low concentrations. Even in advectively dominated systems such as rivers, longitudinal dispersion can be the most important process in diluting peak concentrations. If there were no dispersion, all of the chemical would travel at the mean velocity. With dispersion, some chemical travels faster and some slower than the mean velocity; hence the chemical “spreads out.”

Infiltration of dissolved chemicals. Chemicals associated with the dissolved phase in the runoff will enter the upper soil if the water transporting those chemicals infiltrates. To account for this process, the chemical infiltration flux can be computed from the water infiltration.

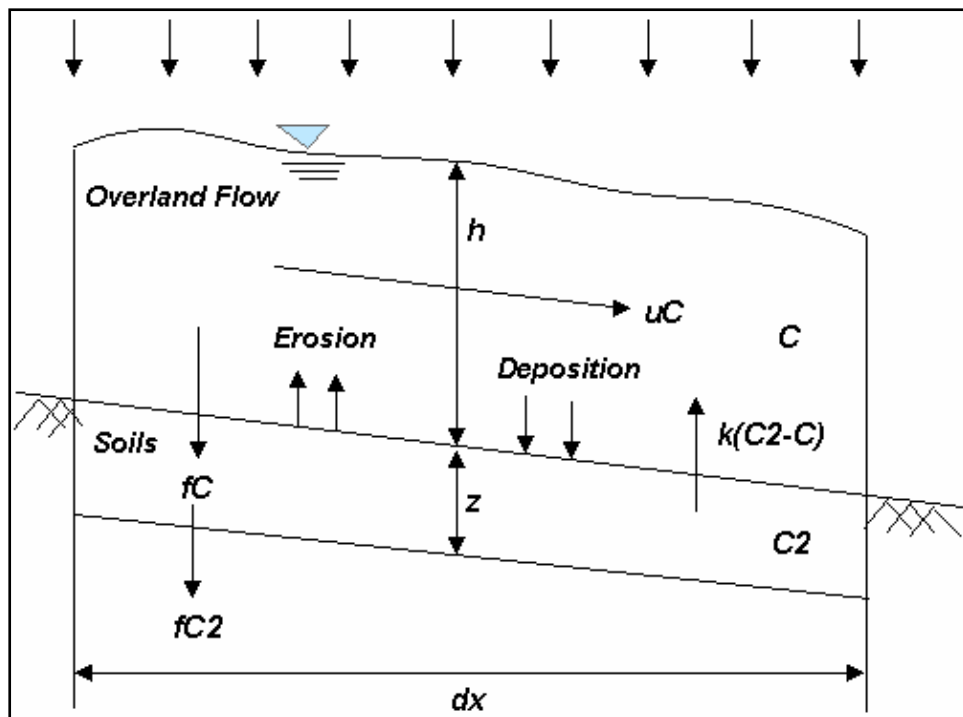


Figure 3. Conceptual transport processes in overland flow and upper soil layer.

Transfer of dissolved chemicals from soil. Surface-applied or soil-incorporated chemicals are often transferred in significant quantities from soil to surface runoff as a result of the rainfall-runoff process. Several dynamic, inter-related processes control chemical transport from soil to runoff during rainfall including ejection of soil water by raindrop impacts, diffusion of chemicals from soil water, infiltration, and soil water-runoff mixing (Zhang et al. 1997, Gao et al. 2004). From early experiments and calculations it has been concluded that only a certain thin soil layer interacts with the rainfall and overland flow. Gao et al. (2004) developed a model that combined the chemical transfer associated with the raindrop impacts and associated with diffusion by assuming raindrop and diffusion processes could be coupled by superposition. This model captured soil-runoff chemical transfer behavior more realistically than either mixing-layer models or diffusion-based models. Thus the formulation used by Gao et al. (2004) will be implemented within the CTT&F sub-model.

Erosion of particulate chemicals. Chemicals sorbed on particles in the sediment bed are subsequently entrained into the water column as these particles are eroded (resuspended) by the moving water. Surface erosion rates by overland flow may be estimated from site-specific erosion rate studies or, in general, from the difference between sediment transport capacity and advective fluxes.

Deposition of particulate chemicals. If the sediment transport capacity is lower than the sediment load, sediment deposition occurs. Chemicals associated with particles in the runoff will enter the upper soil layer if those particles settle. The deposition process is influenced by many factors including particle density, diameter, shape, and fluid turbulence.

Transport Processes in Channels: Internal transport of a chemical occurs in the channel via advective and dispersive movement of dissolved, sediment-sorbed, and solid materials, exchanges between bed sediments and overlying waters, and by transmission losses (Figure 5). Advection, the downstream transport of solute mass at a mean velocity, and dispersion, the spreading of solute mass due to shear stress and molecular diffusion, are considered in most mechanistic models of stream-water quality and solute transport. Consideration of these important mechanisms leads to the familiar 1D advection-dispersion equation. Within the CTT&F sub-model, additional terms are added to the advection-dispersion equation to account for the effects of bed sediments and lateral inflow.

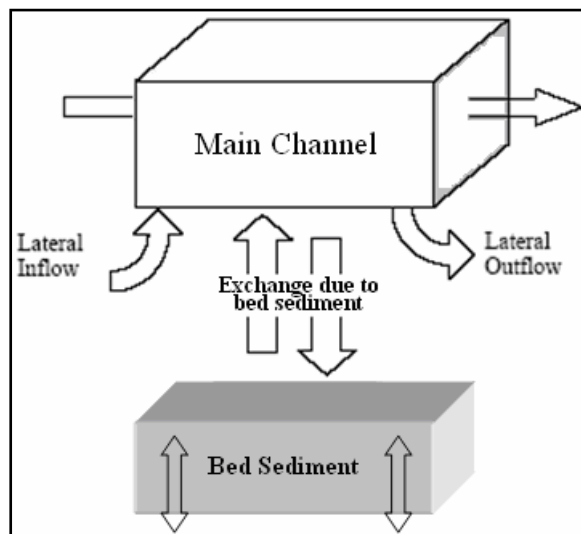


Figure 5. Conceptual transport processes in channels.

The bed sediment plays an important role in the transport of chemicals. Within the bed, dissolved chemicals migrate downward or upward through percolation and pore water diffusion. Sediment-sorbed chemicals may be buried in the bed by deposition and sedimentation, or they may be released to the water column by scour. Lateral inflow is any water that is added to the stream due to overland flow, groundwater inflow, or small springs. These flows act to dilute (or concentrate) solutes in the stream channel if they carry solute concentrations that are lower (or higher) than the stream-solute concentration. Two conceptual areas are defined within the model: the main channel and the bed sediment. Within the bed sediment, the processes include mass transfer across the sediment-water interface, resuspension to the water column, settling of suspended particles from the water column, and burial to lower sediment layers. The exchange of solute mass between the main channel and the bed sediment is modeled as a first-order mass transfer process.

Model Inputs and Outputs

Hydrologic and Sediment Inputs: To simulate the chemical transport in watersheds, it is necessary to estimate beforehand the flow and the suspended sediment transport flux driven by the hydrologic processes and sediment processes governing surface erosion and water and sediment transport. The following minimum data are required to run general distributed watershed hydrologic models:

- Topography (DEM).
- Soil distribution and properties.
- Land use/cover and properties.
- Channel properties.
- Meteorological data including rainfall.
- Watershed characteristics, initial and boundary conditions.

CTT&F Inputs: The CTT&F sub-model input consists of a series of raster GIS layers and chemical parameters, including:

- A set of chemical loadings on each sector of the watershed. The initial condition of each chemical can be specified as a constant concentration throughout the model domain or defined spatially with an input file.
- Molecular weight, partitioning coefficient, and solubility of the chemical.
- Sediment sorption and soil sorption parameters, biomasses, benthic water contents and bulk densities, organic carbon, and ion exchange capacities.
- Parameters defining strength and direction of advective and dispersive transport pathways.
- Biochemical degradation: rate constants or half-life and bacterial population densities.
- Volatilization: Henry's Law constant or vapor pressure data, wind speeds, and reaeration rates.
- Photolysis: reaction quantum yields, absorption spectra, stratospheric ozone, cloudiness, relative humidity, atmospheric dust content and air-mass type, scattering parameters, suspended sediments, chlorophyll, and dissolved organic carbon.
- Hydrolysis: second-order rate constants or Arrhenius functions for the relevant molecular species, pH, and pOH.
- Oxidation: rate constants, surface oxidant concentrations, dissolved organic carbon, and oxygen tension.

Although the potential amount and variety of data used by CTT&F is large and the model allows for the entry of extensive environmental data, data requirements for any particular simulation can be quite small. Thus the model can be executed with a much smaller data set. For example, it is possible to simulate a chemical using no reactions, or using only sorption and one or two transformation reactions that significantly affect a particular chemical. CTT&F allows the user to specify reaction rates for the transformation processes of each of the chemicals simulated.

Hydrologic and Sediment Outputs: Distributed watershed hydrologic models produce the following outputs:

- Tabular outputs of flow and sediment concentration at specified points (grids) over time.
- Spatial distribution of infiltration, water depth, and flow discharge at various times.
- Spatial distribution of sediment concentration and flux at various times.

CTT&F Outputs: Each time CTT&F is executed, the model produces an echo file that echoes the input data to allow the user to verify the accuracy of the specified parameters, flags, and options, plus optional output files as requested by the user. These include spatial distribution of

multiphase concentrations of the chemical or chemicals under study and time-based concentrations and fluxes exported at watershed outlets. The model generates a summary report of a variety of process results that contain the mass balance information obtained.

CTT&F SUBMODEL APPLICATION: Given data from field studies, CTT&F can be used to assess the fate of explosive compounds in watershed systems. High explosives can enter the environment from sites where they are manufactured, stored, disposed, or used in military training. Besides causing possible physical injury and property damage by detonation, several high explosive compounds have been found to have detrimental health effects as well. Human exposure can occur by drinking contaminated water, breathing contaminated air, or coming in contact with contaminated soil. Health effects associated with exposure to high explosive compounds vary by explosive type. TNT (2,4,6-trinitrotoluene) has been associated with liver and blood damage, anorexia, and anemia. RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) has been associated with systemic poisoning, usually affecting bone marrow and the liver. Both TNT and RDX have been classified as possible human carcinogens. Risk assessments should adequately link a contaminant source, transmission pathways, and exposure potential. The objective of this application was to illustrate the use of CTT&F to quantify transport, transformation, and fate of contaminants in watersheds. Of interest are the explosive compounds RDX and TNT used by the military and their resulting presence in the environment.

Experiment Setup: In order to verify the general performance of the model, an experiment was conducted which simulated rainfall and overland flow in a laboratory. The discharge, sediment and contaminant were measured and related to the hydraulic and transport conditions. The experiment plot was 9.0 ft × 7.5 ft. The bed slope of the plot was 2 percent. Two land covers were used for the experiments to simulate two different surface roughnesses. Uniform rainfall was simulated. The simulator was supplied with tap water through a rotameter so that the total discharge was measured and kept constant. During the experiment, precipitation intensity was kept constant at 2.8 in./hr; the rainfall event lasted 30 ± 60 min. Runoff and sediment data were collected at the downstream end of the plot and measured volumetrically. The RDX and TNT were simulated by spreading explosive composition B (Comp B) over the surface. Comp B is a 60/39 mixture of RDX and TNT that contains 1 percent wax (Lever et al. 2005). It has been used in munitions since World War II for its high explosive yield. The RDX and TNT concentrations in the runoff were measured by collecting 4-L samples at the measuring points.

The experiment plot domain consisted of 30 grids (the size of the grids was 1.5 ft), and the Manning roughness coefficient was set to 0.015 for an unvegetated surface. The time interval for the simulation was 0.5 sec, with the following values (Table 1) for the relevant parameters being adopted (Lever et al. 2005), and an initial Comp B density of 500 g. Previous research has identified variables and their plausible ranges of values in describing explosive Comp B dissolution rates. This study gives the result in predicted solid persistence and flux loading from this solid into solution for TNT and RDX.

Table 1			
Model parameters for RDX and TNT in water at 25°C			
Parameter	Comp B	RDX	TNT
S (g/cm ³)		4.6×10^{-5}	1.3×10^{-4}
D (cm ² /s)		2.2×10^{-6}	6.7×10^{-6}
ρ (g/cm ³)	1.65		
S = solubility D = diffusion coefficient ρ = density			

Results: Numerical results were obtained from running the CTT&F sub-model. In this experiment, overland flow caused erosion and dissolution of the solid Comp B, a fraction of which infiltrated into the soil while the remainder was transported downstream. Even though distributed observations for RDX and TNT concentrations were not measured in this study, the sources of RDX and TNT transport and transformation can be inferred using the model. As expected, the onset of rainfall results in dissolution of the solid explosive, with infiltration and washoff resulting in removal of the solid within a short period of time. The graphical representation of the spatial variation of dissolved chemical concentration as a function of time also confirms the generally expected behavior that with increasing time, the peak concentration decreases as it migrates downstream. During this movement, infiltration also occurs so that contamination of the surrounding subsurface area occurs. Obviously, some modifications to these results are to be expected when other transformation effects are incorporated into the model. The model results also provide quantitative information on the amount of contaminant infiltrating into the subsurface. These are important in investigating the loss of explosives due to the transport and transformation of distributed sources.

Figures 6 to 9 compare simulated and measured results over time for surface runoff discharge, total suspended sediment concentration, dissolved RDX, and TNT concentrations. Given the complexity of the process, there is some deviation between simulated and measured results.

Accurate modeling of explosive compound transport and transformation in the field environment depends on mathematically replicating natural processes. The model is complicated by the need to select the correct transformation process description and then select the correct coefficient for each variable supporting the model. Chemical fate and transport at sites contaminated with multiple explosive compounds from more than one type of explosive formulation will be challenging to simulate with a model. Each specific explosive formulation is expected to dissolve differently depending on composition and manufacturing process. Although not investigated in this study, the behavior, transport and ultimate fate of distributed Comp B in watersheds may be affected by their diffusion, hydrolysis, other reactions, and related phenomena. These effects are currently being incorporated into the model. There is also a need for more careful laboratory experimentation to further verify the model.

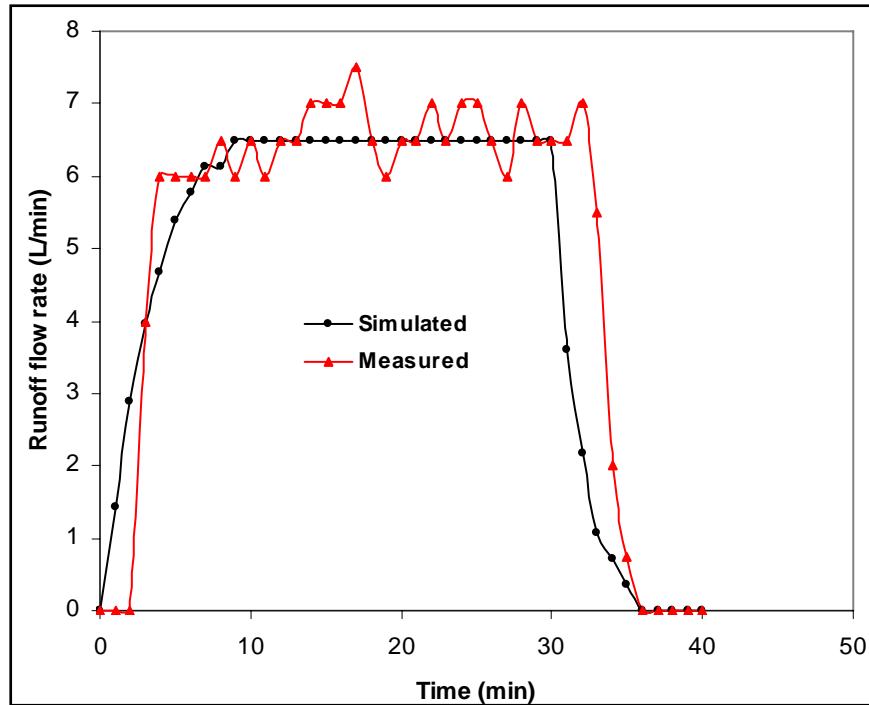


Figure 6. Comparison of simulated and experiment results over time for surface runoff discharge from the unvegetated land.

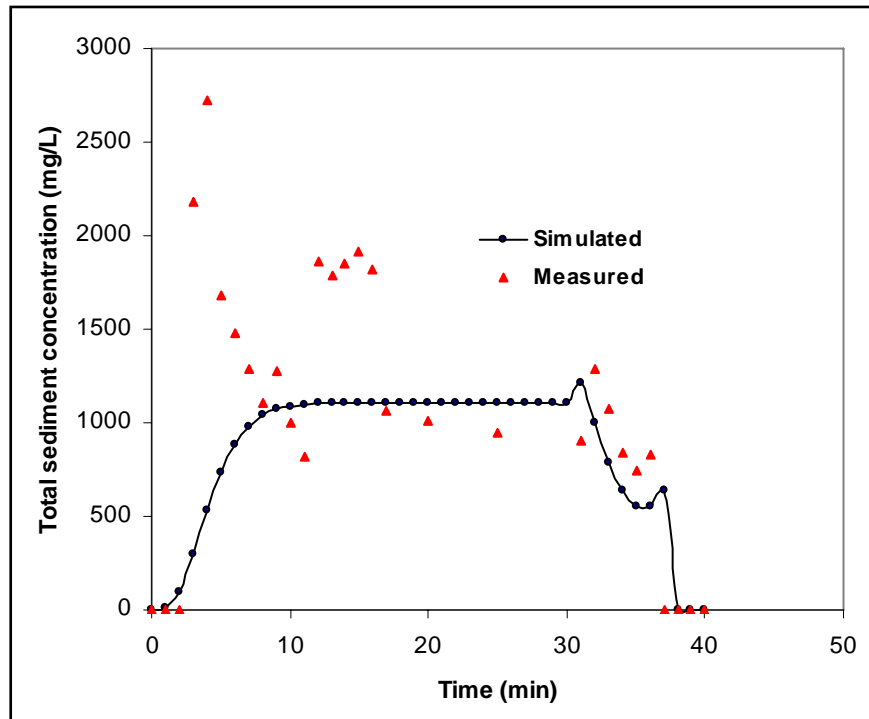


Figure 7. Comparison of simulated and experiment results over time for total suspended sediment concentration from the unvegetated land.

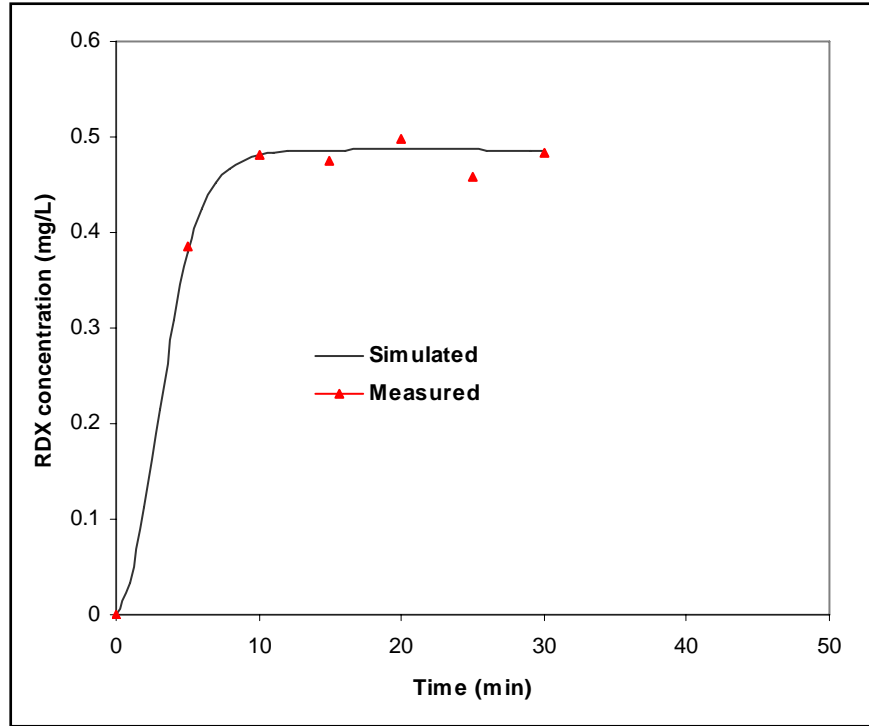


Figure 8. Comparison of simulated and experiment results over time for dissolved RDX concentration from the unvegetated land.

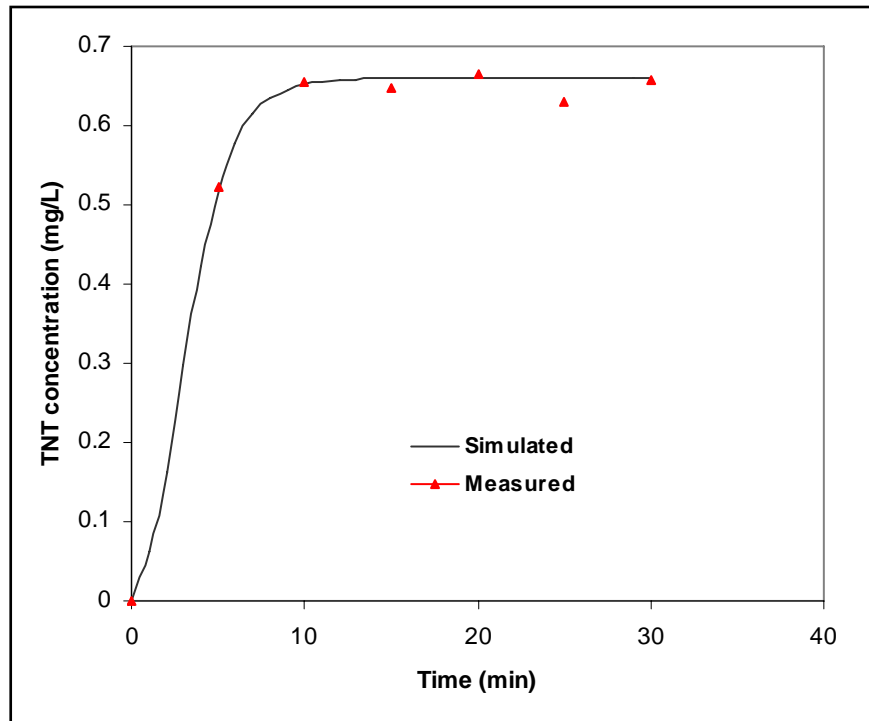


Figure 9. Comparison of simulated and experiment results over time for dissolved TNT concentration from the unvegetated land.

CONCLUSIONS: A contaminant transport, transformation and fate sub-model, CTT&F, has been developed for simulating distributed sources from military installations. The CTT&F equations that were developed are comprehensive, self consistent, and fully compatible with the physically based, distributed watershed hydrologic models, which provide the required hydrological and sediment variables. With a watershed, CTT&F is able to simulate both surface runoff and channel processes of contaminants. CTT&F generates time-series outputs of model state variables at specified points in space over time. The sub-model also provides the temporal variation and spatial distribution of contaminant sources in different phases. CTT&F was validated using an experiment plot in a laboratory. The hydrologic, sediment and contaminant variables of the model have been calibrated using the overland outlet data.

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POINTS OF CONTACT: The CTT&F sub-model is written in a modular/process structure that facilitates modifications to the source code and can run on a variety of computer platforms, including Unix and personal computers. Documentation of CTT&F theory is available as an ERDC-EL Technical Report (Johnson and Zhang, in preparation). For additional information, contact: Dr. Billy E. Johnson (601-634-3714, Billy.E.Johnson@erdc.usace.army.mil) or Dr. Zhonglong Zhang (601-634-3337, Zhonglong.Zhang@erdc.usace.army.mil), Environmental Laboratory, U.S. Army Engineer Research and Development Center, 3909 Halls Ferry Road, Vicksburg, MS 39180. This technical note should be cited as follows:

Johnson, B. E., and Z. Zhang. 2006. "CTT&F: Distributed sources chemical transport, transformation and fate sub-model." ERDC TN-EQT-06-1, Vicksburg, MS: U.S. Army Engineer Research and Development Center.

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