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Development of a Distributed Source Contaminant Transport, Transformation, and Fate (CTT&F) Sub-Model for Military Installations

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Abstract: One of the responsibilities of the U.S. military is to operate munitions test and live-fire training ranges. As a result of this testing and training, many explosives and their degradation products persist in the environment. Ecosystem management by military installations can be met only by providing the tools necessary to actively manage watersheds. Water quality and related aquatic ecosystems are major end-points and are insufficiently understood components of natural resource management.

Numerical modeling, as part of watershed management, is not new. Considerable advances have been made in physically based distributed watershed hydrologic modeling in the past few years; however, few physically based, distributed models simulate contaminant transformation and transport processes. This report summarizes the development of overland and channel contaminant fate and transport modules for linkage with a variety of hydraulic and hydrologic modeling systems.

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Preface

This report summarizes the development of overland and channel contaminant fate and transport modules for linkage with a variety of hydraulic and hydrologic modeling systems. This development effort was performed by the Engineer Research and Development Center (ERDC), Vicksburg, MS. Funding was provided under the Environmental Quality Technologies (EQT) Research Program. Appreciation is extended to all those who assisted in the formulations and review of the process descriptions implemented within the contaminant transport, transformation, and fate (CTT&F) sub-model.

Principal Investigators for this study were Dr. Billy E. Johnson of the Water Quality and Contaminant Modeling Branch (WQCMB), Environmental Laboratory (EL), and Dr. Zhonglong Zhang of SpecPro Inc., Huntsville, AL. Dr. Zhang was funded as an onsite contractor under Task Order Contract W912HZ-05-D-0011 on Military Delivery Order No. 1. Dr. Johnson conducted his portion of the study under the general supervision of Dr. Barry W. Bunch, Chief, WQCMB, and under the general supervision of Dr. Richard E. Price, Chief, Environmental Processes and Engineering Division, EL, and Dr. Beth C. Fleming, Director, EL.

COL Richard B. Jenkins was Commander and Executive Director of ERDC. Dr. James R. Houston was Director.

1 Introduction

Background

One of the responsibilities of the U.S. military is to operate munitions test and live-fire training ranges. Munitions fired, dropped, and disposed of on those ranges pose a dual threat: First and most immediate, literally millions of bombs, shells, rockets, grenades, and other items lying on the surface, resting underwater, or buried beneath soil may explode if disturbed. Second and perhaps equally significant in the long run, the explosives and energetics constituents and explosive byproducts of those munitions pose a potentially toxic threat to public health and natural ecosystems as they move through the environment. Many military installations contain soil, sediment, surface water, and groundwater environments contaminated with explosives (Brannon and Myers 1997). Besides the Department of Defense (DoD), the Department of Energy (DoE) also has lands that are contaminated with explosive compounds. Low-order detonations (in which the munition does not explode completely) produce greater amounts of explosives contamination than high-order (complete) detonations, which fully combust the explosives compound.

Many explosives and their degradation products persist in the environment for a long time. Even when munitions detonate as designed, heavy metals including lead, cadmium, chromium, nickel, copper, and barium remain and can contaminate soil and water. The potentially widespread areal nature of resulting contamination makes remedial actions difficult. Compliance with environmental regulations is becoming increasingly important at military installations. Ecosystem management to provide for sustained and future sustainable mission capacity is an important consideration for military installations. The ecosystem management expectation can be met only by providing the tools necessary to actively manage watersheds. Water quality and related aquatic ecosystems are major endpoints and are insufficiently understood components of natural resource management, particularly for military installations (SERDP 2005).

Numerical modeling, as part of watershed management, to meet water quality goals is not new. Numerous models have been developed that attempt to simulate contaminant transport characteristics and predict the fate of contaminants with research continuing in earnest (e.g., Akan 1987;

Wallach and Van Genuchten 1990; Havis et al. 1992; Bouraoui and Dillaha 1996; Ramireddygari et al. 1996; Hjelmfelt and Wang 1999; Singh 2002; Yan and Kahawita 2000; Garcia-Navarro et al. 2000; Kivva 2000; Birkinshaw and Ewen 2000; Wallach et al. 2001; Bingner 2002; Yeh et al. 2003). These models have implemented a variety of numerical solution techniques. Most of these models are based on finite difference schemes where the models are focused on nutrients, pesticides, and other conservative contaminants. One exception is Yeh et al. (2003), who used a Eulerian-Lagrangian finite element method. The major areas of current application of distributed watershed models are in predicting the effects of complex land use change, the effects of spatially variable inputs and outputs, the movement of sediments and contaminants, and hydrologic response of ungauged catchments (Beven 1985).

Considerable advances have been made in physically based distributed watershed hydrologic modeling in the past few years; however, few physically based, distributed models simulate contaminant transformation and transport processes. Most current watershed models were developed and tested decades ago. Models that reflect hydrologic and aquatic impacts from military conditions are rare. Watershed models that enable diagnostic, predictive, and operational applications in conjunction with monitoring and data collection programs are virtually non-existent across the board and are urgently needed within the scientific and modeling communities (SERDP 2005). To date little effort has been devoted to consideration of explosive compounds and the multi-phase partitioning specification of the contaminant in watershed modeling. Given the complex nature of a watershed system, as well as the spatial nature of contaminant distribution, the inadequacies of existing models in addressing various contaminant processes in the context of the watershed environment motivated the development of a comprehensive distributed-source contaminant model to accurately account for the transport and transformation of contaminants through the various landscape media where lumped parameter models are not applicable.

Approach

To meet the need described above, a physically based, distributed-source Contaminant Transport, Transformation, and Fate (CTT&F) sub-model was developed to simulate both point and nonpoint sources across a watershed. The sub-model operates on a grid basis where the grid cells are uniformly square areas subdividing the watersheds, allowing analyses at

any point within the watershed. Potential contaminants are routed through grids from the watershed divide to the outlet. The distributed, process-oriented structure of CTT&F enables the sub-model to be used for identifying critical source areas of contaminants. The CTT&F sub-model can be linked to any physically-based distributed watershed model (e.g., CASC2D and GSSHA). The hydrologic model must provide the required hydrological and sediment variables in order to provide the driving forces for the CTT&F sub-model. Although designed explicitly for explosive contaminants, the CTT&F formulations are described in a physical way such that other contaminants of concern, including heavy metals, can be handled by the sub-model. The aim of the sub-model is to fully address the transport and transformation of distributed sources and facilitate the exposure assessment and risk management of explosives-contaminated soil in the watershed environment. The expectation is that a sub-model of this type can be implemented for military installation compliance as well as long-term watershed planning and management.

This report provides a technical description of the CTT&F sub-model for simulating contaminant transport and transformation in the overland regime and channel networks within a watershed. The key transport and transformation processes taken into account in CTT&F modeling framework are discussed, and the governing equations solved by the sub-model are stated in detail. A brief overview is given of the sub-model computational structure and numerical solution. The report also includes an example of a CTT&F validation application.

2 Hydrologic and Sediment Transport Descriptions

To simulate the contaminant transport processes in watersheds, it is necessary to estimate beforehand the watershed flow and sediment transport driven by the hydrological processes. The hydrologic variables required to drive CTT&F can be calculated using any physically based distributed watershed model capable of producing a reasonable simulation of the watershed flow and sediment transport fields. These include (1) for surface transport: overland flow depth, flow in the coordinate directions, sediment load, and sediment concentration and (2) for subsurface transport: soil moisture and hydraulic head at various depths in the soil. The major components of the fully distributed watershed model framework are hydrology, sediment transport, and contaminant transport. Each of the major components can be viewed as sub-models within the overall framework as presented in the SHETRAN model (Ewen et al. 2000). The calculations for each process at any time level are independent, and information is carried forward from hydrology to sediment transport to contaminant transport in order to generate a solution. At any time level, flow is assumed to be unaffected by sediment and contaminant transport, and sediment transport is unaffected by contaminant transport, so calculations for these three components (sub-models) have a natural hierarchy (Figure 1).

Several distributed watershed models simulate hydrologic and sediment transport processes. The U.S. Army Corps of Engineer's GSSHA (Gridded Surface Subsurface Hydrologic Analysis) is a physically based, distributed-parameter, structured grid, hydrologic model that simulates the hydrologic response and sediment transport of a watershed subject to given hydro-meteorological inputs. The model incorporates two dimensional (2D) overland flow, one dimensional (1D) stream flow, 1D unsaturated flow, and 2D groundwater flow components. The watershed is divided into grid cells in a uniform finite difference grid. GSSHA is a reformulation and enhancement of the 2D model CASC2D (Figure 2). The GSSHA model employs mass conservation solutions of partial differential equations and closely links the hydrologic components to assure an overall mass balance.

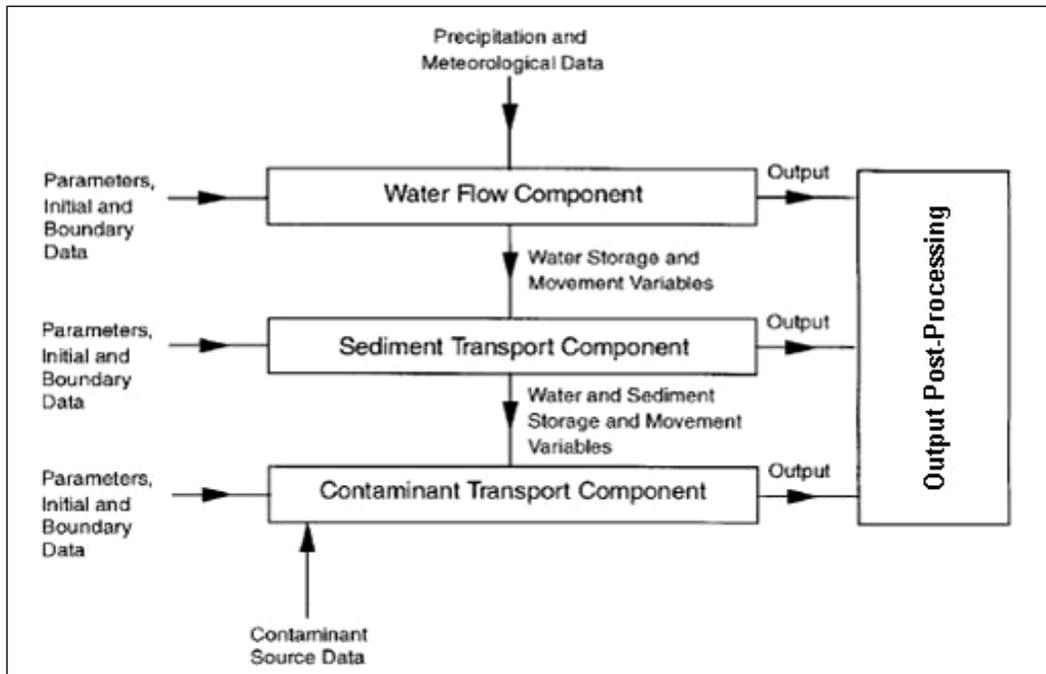


Figure 1. Watershed model hierarchy and information flows.

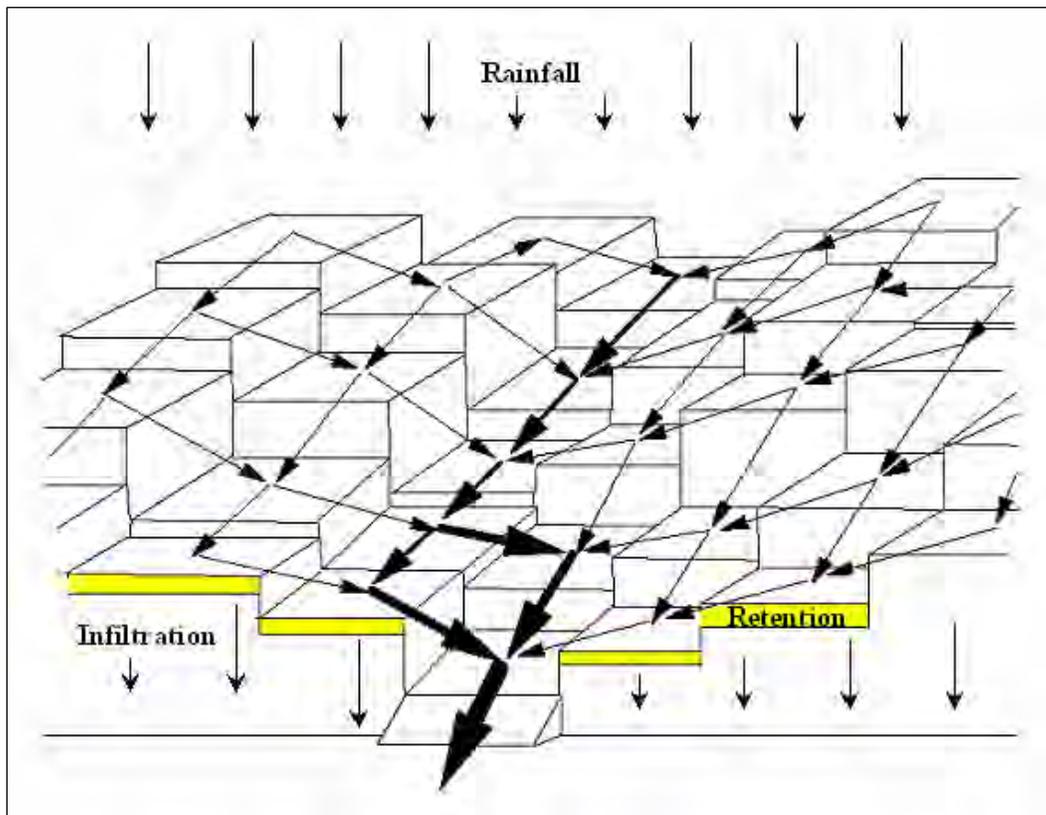


Figure 2. Topographical representation of overland flow and channel routing schemes within a watershed.

A brief introduction includes a review of hydrologic and sediment transport process descriptions that is informative to illustrate the physics behind individual process representations and specific to those needed to drive a full contaminant transport, transformation, and fate sub-model.

Hydrologic processes

The hydrologic processes simulated and the approximations used in GSSHA are listed as follows (Downer and Ogden 2004):

- Precipitation distribution: Thiessen polygon method, inverse distance square method
- Snowfall accumulation and melting: Energy balance
- Precipitation interception: Two parameter
- Overland water retention: Specified depth
- Infiltration: GA (Green and Ampt), multilayered GA, GAR (Green and Ampt with Redistribution), RE (Richards Equation)
- Overland flow routing: 2D diffusive wave equation
- Channel routing: 1D diffusive wave equation
- Evapotranspiration: Deardorff, Penman-Montheith with seasonal canopy resistance
- Soil moisture in the vadose zone: Bucket, RE
- Lateral groundwater flow: 2D vertically averaged equation
- Stream/groundwater interaction: Darcy's law
- Exfiltration: Darcy's law.

GSSHA uses two-step, finite-volume schemes to route water for both 2D overland flow and 1D channel flow, where flows are computed based on heads and volumes are updated based on the computed flows. Several modifications were made to both the GSSHA channel routing and the overland flow routing schemes to improve stability and allow interaction between the surface and subsurface components of the model. The combination of improvements in the stability of the overland and channel routing schemes has allowed significant increases in model computational time steps over CASC2D.

Overland flow routing

Water flow across the land surface is shallow, unsteady, and non-uniform. This flow regime can be described by the Saint-Venant equations, which are derived from physical laws regarding the conservation of mass and

momentum. Overland flow routing in GSSHA uses the 2D diffusive wave equation, which allows for backwater and reverse flow conditions. The 2D (vertically integrated) continuity equation for gradually varied flow over a plane in rectangular (x, y) coordinates is (Julien et al. 1995):

$$\frac{\partial h}{\partial t} + \frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} = i_e \quad (1)$$

where:

$$\begin{aligned} h &= \text{surface water depth [L]} \\ q_x, q_y &= \text{unit discharge in the } x \text{ or } y \text{ direction [L}^2\text{/T]} \\ i_e &= \text{excess precipitation rate [L/T]}. \end{aligned}$$

The diffusive wave momentum equations for the x and y directions are written as:

$$S_{fx} = S_{0x} - \frac{\partial h}{\partial x} \quad (2a)$$

$$S_{fy} = S_{0y} - \frac{\partial h}{\partial y} \quad (2b)$$

where:

$$\begin{aligned} S_{fx}, S_{fy} &= \text{friction slope (energy grade line) in the } x \text{ or } y \text{ direction} \\ S_{0x}, S_{0y} &= \text{ground surface slope in the } x \text{ or } y \text{ direction.} \end{aligned}$$

In GSSHA, $\Delta x = \Delta y$, thus the computational grid cells are considered to be squares. Intercell discharges per unit width in the x and y directions, q_x and q_y , respectively, are computed in cell ij from the depth, h_{ij} , at the n th time level using the Manning equation with spatially varied roughness coefficients n_{ij} for the head-discharge relationship in the x and y directions, respectively, as:

$$(q_x)_{ij}^n = \frac{1}{n_{ij}} (h_{ij}^n)^{5/3} (S_{fx}^n)^{1/2} \quad (3a)$$

$$(q_y)_{ij}^n = \frac{1}{n_{ij}} (h_{ij}^n)^{5/3} (S_{fy}^n)^{1/2} \quad (3b)$$

where n is Manning roughness coefficient $[T/L^{1/3}]$.

$$S_{fx}^n = S_{0x}^n - \frac{h_{i+1,j}^n - h_{ij}^n}{\Delta x} \quad (4a)$$

$$S_{fy}^n = S_{0y}^n - \frac{h_{i,j+1}^n - h_{ij}^n}{\Delta x} \quad (4b)$$

Depths in each cell are calculated at the $n+1$ time level based on the flows for each cell (Downer and Ogden 2004):

$$h_{ij}^{n+1} = h_{ij}^n + \frac{\Delta t}{\Delta x} [(q_x)_{i-1,j}^n + (q_y)_{i,j-1}^n - (q_x)_{ij}^n - (q_y)_{ij}^n] \quad (5)$$

In addition to this scheme, other numerical solution schemes such as Alternating Direction Explicit (ADE) and ADE with prediction correction (ADEPC) are also included in GSSHA.

Channel flow routing

Channel flow routing in GSSHA employs the 1D diffusive wave equation. The 1D (laterally and vertically integrated) continuity equation for gradually varied flow along a channel is (Julien et al. 1995):

$$\frac{\partial A}{\partial t} + \frac{\partial Q}{\partial x} = q_l \quad (6)$$

where:

- A = cross sectional area of channel flow $[L^2]$
- Q = total discharge $[L^3/T]$
- q_l = lateral flow into or out of the channel $[L^2/T]$.

Intercell flows $Q_{i-1/2}$ and $Q_{i+1/2}$ in the longitudinal, x , direction are computed from depths, h , at the n time level using the Manning equation for the head discharge relationship:

$$Q_{i+0.5}^n = \frac{1}{n} A_i^n (R_{nij}^n)^{2/3} (S_{fxi+0.5}^n)^{0.5} \quad (7a)$$

$$Q_{i-0.5}^n = \frac{1}{n} A_i^n (R_{hij}^n)^{2/3} (S_{fxi-0.5}^n)^{0.5} \quad (7b)$$

where:

R_h = hydraulic radius of flow A/P [L]

P = wetted perimeter of channel flow [L].

$$S_{fxi+0.5}^n = S_{0xi+0.5}^n - \frac{h_{i+1}^n - h_i^n}{\Delta x} \quad (8a)$$

$$S_{fxi-0.5}^n = S_{0xi-0.5}^n - \frac{h_i^n - h_{i-1}^n}{\Delta x} \quad (8b)$$

If adverse (reverse) flow occurs (flow in the topographically upstream direction), the head in the downstream cell is used to calculate the flow. Inter-node fluxes are used to calculate the volume, V , in each node as:

$$V_i^{n+1} = V_i^n + \Delta t (\Delta x q_i^{n+1} + \Delta x q_{recharge}^{n+1} + Q_{i-0.5}^n - Q_{i+0.5}^n) \quad (9)$$

where $q_{recharge}$ is exchange between the groundwater and channel. These new volumes are used to compute nodal values of A , h , and P at the $n+1$ time level. Calculations proceed from the upstream boundary to the downstream boundary.

Sediment erosion and transport processes

The movement of water across the overland plane or through a channel network can transport and redistribute soil and sediment throughout a watershed. Within GSSHA, sediment erosion and transport processes take place both on the land and within the channel. Sediment erosion and transport are potentially very important processes in watersheds. Excess sediment can affect water quality directly by itself. Sediment transport also influences contaminant transport and fate processes. Suspended sediments act as a carrier of contaminants in the watershed flow. Many contaminants sorb strongly to sediment and thus undergo settling, scour, and sedimentation. Sorption also affects a contaminant's transfer and transformation rates. The amount of contaminants transported by the sediments depends on the suspended sediment concentration and the sorption coefficient. Both sediment transport rates and concentrations must be

estimated in most toxic contaminant studies. The main processes in the soil erosion and sediment transport sub-model include:

- Advection-diffusion transport
- Erosion
- Deposition
- Bed processes (bed elevation dynamics).

Governing equations

The sediment transport models are based on the suspended sediment mass conservation equation (advection-diffusion equation with the sink-source term describing sedimentation resuspension rate) and the equation of bottom deformation. For the overland plane in 2D, the concentration of particles in a flow is governed by conservation of mass (sediment continuity) (Julien 1998):

$$\frac{\partial C_s}{\partial t} + \frac{\partial \hat{q}_{tx}}{\partial x} + \frac{\partial \hat{q}_{ty}}{\partial y} = \hat{J}_e - \hat{J}_d + \hat{W}_s = \hat{J}_n \quad (10)$$

where:

- C_s = concentration of sediment particles in the flow [M/L³]
 \hat{q}_{tx} , \hat{q}_{ty} = total sediment transport areal flux in the x or y direction [M/L²T]
 \hat{J}_e = sediment erosion volumetric flux [M/L³T]
 \hat{J}_d = sediment deposition volumetric flux [M/L³T]
 \hat{W}_s = sediment point source/sink volumetric flux [M/L³T]
 \hat{J}_n = net sediment transport volumetric flux [M/L³T].

The total sediment transport flux in any direction has three components, advective, dispersive (mixing), and diffusive, and may be expressed as (Julien 1998):

$$\hat{q}_{tx} = u_x C_s - (R_x + D_x) \frac{\partial C_s}{\partial x} \quad (11a)$$

$$\hat{q}_{ty} = u_y C_s - (R_y + D_y) \frac{\partial C_s}{\partial y} \quad (11b)$$

where:

u_x, u_y = advective flow velocity in the x or y direction [L/T]

R_x, R_y = dispersion (mixing) coefficient the x or y direction [L²/T]

D_x, D_y = sediment dispersion coefficient in the x or y direction [L²/T].

The dispersive and diffusive flux terms in Equations (11a) and (11b) are negatively signed to indicate that mass is transported in the direction of decreasing concentration gradient. Note that both dispersion and diffusion are represented in forms that follow Fick's Law. However, dispersion represents a relatively rapid turbulent mixing process, while diffusion represents a relatively slow Brownian motion, random walk process (Holley 1969). In turbulent flow, dispersive fluxes are typically several orders of magnitude larger than diffusive fluxes. Further, flow conditions for intense precipitation events are usually advectively dominated as dispersive fluxes are typically one to two orders smaller than advective fluxes. As a result, both the dispersive and diffusive terms may be neglected.

Similarly, the suspended sediment transport in channels is described by the 1D advection-diffusion equation that includes a sink-source term describing sedimentation and resuspension rates and laterally distributed inflow of sediments. The concentration of particles in flow is governed by the conservation of mass (Julien 1998):

$$\frac{\partial C_s}{\partial t} + \frac{\partial \hat{q}_{tx}}{\partial x} = \hat{J}_e - \hat{J}_d + \hat{W}_s = \hat{J}_n \quad (12)$$

Individual terms for the channel advection-diffusion equation are identical to those defined for the overland plane. Similarly, the diffusive flux term can be neglected. The dispersive flux is expected to be larger than the corresponding term for overland flow. However, the channel dispersive flux still may be neglected relative to the channel advective flux during intense runoff events.

Soil and sediment bed processes

The soil sediment bed plays an important role in the transport of contaminants. Once a particle erodes, it becomes part of the flow and is transported downstream. The fluxes of the sedimentation and the resuspension control the dynamics of the uppermost contaminated layer of the bottom

sediments. Particles and associated contaminants in the surficial sediments may enter deeper sediment layers by burial or be returned to the water column by scour. Whenever burial/scour occurs, particles and associated contaminants are transported through each subsurface sediment segment within a vertical stack. In response to the difference between bed form transport, erosion, and deposition fluxes, the net addition (burial) or net loss (scour) of particles from the bed causes the bed surface elevation to increase or decrease. The rise or fall of the bed surface is governed by the sediment continuity (conservation of mass) equation, various forms of which are attributed to the Exner equation (Simons and Sentürk 1992). Julien (1998) presents a derivation of the bed elevation continuity equation for an elemental control volume that includes vertical and lateral (x and y direction) transport terms. Neglecting bed consolidation and compaction processes, and assuming that only vertical mass transport processes (erosion and deposition) occur, the sediment continuity equation for the change in elevation of the soil or sediment bed surface may be expressed as:

$$\rho_b \frac{\partial z}{\partial t} + v_{se} C_s - v_r C_{sb} = 0 \quad (13)$$

where:

- ρ_b = bulk density of soil or bed sediments [M/L³]
- z = elevation of the soil surface [L]
- v_{se} = effective settling (deposition) velocity [L/T]
- v_r = resuspension (erosion) velocity [L/T]
- C_{sb} = concentration of sediment at the bottom boundary (in the bed) [M/L³].

3 CTT&F Sub-model

Within this chapter the mathematical equations and algorithms needed to implement the CTT&F sub-model are developed. The sub-model described below is designed to provide a broad framework applicable to many contamination problems (e.g., explosives, heavy metals, etc.) within the watershed and to allow the user to match the model complexity with the requirements of the problem.

Model framework

From a spatial perspective, contaminants enter the watershed environment through point and nonpoint sources. Nonpoint sources are sources of contaminants that are distributed along the watershed. These sources are often diffuse, in that mass entering at any one point in space is relatively small, yet the aggregate mass loading rate is significant. During precipitation events, the movement of water and sediment across the overland plane or through a channel network can transport and redistribute contaminants throughout a watershed. The mass balance for contaminants in the watershed is computed in the CTT&F sub-model. This sub-model describes contaminant transport, intermedia exchange, phase distribution, and biochemical transformations, in both the water column and soils/sediments.

A variety of processes determine the fate of contaminants within watersheds. Physical processes include advection, diffusion or dispersion, erosion (resuspension), and deposition. Physical transport mechanisms will affect the location of contaminant mass. Partitioning and biochemical reactions, meanwhile, determine the distribution of contaminant mass among different phases and thereby affect the amount of mass available for transport. Several biochemical processes can affect the transport and fate of contaminants in the watershed environment. Some contaminants undergo a complex set of reactions, while others behave in a more simplified manner. A generalized conceptual framework for the CTT&F sub-model is presented in Figure 3, where the system is represented as two compartments: water column and sediment deposition. The pathways that affect contaminant movements and transformations in the watershed

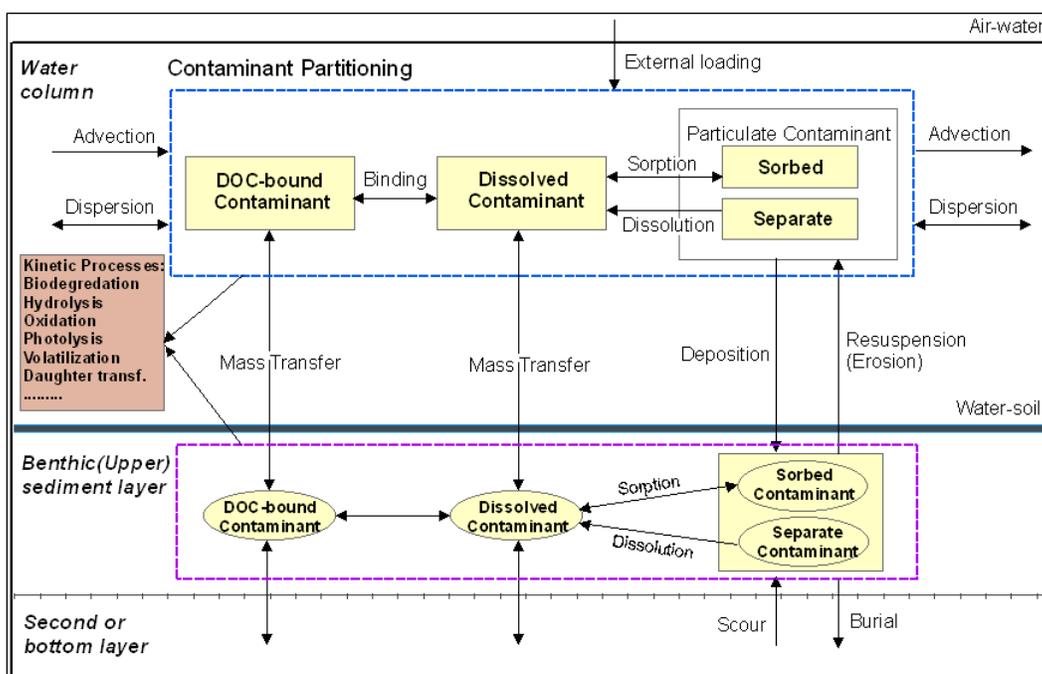


Figure 3. Schematic of the key processes of CTT&F sub-model.

environment depend on the phase in which the contaminants are present and on the environmental media. The CTT&F sub-model allows the simulation of a variety of processes that may affect contaminants. Key processes taken into account in the CTT&F sub-model are:

- contaminant partitioning and phase distribution
- contaminant advection-diffusion
- contaminant infiltration
- contaminant transfer from the soil
- contaminant erosion (resuspension) from the surface
- contaminant deposition into the soil (sediment) surface
- contaminant buried via sedimentation
- contaminant transformation (reaction)
- contaminant volatilization.

In watersheds, these processes are closely coupled. In considering these important processes, the governing equations for contaminants are established over a differential control volume through which the fluid is flowing. A basic principle of many contaminant transport models is the conservation of mass. This principle requires that the mass of each constituent being investigated must be accounted for in one way or another. When diffusion effects are significant, the use of Fick's law of dispersion

results in the appearance of additional terms. Also, when diffusion is not dominant, the transport problem can be considered as a linear advection problem in which the advection velocity is the flow velocity. This general modeling framework is employed for each of the contaminant phases for overland flow and channel flow within a watershed. The amount of contaminant in the flow is specified by concentration C , that is, the mass of contaminant per unit volume of flow. The overland and channel flow has been routed solving 2D and 1D mass conservation equations that are functions of time and space. These equations are given in the following sections.

Contaminant partitioning and transformation processes

Partitioning is a process that can and does occur in any environment, although the relative significance of partitioning in relation to other processes may vary. On the land surface and in channel environments, contaminants may exist in four phases:

- free dissolved in water
- bound to dissolved organic compounds (DOC)
- sorbed to solid particles
- separate solid particulate (not necessary sorbed to solid particles).

In a watershed, contaminants may be transferred between phases and may be degraded by any of a number of chemical and biological processes. CTT&F accounts for equilibrium partitioning of mass among particulate (sorbed) phase, aqueous (dissolved) phase, and bound with DOC or other binding ligands or complexation agents. The separate solid contaminant is assumed to be a separate phase and is modeled as a reactive sediment particle. The sub-model describes contaminant partitioning between dissolved and particulate sorbents, including multiple particle types, using an organic carbon-based equilibrium assumption.

Equilibrium partitioning process

Many contaminants were thought to exist in equilibrium between the dissolved and sediment phases in water. However, recent research has shown that contaminants also sorb to nonsettling microparticles (colloids) and DOC so that three phases (Figure 4) must be considered for realistic contaminant transport modeling. Partitioning reactions are usually fast relative to other environmental processes, and local equilibrium may be

assumed to exist. At equilibrium, then, the distribution among the phases is controlled by the partition coefficients. In this fashion, the concentration of the contaminant in any phase can be calculated from the total contaminant concentration. Therefore, only a single-state variable representing total concentration is required for each contaminant.

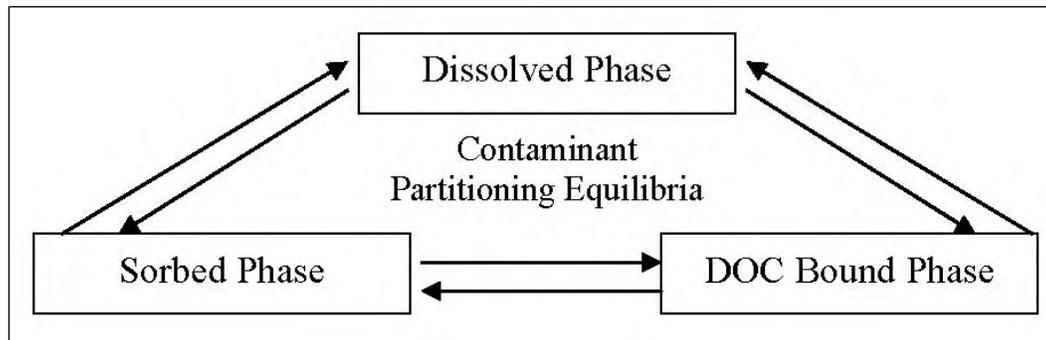


Figure 4. Three phases of contaminant transport.

Contaminants may partition to all particle types (sorbents) present in a solution. The equilibrium partition (distribution) coefficient to any particle is defined as (Thomann and Mueller 1987):

$$\mathcal{K}_{pn} = K_{pn} = f_{ocn} K_{oc} \quad (14)$$

where:

- \mathcal{K}_{pn} , K_{pn} = equilibrium partition (distribution) coefficients for particle "n"
[L³/M]
- f_{ocn} = fraction organic carbon of particle "n"
- K_{oc} = organic carbon normalized partition coefficient [L³/M].

For sorbed phases in the water column, equilibrium partition coefficients vary with the concentration of suspended solids as a result of particle interactions. Particle-dependent partition coefficients are described as (DiToro 1985):

$$\mathcal{K}_{pxn} = \frac{\mathcal{K}_{pn}}{1 + m_n \mathcal{K}_{pn} / \nu_x} = \frac{f_{ocn} K_{oc}}{1 + m_n f_{ocn} K_{oc} / \nu_x} \quad (15)$$

where:

- $\mathcal{K}_{\rho \times n}$ = particle-dependent partition coefficient [L³/M]
- n = particle index = 1, 2, 3, etc.
- m_n = concentration of particle “ n ” [M/L³]
- v_x = particle interaction parameter.

For the bound phase, the equilibrium binding coefficient is defined as:

$$\mathcal{K}_b = D_e f_{ocD} K_{oc} \quad (16)$$

where:

- \mathcal{K}_b = equilibrium binding coefficient [L³/M]
- D_e = DOC-binding effectiveness coefficient
- f_{ocD} = fraction organic carbon of DOC.

Conceptually, DOC are composed entirely of organic carbon ($f_{ocD} = 1$). Under those conditions, the equilibrium-binding coefficient would equal the organic carbon partition coefficient. However, at least for neutral organic contaminant binding in some surface waters (e.g., the Great Lakes), observed binding coefficients were up to 100 times smaller than K_{oc} (Eadie et al. 1990 and 1992). Also, in sediment, observed binding coefficients were up to 10 times smaller than K_{oc} (Landrum et al. 1987; Capel and Eisenreich 1990). One explanation for decreased binding efficiency is photobleaching of DOC by ultraviolet (UV-B) radiation (Kashian et al. 2004).

The equilibrium partition coefficient can be used to describe the fraction of the total contaminant that is associated with each phase as follows (Thomann and Mueller 1987; Chapra 1997):

$$f_d = \frac{1}{1 + D_{oc} \mathcal{K}_b + \sum_{n=1}^N m_n \mathcal{K}_{\rho \times n}} \quad (17a)$$

$$f_b = \frac{D_{oc} \mathcal{K}_b}{1 + D_{oc} \mathcal{K}_b + \sum_{n=1}^N m_n \mathcal{K}_{\rho \times n}} \quad (17b)$$

$$f_{pn} = \frac{m_n \rho_{pn}}{1 + D_{oc} \rho_b + \sum_{n=1}^N m_n \rho_{pn}} \quad (17c)$$

$$f_d + f_b + \sum_{n=1}^N f_{pn} = 1 \quad (17d)$$

where:

- f_d = fraction of the total contaminant in the dissolved phase
- D_{oc} = dissolved organic carbon concentration [M/L³].
- f_b = fraction of the total contaminant in the DOC-bound phase
- f_{pn} = fraction of the total contaminant in the sorbed phase associated with particle “n”

Equations (17a)-(17c) are presented for the water column. For the soils or bed sediments, the fractions associated with dissolved, DOC, and sorbed, respectively, are derived by using porosity. ρ_{pn} is used in place of ρ_{pxn} .

$$f_d = \frac{1}{\phi + \phi D_{oc} \rho_b + (1 - \phi) \rho_s \rho_{pn}} \quad (18a)$$

$$f_b = \frac{D_{oc} \rho_b}{\phi + \phi D_{oc} \rho_b + (1 - \phi) \rho_s \rho_{pn}} \quad (18b)$$

$$f_{pn} = \frac{(1 - \phi) \rho_s \rho_{pn}}{\phi + \phi D_{oc} \rho_b + (1 - \phi) \rho_s \rho_{pn}} \quad (18c)$$

where:

- ϕ = porosity of the soils or bed sediments
- ρ_s = density of the soils or bed sediments [M/L³].

These fractions are determined in time and space throughout a simulation from the partition coefficients, internally calculated porosities, and simulated sediment concentrations and DOC concentrations. Given the total concentration and the three phase fractions, the dissolved, bound, and sorbed concentrations at equilibrium are uniquely determined as follows:

$$C_d = f_d C_T \quad (19a)$$

$$C_b = f_b C_T \quad (19b)$$

$$C_p = \sum_{n=1}^N C_{pn} = \sum_{n=1}^N f_{pn} C_T \quad (19c)$$

$$C_T = \left(1 + D_{oc} \mathbb{1}_b + \sum_{n=1}^N m_n \mathbb{1}_{pxn} \right) C_d \quad (19d)$$

where:

C_d = free dissolved contaminant concentration [M/L³]

C_b = DOC bound contaminant concentration [M/L³]

C_p = sorbed contaminant concentration [M/L³]

C_T = total contaminant concentration [M/L³].

In addition to the assumption of instantaneous equilibrium, implicit in the use of these equations is the assumption of reversibility. Whether the sorption is reversible or irreversible will depend on environmental and contaminant conditions as well as the nature of the sorbing material. Laboratory data for very hydrophobic chemicals suggest, however, that a hysteresis exists, with desorption being a much slower process than adsorption. This effect may be the result of intraparticle kinetics in which the contaminant is slowly incorporated into components of the sorbent (Karickhoff et al. 1979). This phenomenon is not well understood, however, and no quantitative modeling framework is available to characterize it.

Solid phase compounds may exist on the surface separately. They can enter the environment through several mechanisms: (1) explosives manufacture, (2) munitions load, assembly, and pack, (3) munitions maintenance/demilitarization, and training activities (Brannon and Pennington 2002). Considering the separate solid phase, the total contaminant concentration becomes:

$$C_T = C_d + C_b + C_p + C_c \quad (20)$$

where C_c is the separate solid phase contaminant concentration [M/L³].

When the equilibrium case is not warranted, governing equations for CTT&F are formulated in terms of contaminant components. The dissolved and sorbed contaminant concentrations needed to be simulated separately by incorporating non-equilibrium kinetics approaches.

Transformation processes

Beyond partitioning and mass transport processes, the fate of contaminants is potentially influenced by a number of biochemical transformation processes that include, but are not limited to, biodegradation, hydrolysis, oxidation, photolysis, volatilization, and user-defined reaction. All processes may not be operative in all environmental settings. Some contaminants undergo a complex set of reactions, while others behave in a more simplified manner. The importance of any particular process is highly dependent on the contaminant of interest and environmental settings. For example, during subsurface transport of contaminants, photolysis would be inactive and volatilization should be minimal. The CTT&F sub-model allows the simulation of a variety of processes that may affect contaminants. The sub-model is designed to provide a broad framework applicable to many environmental problems and to allow the user to match the model complexity with the requirements of the problem. The contaminants may be independent or they may be linked with reaction yields, such as a parent compound-daughter product sequence. However, transformation process descriptors for explosives are poorly developed because specific reaction mechanisms and their interrelations are poorly understood (McGrath 1995). Additional research is needed to delineate transformation parameters for explosives compounds for which data are limited. 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). Both WASP and IPX model the water body's water quality constituents transport and transformation.

Contaminant biodegradation

Biodegradation encompasses the broad and complex processes of enzymatic attack by organisms on contaminants. Dehalogenation, dealkylation, hydrolysis, oxidation, reduction, ring cleavage, and condensation reactions are all known to occur. If these processes follow pseudo first-order kinetics, which means that the rate of loss of mass at any given time is directly proportional to the mass present at that time, the rate coefficients may be

combined into a single decay coefficient. The contaminant mass rate equation is then given by:

$$J_{bio} = k_{bio} C_T \quad (21a)$$

where:

J_{bio} = total decay rate for a contaminant in water or soil [M/L³/T]
 k_{bio} = lumped first order decay rate in soil or sediment [1/T].

When dealing with first-order degradation reactions, the use of a half-life rather than a rate is often convenient. If a half-life is specified for the transformation processes, then it is converted to first-order rate constant:

$$k_{bio} = \frac{\ln 2}{t_{1/2}} \quad (21b)$$

Not all phases will necessarily biodegrade at the same rate. In addition, the overall biodegradation rate may vary as a function of the concentration of degrading organisms as well as the medium (water, soil, or sediment) in which the reaction occurs. To account for these factors, the first-order biodegradation rate for any media can be expressed as a second-order process:

$$k_{bio} = C_{bio} \sum_i k'_{bioi} f_i \quad (21c)$$

where:

C_{bio} = concentration of degrading organisms [cells/mL]
 k'_{bioi} = second-order biodegradation rate for contaminant in phase i
 [mL/cell-day]
 f_i = fraction of total contaminant in phase i [dimensionless].

Contaminant hydrolysis

Hydrolysis, or reaction of the contaminant with water, is known to be another major pathway for degradation of many toxic contaminants. Hydrolysis is a reaction in which cleavage of a molecular bond of the contaminant occurs and a new bond is formed with either the hydrogen or

the hydroxyl component of a water molecule. Contaminants in water may react with positively charged hydronium ions $[H^+]$, negatively charged hydroxide ions $[OH^-]$, or neutral water molecules. The reactions are first order for the neutral contaminant and second order for the acidic or basic forms of the contaminant. Not all phases of a contaminant will necessarily hydrolyze at the same rate. Hydrolysis by specific-acid-catalyzed, neutral, or base pathways is considered for the various species and phases of each contaminant as:

$$k_{hyd-N} = \sum_j k_{nj} f_j \quad (22a)$$

$$k_{hyd-H} = \sum_j k_{aj} [H^+] f_j \quad (22b)$$

$$k_{hyd-OH} = \sum_j k_{bj} [OH^-] f_j \quad (22c)$$

where:

k_{hyd-N} = net neutral hydrolysis rate constant, day⁻¹ [1/T]

k_{nj} = neutral rate constant for contaminant in phase j, day⁻¹ [1/T]

f_j = fraction of contaminant in phase j.

k_{hyd-H} = net acid catalyzed hydrolysis rate constant, day⁻¹ [1/T]

k_{hyd-OH} = net base catalyzed hydrolysis rate constant, day⁻¹ [1/T]

k_{aj}, k_{bj} = specific acid catalyzed and base rate constants for contaminant in phase j, respectively, L/mol-day [L³/M/T]

The total rate of hydrolysis transformation of a contaminant is computed by the sub-model as the sum of three contributing processes.

$$k_{hyd} = k_{hyd-N} + k_{hyd-H} + k_{hyd-OH} \quad (22d)$$

where:

k_{hyd} = overall (first-order) hydrolysis rate [1/T].

Contaminant oxidation

Contaminant oxidation in aquatic systems can be a consequence of interactions between free radicals and the contaminants. Free radicals can be

formed as a result of photochemical reactions. Free radicals that have received some attention in the literature include alkylperoxy radicals, RO_2 , OH radicals, and singlet oxygen. Not all phases of a contaminant will necessarily oxidize (or be reduced). Further, oxidation and reduction rates for each contaminant phase may vary as a function of oxidant or reductant concentrations. To account for these factors, oxidation is modeled as a general second-order process for the various species and phases of each contaminant. The overall oxidation or reduction rate of a contaminant is computed as:

$$k_{oxi} = [RO_2] \sum_j k_{oj} f_j \quad (23)$$

where:

k_{oxi} = net oxidation rate constant, day^{-1} [1/T]

$[RO_2]$ = molar concentration of oxidant, mol/L [M/L³]

k_{oj} = second order oxidation rate constant for contaminant in phase j, L/mol-day [L³/M/T].

Contaminant photolysis (photodegradation)

Photolysis is the transformation or degradation of a contaminant that results directly from the adsorption of light energy. It is a function of the quantity and wavelength distribution of incident light, the light adsorption characteristics of the contaminant, and the efficiency at which absorbed light produces a contaminant reaction. Photolysis is classified into two types that are defined by the mechanism of energy absorption. Direct photolysis is the result of direct absorption of photons by the toxic contaminant molecule. Indirect or sensitized photolysis is the result of energy transfer to the toxic contaminant from some other molecule that has absorbed the radiation. Not all phases of a photo-reactive compound necessarily react. In addition, the overall photolysis rate depends on the depth to which reactive light wavelengths penetrate. For soils and exposed sediments, light does not penetrate the particle matrix to any significant depth, so photolysis is limited to a thin layer at the very surface of the matrix. In surface waters, light can penetrate to some depth but is attenuated. The first order rate coefficient for photolysis can be calculated from the absorption rate and the quantum yield for contaminant in each phase:

$$k_{pht} = \sum_j k_{aj} \phi_j f_j \quad (24)$$

where:

k_{pht} = first order photolysis rate coefficient at ambient light intensity, day⁻¹ [1/T]

k_{aj} = specific sunlight absorption rate for contaminant in phase j, E/mol-day [E/M/T]

ϕ_j = reaction quantum yield for contaminant in phase j, mol/E [M/E].

Dissolved contaminant volatilization

Volatilization rate from water column. Volatilization is the process by which contaminants dissolved in water are transferred from the aqueous phase into the vapor phase across the air-water interface. Only dissolved contaminants can be transported across the interface, and sorption to particulate or DOC reduces volatilization. In the CTT&F sub-model, the method for estimating the flux of volatile components across the air-water interface is based on the two film concept, and uses a finite difference approximation to Fick's law of diffusion:

$$J_{vlt} = k_{vlt} \Delta C = k_v \left(f_d C_T - \frac{C_a}{k_H} \right) \quad (25a)$$

where:

J_{vlt} = volatilization rate for a contaminant [M/L³/T]

k_{vlt} = net volatilization rate, day⁻¹ [1/T]

k_v = mass transfer rate (conductivity), m/day [L/T]

C_a = atmospheric concentration, ug/L [M/L³]

k_H = Henry's constant, i.e., distribution coefficient between liquid and vapor phase.

Volatile contaminant concentrations in the atmosphere are often much lower than partial pressures equilibrated with water concentrations. If this concentration is 0, then volatilization will always cause a loss of contaminant from the water body. In such a case, volatilization reduces to a first-

order process with a rate proportional to the conductivity and surface area divided by volume:

$$k_{vit} = k_v \frac{1}{D} = k_v \frac{A_s}{V} \quad (25b)$$

where:

k_v = mass transfer rate (conductivity), m/day [L/T]

D = water column depth, m [L]

A_s = surface area of water column, m² [L²]

V = volume of water column, m³ [L³].

The two-resistance method assumes that two “stagnant films” are bounded on either side by well-mixed compartments. Concentration differences serve as the driving force for the water layer diffusion. Pressure differences drive the diffusion for the air layer. From mass balance considerations, it is obvious that the same mass must pass through both films, thus the two resistances combine in series, so that the conductivity is the reciprocal of the total resistance:

$$k_v = (R_L + R_G)^{-1} = (K_L^{-1} + K_G^{-1})^{-1} \quad (25c)$$

where:

R_L = liquid phase resistance, day/m [T/L]

R_G = gas phase resistance, day/m [T/L]

K_L = liquid phase transfer coefficient, m/day [L/T]

K_G = gas phase transfer coefficient, m/day [L/T].

For a flowing system, the mass transfer rates are controlled by flow-induced turbulence, which is primarily a function of the stream velocity. For stagnant waterbodies, wind shear may dominate. Several formulations are available for computing liquid phase mass transfer rates. The liquid phase transfer rate can be estimated from reaeration formulae. Reaeration is caused by turbulence near the water surface because of flow and wind.

$$K_L = K_a \left(\frac{32}{MW_c} \right)^{0.5} \quad (25d)$$

where:

$$K_a = \text{oxygen reaeration rate, m/day [L/T]}$$

$$MW_C = \text{molecular weight of contaminant, g/mol [M/M].}$$

For water column with depths less than 0.61 m the Owens formula is used to calculate the oxygen reaeration rate:

$$K_a = 5.349 \frac{u^{0.67}}{D^{0.85}} \quad (25e)$$

where u is velocity of the water, m/sec [L/T].

For water column where the velocity is less than 0.52 m/sec or the depth is greater than $13.584 u^{2.9135}$ m, the modified form of the O'Connor-Dobbins formula is used:

$$K_a = 8.64 \cdot 10^4 \left(\frac{D_w u}{D} \right)^{0.5} \quad (25f)$$

where $D_w = 22 \cdot 10^{-9} / MW_C^{2/3}$ is diffusivity of contaminant in water, cm^2/sec [L^3/T].

In all other cases, the Churchill formula is used to estimate reaeration rate:

$$K_a = 5.049 \frac{u^{0.969}}{D^{0.673}} \quad (25g)$$

For flowing systems, Ambrose et al. (1993) assume that the gas phase mass transfer rate is constant at 100 m/day. As wind speeds decrease, mass transfer rates in the gas phase also decrease. Under still-air conditions, Mackay and Leinonen (1975) suggested that K_G is 86.4 m/day (0.001 m/sec), representing a minimum rate of gas phase mass transfer.

Volatilization rate from soils. Volatilization from soil is a more complex process, requiring the balancing of several processes. A contaminant in soil will partition between the soil water, soil air, and the soil constituents. The rate of volatilization will therefore depend on factors such as desorption kinetics, water-air interfacial transfer, solid-air interfacial transfer, and evaporation (Jury et al. 1990). In the CTT&F sub-model, the

volatilization from soils is assumed to proceed through a surface stagnant air boundary layer and involve desorption of the contaminant from soil, movement to the soil surface in the water or air phase, and vaporization into the atmosphere (Figure 5). Assuming zero vapor concentration above the surface, using Fick's Law, the volatilization rate from soil can be estimated by:

$$k_{vit} = k_H \frac{D_a A_s}{d} \left(\frac{1}{V} \right) \quad (25h)$$

where:

$D_a = 1.9 \cdot 10^{-4} / MW_c^{2/3} =$ diffusivity of contaminant in air, cm^2/s
 $[\text{L}^2/\text{T}]$

$A_s =$ surface area of soil column, m^2 $[\text{L}^2]$

$d =$ thickness of stagnant air boundary layer $[\text{L}]$. Jury et al. (1983) suggested a value of 0.5 cm for d , which in general varies with both evaporation and relative humidity

$V =$ volume of upper soil layer, m^3 $[\text{L}^3]$.

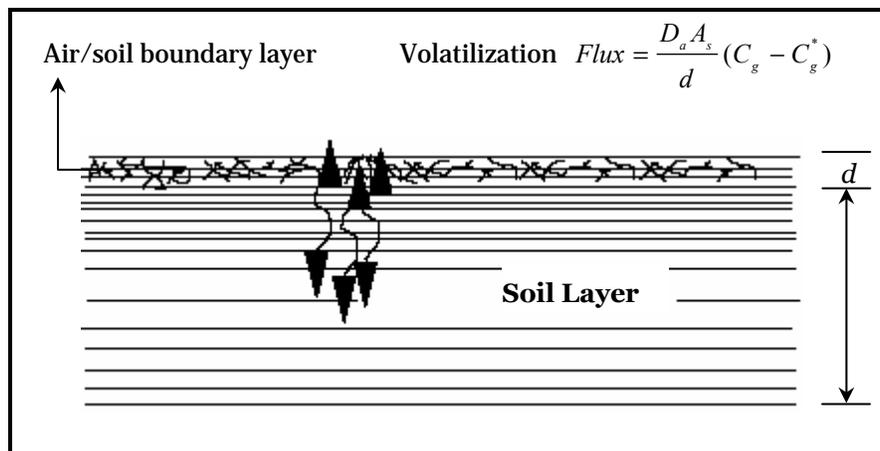


Figure 5. Schematic representation of contaminant volatilization process from soils.

User-defined extra reaction

An extra user-defined second-order reaction for the various phases of each contaminant is included. The second-order reaction allows the user to simulate the effect of processes not considered by the sub-model. The reaction depends upon a rate constant and an environmental parameter

that may be taken to represent, for example, some reducing or oxidizing agent.

$$k_{urd} = [E] \sum_j k_{ej} f_j \quad (26)$$

where:

- k_{urd} = net user-defined reaction rate constant, day⁻¹ [1/T]
- $[E]$ = intensity of environmental property driving the reaction
- k_{ej} = second order rate constant for contaminant in phase j, [E]⁻¹day⁻¹.

Transformations and daughter products

The contaminants simulated by the sub-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 contaminants and by specifying appropriate yield coefficients for each process:

$$J_{kji} = \sum_j \sum_k k_{kj} C_j Y_{kji} \quad (27)$$

where:

- J_{kji} = production of contaminant “i” from contaminant “j” undergoing reaction “k,” mg/L-day [M/L³/T]
- k_{kj} = effective rate coefficient for contaminant “j,” reaction “k,” day⁻¹ [1/T]
- Y_{kji} = yield coefficients for production of contaminant “i” from contaminant “j” undergoing reaction “k,” mg/mg [M/M].

Transport and transformation of contaminants in 2D overland regime

Overland transport of contaminants is vital for quantifying a distributed source. On the land surface, contaminants may exist on the soil surface as well as below it. The movement of water and sediment across the overland plane can transport and redistribute contaminants. The contaminant transport in dissolved phase is a result of the transfer of the contaminant from soil water to the surface runoff water, desorption from the suspended

sediments and dissolution from the separate solid phase. The amount of the contaminant desorbed from eroded sediment is generally much less than the amount desorbed from the soil in place. Furthermore, the contaminant present on the sediment is likely to have been desorbed partially before the sediment was dislodged. The infiltration and kinetics of the soil control the contaminant mass advection and diffusion. The sorbed contaminant on the suspended sediments is a result of detachment of contaminated particles from the top soil and/or adsorption from the dissolved phase. The contaminant mass balance governing equations track all sources, losses, and internal transformations of the contaminant in overland regime. Mathematical modeling of contaminant transport involves the solution of governing equations of both overland flow and upper soil layer simultaneously. Within CTT&F, the upper soil layer is well-mixed and can be characterized by a single concentration throughout the layer. Contaminants are exchanged with the overlying runoff through settling of the sorbed fraction and transfer of the dissolved fraction. Diffusion of contaminants from the soil below the upper layer is neglected in this sub-model.

Governing equations for contaminants with equilibrium partitioning

Several processes that govern the transport of contaminants in the overland plane are considered in CTT&F, in which advection, dispersion, infiltration, erosion, and deposition are the dominant hydrologic transport mechanisms. Consideration of these important mechanisms leads to the 2D advection-dispersion equation. Assuming the sorption-desorption kinetics between the sorbed and dissolved contaminant phases are rapid and lead to a local equilibrium, the mass conservation equations of the contaminant transport and kinetic processes considered in overland regime are written for the total contaminant concentration as follows.

Overland flow

$$\begin{aligned} \frac{\partial(hC_T^r)}{\partial t} + \frac{\partial(q_x C_T^r)}{\partial x} + \frac{\partial(q_y C_T^r)}{\partial y} - \frac{\partial}{\partial x} \left(hD_x \frac{\partial C_T^r}{\partial x} \right) - \frac{\partial}{\partial y} \left(hD_y \frac{\partial C_T^r}{\partial y} \right) \\ = -J_{df} + J_{dm} + J_{pe} - J_{pd} + \sum S_k \end{aligned} \quad (28)$$

Upper Soil Layer

$$\frac{\partial(z_m C_{T2}^r)}{\partial t} = J_{df} - J_{dm} - J_{pe} + J_{pd} + \sum S_k \quad (29)$$

where:

C_T^r = total contaminant concentration in the overland flow [M/L³]

C_{T2}^r = total contaminant concentration in the upper soil layer [M/L³]

D_x, D_y = contaminant dispersion coefficient in the x or y direction [L²/T]

z_m = depth of the upper soil layer [L]

J_{df} = dissolved contaminant infiltration flux [M/L²/T]

J_{dm} = dissolved contaminant mass transfer flux between surface water and upper soil layer [M/L²/T]

J_{pe} = sorbed contaminant erosion flux [M/L²/T]

J_{pd} = sorbed contaminant deposition flux [M/L²/T]

$\sum S_k$ = total contaminant kinetics transformation flux; positive indicates a source, negative a sink [M/L²/T].

Contaminant transport processes in the overland plane consist of the following six types.

- Contaminant advection
- Contaminant dispersion
- Dissolved contaminant infiltration
- Dissolved contaminant transfer from soils
- Particulate contaminant erosion
- Particulate contaminant deposition.

Contaminant advection

Advective transport is the process by which contaminants are transported by flowing water at its mean velocity. Advective flow transports all contaminant phases downstream with the water. The contaminant advective flux ($\partial(q_x C_T)/\partial x, \partial(q_y C_T)/\partial y$) is calculated based on the flow velocity.

Contaminant dispersion

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 contaminant would travel at the mean velocity. With dispersion, some contaminant travels faster and some slower than the mean velocity; the contaminant “spreads out.” The dispersion coefficient for transport in soils can generally be described by (Bear 1972):

$$\theta D_x = D_l q_x + \theta D_d \tau_0 \quad (30a)$$

$$\theta D_y = D_t q_y + \theta D_d \tau_0 \quad (30b)$$

where:

D_l = longitudinal dispersivity [L]

D_d = molecular diffusion in free water [L^2/T].

τ_0 = tortuosity factor

D_t = transverse dispersivity [L]

For overland flow, letting $\theta = 1$ and $\tau = 1$, Equation (30) simplifies to:

$$D_x = D_l u_x + D_d \quad (31a)$$

$$D_y = D_t u_y + D_d \quad (31b)$$

Dissolved contaminant infiltration

Contaminants associated with the dissolved phase in the runoff will enter the upper soil if the water transporting those contaminants infiltrates. To account for this process, the contaminant infiltration flux can be computed from the water infiltration:

$$J_{df} = f(f_d + f_b)C_T^r \quad (32)$$

where f is the infiltration rate [L/T].

Dissolved contaminant transfer from soils

Surface-applied or soil-incorporated contaminants are often transferred in significant quantities from the soil matrix to surface runoff as a result of the rainfall-runoff process. Several dynamic, interrelated processes control contaminant transport from soil to runoff during rainfall, including ejection of soil water by raindrop impacts, diffusion of contaminants 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 (Ahuja and Lehman 1983; Snyder and Woolhiser 1985). Effective soil depth of interaction is related to the degree of soil aggregation, and it increases with soil slope, kinetic energy of raindrops, and rainfall intensity. Gao et al. (2004) developed a model that combined the contaminant transfer associated with the raindrop impacts and diffusion by assuming raindrop and diffusion processes could be coupled by superposition. This model captured soil-runoff contaminant transfer behavior more realistically than either mixing-layer models or diffusion-based models. From this model, the mass transfer flux of the dissolved contaminant between the overland flow and the soil water can be expressed:

$$J_{dm} = k_e (f_d + f_b) (C_{T2}^r - C_T^r) \quad (33)$$

where:

$$k_e = k_m + \frac{ai\theta}{\rho_b} = \text{effective mass transfer coefficient [L/T]} \quad (\text{Gao et al. 2004})$$

k_m = diffusive mass transfer coefficient [L/T], which was derived by the concentration gradient across the hydrodynamic boundary layer (Wallach et al. 1988, 1989). Diffusion between the upper soil and surface runoff may be neglected since the diffusivity is much smaller than the rainfall induced mass transfer rate (Gao et al. 2004)

a = soil detachability [M/L³]

i = rainfall intensity rate [L/T]

θ = volumetric water content.

Particulate contaminant erosion

Contaminants sorbed on the soil particles are subsequently entrained into surface runoff as these particles are eroded by the moving water. Surface erosion by overland flow is comprised of two processes: splash erosion and hydraulic erosion. The erosion flux of sorbed contaminant due to runoff is computed by:

$$J_{pe} = \sum_1^N f_{pn} v_r C_{T2}^r \quad (34a)$$

where v_r is resuspension (erosion) velocity [L/T], with its calculation being adapted as follows, in part, from the IPX User's Guide (Velleux et al. 2001).

Entrained material may be transported as either bedload or suspended load. However, for overland sheet and rill flows, bedload transport by rolling and sliding may predominate as the occurrence of saltation and full suspension may be limited (Julien and Simons 1985). Entrainment rates may be estimated from site-specific erosion rate studies or, in general, from the difference between sediment transport capacity and advective fluxes:

$$v_r = \frac{J_c - v_a C_s}{\rho_b} \quad \text{for: } J_c > v_a C_s$$

$$v_r = 0 \quad \text{for: } J_c \leq v_a C_s \quad (34b)$$

where:

J_c = sediment transport capacity areal flux [M/L²/T]
 v_a = advective (flow) velocity (in the x or y direction) [L/T].

In the overland plane, particles can be detached from the bulk soil matrix by raindrop (splash) impact and entrained into the flow by hydraulic action when the exerted shear stress exceeds the stress required to initiate particle motion (Julien and Simons 1985). The overland erosion process is influenced by many factors including precipitation intensity and duration, runoff length, surface slope, soil characteristics, vegetative cover, exerted shear stress, and particle size. Raindrop impact may generally be neglected

when flow depths are greater than three times the average raindrop diameter (Julien 2002). Julien and Simons (1985) summarize numerous relationships to describe the transport capacity of overland flow. Julien (1998, 2002) recommends a modified form of the Kilinc and Richardson relationship that includes soil erodibility terms from the Universal Soil Loss Equation (USLE) for estimating the overland sediment transport capacity (for both the x and y directions):

$$q_s = 1.542 \times 10^8 (q - v_c h)^{2.035} S_f^{1.66} KCP \quad (34c)$$

$$J_c = \frac{q_s}{B_e} \quad (34d)$$

where:

q_s = sediment transport capacity (kg/m·s) [M/L·T]

q = unit flow rate of water = $v_a h$ [L²/T]

v_c = critical velocity for erosion overland [L/T]

K = USLE soil erodibility factor

C = USLE soil cover factor

P = USLE soil management practice factor

B_e = width of eroding surface in flow direction [L].

In channels, sediment particles can be entrained into the flow when the exerted shear stress exceeds the stress required to initiate particle motion. For noncohesive particles, the channel erosion process is influenced by factors such as particle size, particle density, and bed forms. For cohesive particles, the erosion process is significantly influenced by interparticle forces (such as surface charges that hold grains together and form cohesive bonds) and consolidation. Total (bed material) load transport capacity relationships account for the both bedload and suspended load components of sediment transport. Yang (1996) and Julien (1998) provide summaries of numerous total load transport relationships. The Engelund and Hansen relationship is considered a reasonable estimator of the total load:

$$C_w = 0.05 \left(\frac{G}{G-1} \right) \frac{(v_a - v_c) S_f}{[(G-1)gd_p]^{0.5}} \left[\frac{R_h S_f}{(G-1)d_p} \right]^{0.5} \quad (34e)$$

$$J_c = \frac{v_a C_t}{A} \quad (34f)$$

where:

C_w = concentration of entrained sediment particles by weight at the transport capacity

G = particle specific gravity

g = gravitation acceleration [L/T²]

d_p = particle diameter [L]

C_t = concentration of entrained sediment particles at the transport

$$\text{capacity} = \frac{10^6 G C_w}{G + (1 - G) C_w} \text{ (g/m}^3\text{) [M/L}^3\text{].}$$

Particulate contaminant deposition

If the sediment transport capacity is lower than the sediment load, the sediment deposition occurs. Contaminants associated with particles in the runoff will enter the upper soil layer if those particles settle. The deposition flux of sorbed contaminant in overland flow is computed by:

$$J_{pd} = \sum_1^N f_{pn} v_{se} C_T^r \quad (34g)$$

where v_{se} is the effective settling (deposition) velocity [L/T], with its calculation being adapted as follows, in part, from the IPX User's Guide (Velleux et al. 2001).

The process of deposition is highly selective, the settling velocity of an aggregate or particle being a function of its size, shape, and density. Coarse particles (>62 μm) are typically inorganic, noncohesive, and generally have large settling velocities under quiescent conditions. Numerous empirical relationships to describe the noncohesive particle-settling velocities are available. Summaries of relationships and settling velocities are presented by Yang (1996) and Julien (1998). For noncohesive (fine sand) particles with diameters from 62 μm to 500 μm , the settling velocity can be computed as (Cheng 1997):

$$v_{sq} = \frac{\nu}{d_p} \left[(25 + 1.2 d_*^2)^{0.5} - 5 \right]^{-1.5} \quad (34h)$$

$$d_* = d_p \left[\frac{(G-1)g}{\nu^2} \right]^{1/3} \quad (34i)$$

where:

- v_{sq} = quiescent settling velocity [L/T]
- ν = kinematic viscosity of water [L²/T]
- d_* = dimensionless particle diameter.

Medium particles ($10 \mu\text{m} < d_p < 62 \mu\text{m}$) can vary in character. Inorganic particles may behave in a non-cohesive manner. In contrast, organic particles (potentially including particles with organic coatings) may behave in a cohesive manner. Fine particles ($< 10 \mu\text{m}$) often behave in a cohesive manner. If behavior is largely noncohesive, settling velocities may be estimated as described by Julien (1998). If the behavior is cohesive, flocculation may occur. Floc size and settling velocity depend on the conditions under which the floc was formed (Burban et al. 1990; Krishnappan 2000; Haralampides et al. 2003). When flocculation occurs, settling velocities of cohesive particles can be approximated by relationship of the form (Burban et al. 1990):

$$v_s = a \cdot d_f^m \quad (34j)$$

where:

- v_s = floc settling velocity (cm/sec) [L/T]
- a = experimentally determined constant = 8.4×10^{-3}
- d_f = median floc diameter (μm) [L]
- m = experimentally determined constant = 0.024.

However, depending on fluid shear, particle surface charge, and other conditions, fine particles may not flocculate. Under conditions which limit floc formation, fine particles can have very small, near zero settling velocities.

As a result of turbulence and other factors, not all particles settling through a column of flowing water will necessarily reach the sediment-water interface or be incorporated into the sediment bed. Beuselinck et al. (1999) suggested this process also occurs for the overland plane. As a result, effective settling velocities in flowing water can be much less than quiescent settling velocities. The effective settling velocity of a particle can

be described as a reduction in the quiescent settling velocity by the probability of deposition (Mehta et al. 1989):

$$V_{se} = P_{dep} V_s \quad (34k)$$

where P_{dep} is the probability of deposition.

The probability of deposition varies with shear stress near the sediment bed and particle size. As particle size decreases or shear stress increases, the probability of deposition decreases. For noncohesive particles, the probability of deposition has been described as a function of bottom shear stress (Gessler 1967, 1971):

$$P_{dep} = P = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^Y e^{-0.5x^2} dx \quad (34l)$$

$$Y = \frac{1}{\sigma} \left(\frac{\tau_{cd,n}}{\tau} - 1 \right) \quad (34m)$$

where:

P = probability integral for the Gaussian distribution

σ = experimentally determined constant = 0.57

$\tau_{cd,n}$ = critical shear stress for deposition of noncohesive particles, defined as the shear stress at which 50 percent of particles deposit [M/LT²].

τ = bottom shear stress [M/LT²].

For coarse particles, the critical shear stress for deposition can be computed from a force balance following the method of van Rijn (1984a, 1984b) as summarized by Quantitative Environmental Analysis (1999), with the particle diameter equal to the mean diameter for a range of particle size in a class (i.e., $d_p = d_{50}$).

For cohesive particles, the probability of deposition has also been described as a function of bottom shear stress (Partheniades 1992):

$$P_{dep} = 1 - P = 1 - \frac{1}{\sqrt{2\pi}} \int_{-\infty}^Y e^{-0.5x^2} dx \quad (34n)$$

$$Y = \frac{1}{\sigma} \ln \left[0.25 \left(\frac{\tau_{cd,c}}{\tau} - 1 \right) e^{1.27\tau_{cd}} \right] \quad (34o)$$

where:

- σ = experimentally determined constant = 0.49
- $\tau_{cd,c}$ = critical shear stress for deposition of cohesive particles, defined as the shear stress at which 100 percent of the particles deposit [M/LT²].

The probability integrals in Equations (34l) and (34n) can be approximated as (Abramowitz and Stegun 1972):

$$P = 1 - F(Y) (0.4362X - 0.1202X^2 + 0.9373X^3) \quad \text{for: } Y > 0 \quad (34p)$$

$$P = 1 - P(|Y|) \quad \text{for: } Y < 0$$

$$F(Y) = \frac{1}{\sqrt{2\pi}} e^{-0.5Y^2} \quad (34q)$$

$$X = (1 + 0.3327Y)^{-1} \quad (34r)$$

Transformation processes

The kinetics processes considered in the overland regime include decay, hydrolysis, oxidation, photolysis, volatilization, and user-defined extra reaction. The CTT&F sub-model uses different values of the transformation rates for the water column and for the soil layers because these values fit better with the real physical-contaminant behavior of contaminants. Furthermore, the use of the variable transformation rates allow for more flexibility and accuracy in the simulations. The total contaminant kinetics transformation flux is:

$$\begin{aligned} \sum S_k &= H(-J_{bio} - J_{hyd} - J_{oxi} - J_{pht} - J_{vit} - J_{urd} + J_{kji}) \\ &= -H(k_{bio} + k_{hyd}f_d + k_{oxi} + k_{pht} + k_{vit}f_d + k_{udr})C_T + HJ_{kji} \end{aligned} \quad (35)$$

where:

- $H = h$ for overland flow
- $H = z_m$ for upper soil layer [L]
- J_{hyd} = hydrolysis rate for a contaminant [M/L³/T]
- J_{oxi} = oxidation rate for a contaminant [M/L³/T]
- J_{pht} = photolysis rate for a contaminant [M/L³/T]
- J_{vlt} = volatilization rate for a contaminant [M/L³/T]
- J_{udr} = user-defined reaction rate for a contaminant [M/L³/T].

Substituting the above source/sink terms into Equations (28) and (29) leads to:

$$\begin{aligned} & \frac{\partial(hC_T^r)}{\partial t} + \frac{\partial(q_x C_T^r)}{\partial x} + \frac{\partial(q_y C_T^r)}{\partial y} - \frac{\partial}{\partial x} \left(hD_x \frac{\partial C_T^r}{\partial x} \right) - \frac{\partial}{\partial y} \left(hD_y \frac{\partial C_T^r}{\partial y} \right) \\ & = -f(f_d + f_b)C_T^r + k_e(f_d + f_b)(C_{T2}^r - C_T^r) \end{aligned} \quad (36)$$

$$+ \sum_1^N f_{pn} (v_r C_{T2}^r - v_{se} C_T^r) + \sum S_k$$

$$\frac{\partial(z_m C_{T2}^r)}{\partial t} = f(f_d + f_b)(C_T^r - C_{T2}^r) - k_e(f_d + f_b)(C_{T2}^r - C_T^r) \quad (37)$$

$$- \sum_1^N f_{pn} (v_r C_{T2}^r - v_{se} C_T^r) + \sum S_k$$

Governing equations for solids

Previous transport equations assume that contaminants either attach to soil particles or partition to water and DOC when wet. Contaminants can be deposited from the air and applied on the surface in a solid form. As such, solid contaminant particles are carried by runoff and transported through erosion and deposition processes. Within CTT&F, it is necessary to track the mass of a solid phase contaminant. The sediment transport equation assumes the types of “solids” variables are conservative, which indicates that no existing kinetic functions are available or applicable. Therefore, mineralization, dissolution, or other transformation processes need to be considered and applied to solids. CTT&F performs a mass

balance for each solid variable on grid cells based upon specified transport processes, along with special kinetics processes. Mass balance computations are performed in soil/sediment layers as well as the water columns.

Overland flow

$$\begin{aligned} & \overbrace{\frac{\partial(hC_c^r)}{\partial t} + \frac{\partial(q_x C_c^r)}{\partial x} + \frac{\partial(q_y C_c^r)}{\partial y}}^{\text{Solid advection}} - \overbrace{\frac{\partial}{\partial x} \left(hD_x \frac{\partial C_c^r}{\partial x} \right) - \frac{\partial}{\partial y} \left(hD_y \frac{\partial C_c^r}{\partial y} \right)}^{\text{Solid dispersion}} \\ & = J_{ce} - J_{cd} + \sum S_k \end{aligned} \quad (38)$$

Upper soil layer

$$\frac{\partial(z_m C_{c2}^r)}{\partial t} = -J_{ce} + J_{cd} + \sum S_k \quad (39)$$

where:

- C_c^r = solid contaminant concentration in the overland flow [M/L³]
- C_{c2}^r = solid concentration of the contaminant in the upper soil layer [M/L³]
- J_{ce} = solid contaminant erosion flux [M/L²/T]
- J_{cd} = solid contaminant deposition flux [M/L²/T].

Solid contaminant transport processes in the overland plane consist of four types: advection, dispersion, erosion, and deposition.

Solid erosion

In the overland plane, solid contaminants can be detached from the bulk soil matrix by raindrop (splash) impact and entrained into the flow by hydraulic action. Therefore, the contaminant erosion flux may be computed using the same method as soil erosion.

$$J_{ce} = v_r C_{c2}^r \quad (40)$$

Solid deposition

Deposition is the loss of material entrained in a flow to the land surface by gravity. The deposition flux may be expressed as a mass rate of particle

removal from the water column over time and the concentration of contaminant particles that are entrained in the flow:

$$J_{cd} = v_{se} C_c^r \quad (41)$$

Solid contaminant transport capacity can be calculated using a modified sediment transport capacity formula for individual particle size distribution.

Transformation processes

The kinetics processes considered in the overland regime include mineralization and dissolution.

Solid mineralization. Within a watershed, a solid phase is subject to weathering reactions that are a source of contaminants to waters. The solid contaminant mineralization rate is determined by using the first order equation:

$$J_{mnr} = k_{mnr} C_c^r \quad (42)$$

where:

J_{mnr} = mass loss by solid contaminant mineralization [M/L²/T]

k_{mnr} = mineralization rate in water or soil [1/T].

Solid dissolution. When contaminants exist in the solid phase and are not necessarily adsorbed to soil particles, dissolution into water is a primary mechanism by which solid phase contaminant contamination spreads. Once dissolved, the contaminants are available for transfer or transformation. Dissolution rates of solid-phase explosives describe the speed at which the explosives enter the water-soluble phase under optimal conditions of contact between the phases. The maximum aqueous concentration that the contaminant can attain at a specific temperature, if the water and solid phases remain in contact long enough, is the solubility. Not only does inclusion of solid contaminant 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 contaminants. One way to describe the

dissolution rate is the first-order approximation of the dissolution process (Cussler 1997):

$$J_{dsi} = \frac{D}{h} \alpha (S - C_d^r) = k_{dsi} \alpha (S - f_d C_T^r) \quad (43)$$

where:

J_{dsi} = mass loss by solid contaminant dissolution [M/L²/T]

D = aqueous phase diffusion coefficient [L²/T]

h = boundary layer film thickness [L]

$D/h = k_{dsi}$ = also called the mass transfer coefficient [L/T]

α = area available for mass transfer between the solid and liquid [L²]

S = solubility of the contaminant [M/L³].

The selection of dissolution rate equations greatly affects not only the predicted persistence of contaminant compound sources but also their resulting concentrations in solution. For explosive contaminant compounds, dissolution rates have not been widely studied. The dissolution rate for explosives and byproducts has rarely been measured. Laboratory studies to determine the dissolution rates for the primary high explosives trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), and cyclotetramethylene-tetranitramine (HMX) as well as formulations commonly used in munitions are currently in progress at the ERDC. Once available, it will be included in the CTT&F sub-model. Total solid contaminant kinetics transformation flux in the overland regime is:

$$\sum S_k = H(-J_{mnr} + J_{kji}) - J_{dsi} \quad (44)$$

Substituting the all source/sink terms into Equations (38) and (39) leads to:

$$\frac{\partial(hC_c^r)}{\partial t} + \frac{\partial(q_x C_c^r)}{\partial x} + \frac{\partial(q_y C_c^r)}{\partial y} - \frac{\partial}{\partial x} \left(hD_x \frac{\partial C_c^r}{\partial x} \right) - \frac{\partial}{\partial y} \left(hD_y \frac{\partial C_c^r}{\partial y} \right) \quad (45)$$

$$= v_r C_{c2}^r - v_{se} C_c^r + \sum S_k$$

$$\frac{\partial(z_m C_{c2}^r)}{\partial t} = -v_r C_{c2}^r + v_{se} C_c^r + \sum S_k \quad (46)$$

Transport and transformation of contaminants in 1D channel/stream

The 1D channel model is developed to simulate the contaminant transport process in the solute and the solid, on the suspended sediments, and in the bed sediments. The model of the cross-sectionally averaged concentrations of contaminants in channels, within a watershed, is formed by writing mass conservation equations for two conceptual areas: the channel and the bed sediments as follows. Within the channel, contaminants in channel networks are transported by the water flow (advection processes) with the simultaneous influence of the turbulent diffusion processes. The contaminants can interact with the suspended sediments and bed depositions. Particulate contaminants settle through water column segments and deposit to or erode from surficial benthic segments. Advection and dispersion are not included in the bed sediments, where downstream transport is negligible. Within the bed, dissolved contaminants migrate downward or upward through percolation and pore water diffusion. Particulate contaminants migrate downward or upward through net sedimentation or erosion. Bed sediments are envisioned as a single, well-mixed layer. The contaminant mass balance equations track all sources, losses, and internal transformations of contaminants in the channel.

Governing equations for contaminants with equilibrium partitioning

Internal transport of a contaminant 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. Consideration of these important mechanisms leads to the familiar 1D advection-dispersion equation (Environmental Laboratory 1990; Runkel and Broshears 1991). Assuming the local equilibrium kinetics are satisfied, the governing mass conservation equation of the channel contaminant transport model is written for the total contaminant concentration as follows.

Channel flow

$$\begin{aligned} \frac{\partial C_T^w}{\partial t} + \frac{Q}{A} \frac{\partial C_T^w}{\partial x} - \frac{1}{A} \frac{\partial}{\partial x} \left(A D_x \frac{\partial C_T^w}{\partial x} \right) &= \frac{q_l}{A} (C_T^r - C_T^w) \\ &+ \frac{1}{h} (J_{pe} - J_{pd} - J_{dt}) + J_{dd} + \sum S_k \end{aligned} \quad (47)$$

Bed sediments

$$\frac{\partial C_{T2}^w}{\partial t} = \frac{1}{Z_m} (-J_{pe} + J_{pd} - J_{dd}) + \sum S_k \quad (48)$$

where:

C_T^w = total contaminant concentration in the channel flow
[M/L³]

q_l = channel transmission loss rate [L/T]

$J_{pe} = \sum_1^N f_{pn} v_r C_{T2}^w$ = sorbed contaminant resuspension rate of the bed
sediments [M/L²/T]

$J_{pd} = \sum_1^N f_{pn} v_{se} C_T^w$ = sorbed contaminant deposition rate [M/L²/T]

$J_{dt} = q_t (f_d + f_b) C_T^w$ = dissolved contaminant transmission loss flux [M/L²T]
 J_{dd} = pore water diffusion flux of dissolved contaminants
[M/L³/T]

C_{T2}^w = total contaminant concentration in the bed sediments
[M/L³]

$\sum S_k$ = other source/sink term such as hydrolysis, photolysis,
etc. [M/L³/T].

Contaminant transport processes considered in the channel networks include advection, dispersion, erosion, deposition, transmission loss, and pore water diffusion. Depending on the dissolved concentration gradient, pore water diffusion may be a source or sink of contaminants for the overlying water column.

Pore water diffusion

Dissolved and bound constituents can be exchanged between the sediment bed and the water column by pore water diffusion, particularly for relatively soluble contaminants. Depending on the dissolved contaminant concentration gradient, pore water diffusion may be a source or sink of pollutants to overlying waters. The actual diffusive flux is given by:

$$J_{dd} = \frac{EA_s}{L_c} (f_d + f_b) (C_{T2}^w - C_T^w) \quad (49)$$

where:

- E = diffusion coefficient [L^2/T]
- A_s = interfacial area [L^2]
- L_c = characteristic mixing length [L], which is usually taken to be the depth of the surficial sediment segment.

Transformation processes

The kinetics processes considered in the channel networks include decay, hydrolysis, oxidation, photolysis, volatilization, and user-defined extra reaction. Total contaminant kinetics transformation flux is:

$$\begin{aligned} \sum S_k &= -J_{bio} - J_{hyd} - J_{oxi} - J_{pht} - J_{vlt} - J_{urd} + J_{kji} \\ &= -(k_{bio} + k_{hyd}f_d + k_{oxi} + k_{pht} + k_{vlt}f_d + k_{udr})C_T^w + J_{kji} \end{aligned} \quad (50)$$

Substituting all source/sink terms into Equations (46) and (47) leads to:

$$\begin{aligned} \frac{\partial C_T^w}{\partial t} + \frac{Q}{A} \frac{\partial C_T^w}{\partial x} - \frac{1}{A} \frac{\partial}{\partial x} \left(AD_x \frac{\partial C_T^w}{\partial x} \right) &= \frac{q_i}{A} (C_T^r - C_T^w) \\ &+ \frac{1}{h} \left[\sum_1^N f_{pn} (v_r C_{T2}^w - v_{se} C_T^w) - q_t (f_d + f_b) C_T^w \right] \\ &+ EA_s (f_d + f_b) (C_{T2}^w - C_T^w) + \sum S_k \end{aligned} \quad (51)$$

$$\frac{\partial C_{T2}^w}{\partial t} = \frac{1}{z_m} \sum_1^N f_{pn} (v_{se} C_T^w - v_r C_{T2}^w) - EA_s (f_d + f_b) (C_{T2}^w - C_T^w) + \sum S_k \quad (52)$$

Governing equations for solids

For a solid contaminant in channels, due to its solid nature, there is no mass transfer from sediment pore water and volatilization processes. The contaminant transport process is described by the 1D advection-diffusion equation that includes deposition, resuspension, lateral distributed inflow of contaminants, and associated transformation processes.

Channel flow

$$\frac{\partial C_c^w}{\partial t} + \frac{Q}{A} \frac{\partial C_c^w}{\partial x} - \frac{\partial}{\partial x} \left(AD_x \frac{\partial C_c^w}{\partial x} \right) = \frac{q_l}{A} (C_c^r - C_c^w) + \frac{1}{h} (J_{ce} - J_{cd}) + \sum S_k \quad (53)$$

Bed sediments

$$\frac{\partial C_{c2}^w}{\partial t} = \frac{1}{z_m} (-J_{ce} + J_{cd}) + \sum S_k \quad (54)$$

where:

- C_c^w = solid contaminant concentration in the channel flow [M/L³]
- $J_{ce} = v_r C_{c2}^w$ = solid contaminant deposition rate (downward directed flux) [M/L³/T]
- $J_{cd} = v_{se} C_c^w$ = solid contaminant resuspension rate of the bed sediments (upward directed flux) [M/L³/T]
- C_{c2}^w = solid contaminant concentration in the bed sediments [M/L³].

Solid contaminant transport processes in the sub-model consist of four types: advection, dispersion, erosion, and deposition. The kinetics processes considered in the channel networks include mineralization, abrasion, dissolution, and parent-daughter transformation. Total solid contaminant kinetics transformation flux is:

$$\sum S_k = -J_{mnr} + J_{kjl} - H \cdot J_{dsl} \quad (55)$$

Substituting all source/sink terms into Equations (53) and (54) leads to:

$$\frac{\partial C_c^w}{\partial t} + \frac{Q}{A} \frac{\partial C_c^w}{\partial x} - \frac{\partial}{\partial x} \left(AD_x \frac{\partial C_c^w}{\partial x} \right) = \frac{q_l}{A} (C_c^r - C_c^w) + \frac{1}{h} (v_r C_{c2}^w - v_{se} C_c^w) + \sum S_k \quad (56)$$

$$\frac{\partial(z_m C_{c2}^w)}{\partial t} = -v_r C_{c2}^w + v_{se} C_c^w + \sum S_k \quad (57)$$

Solution of the governing equations

The coupled set of CTT&F differential equations is solved by numerical techniques. The CTT&F sub-model follows the same spatial discretization convention used by GSSHA. The general procedure follows for the hydrologic and sediment routing equations, which use a finite difference control volume solution scheme. Flow and sediment are assumed to be unaffected by contaminant transport processes. A watershed system is discretized into a mesh of square grids, the locations of which are described in terms of rows (I), columns (J), and layers (K) as illustrated in Figure 6.

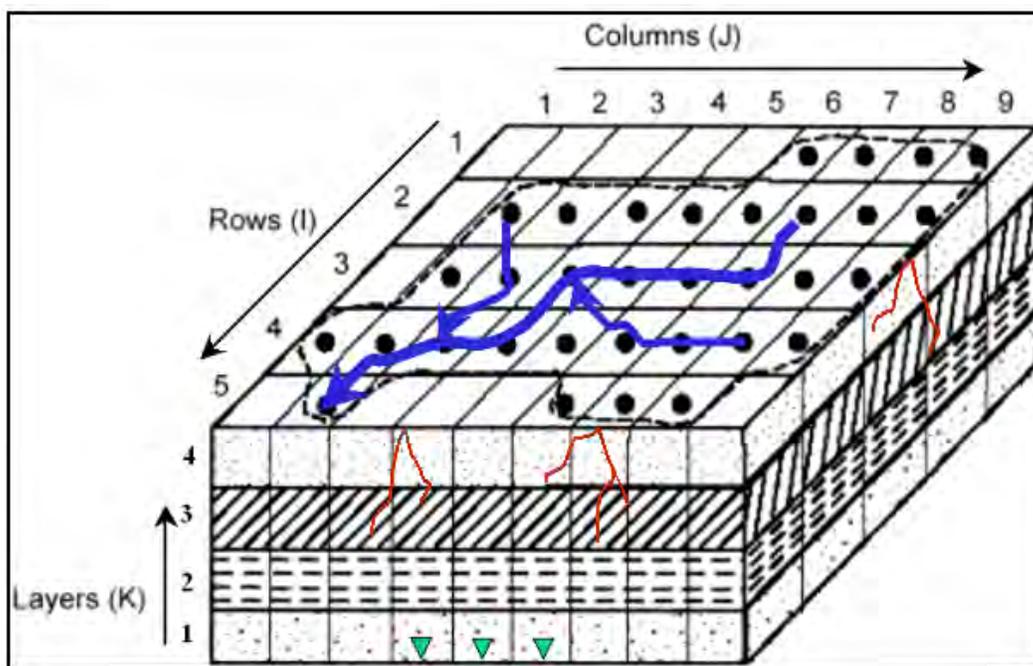


Figure 6. Spatial discretization of a watershed system.

The finite differential equations for contaminant transport and transformation are solved on the square digital elevation map (DEM) representing the watershed land surface and the equations evaluated at each point in space over the temporal evolution of the landform. DEM-derived local drainage directions are used as the basis for channel routing. However, the channel routing is conducted up and down slope lines across the watershed. In the sub-model, contaminant transport and transformation simulation is based on the flow solution provided by a separate hydrologic model. The length of the time-step used for the flow solution is generally

to be used as the length of the time-step for the transport and transformation solution; however, the transport solution's stability constraints and/or accuracy requirements should be satisfied. By using a finite-difference algorithm, solution of the sub-model yields a general equation of the form:

$$C(x, y, t) = \begin{pmatrix} \text{Hydrologic} \\ \text{Transport} \end{pmatrix} + \begin{pmatrix} \text{Contaminant} \\ \text{Transformation} \end{pmatrix} \quad (58)$$

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

This equation describes the spatial and temporal variation in contaminant concentration as a function of several hydrologic and biochemical parameters. The hydrologic processes affect the transport of all water-borne contaminants. Transformation reactions can be sources or sinks for each modeled contaminant.

4 Model Testing and Validation Studies

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, in addition to other explosives, 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 has been associated with liver and blood damage and anemia. RDX has been associated with systemic poisoning usually affecting bone marrow and the liver. Risk assessments should adequately link a contaminant source, transmission pathways, and exposure potential. The objective of this validation study was to illustrate the use of CTT&F to quantify transport, transformation, and fate of contaminants in watersheds and compare the model results with the measured values in the overland flow. Of interest are the explosive compounds RDX and TNT used by the military and their resulting presence in the environment.

Experiment set-up

Given the necessary field data, CTT&F can be used to assess the fate of explosive compounds in watershed systems. Modeling RDX and TNT has begun using data from a Camp Shelby, MS, firing range. Unfortunately, reliable watershed field data are still being collected and were not available for analysis and inclusion in this report. In order to validate the general performance of the model, the CTT&F sub-model has been evaluated by means of a test case study of explosives transport and transformation in a laboratory setting.

A laboratory experiment was conducted using simulated rainfall and overland flow associated with sediment and contaminant transport. The laboratory experiment procedure was designed to mimic field conditions resulting from the direct action of rainwater on distributed sources at military installations. The experimental plot was 9.0 ft by 7.5 ft. The bed slope of the plot was designed with a 2 percent slope for collecting runoff water from the surface of the soil. Two land covers were used for the experiment to simulate two different surface roughnesses: “disturbed”

(unvegetated) and “undisturbed” (vegetated). The soils used in the laboratory experiment were obtained from the Camp Shelby military firing range. The contaminant and physical properties of the soils were analyzed before rainfall was applied.

The rainfall was applied uniformly across the plot using a rainfall simulator. Rainfall intensity for the overall plot area ranged between 2.7 to 2.9 in./hr; giving a mean intensity of 2.8 in./hr. The simulated rainfall events lasted 30 ±, 60 ±, and 90 minutes. Runoff and sediment were collected at the downstream end of the plot and measured volumetrically.

Runoff rates and volumes were collected on a 1-minute time increment and were continued until no appreciable flow was observed at the plot outlet. Samples for total suspended sediment (TSS) were collected every minute for the first 15 minutes of runoff, then every 5 minutes afterward.

To simulate the transport and transformation of RDX and TNT, a total of 500 g of Comp B of varying sizes (less than 1 cm in diameter and 2 mm thick to 3.5 cm in diameter and 2.5 cm thick) was applied uniformly onto the soil surface. After the Comp B application, the soil surface was subjected to a simulated rainfall event, which induced overland flow and contaminant transport. Comp B is commonly present as crystalline solids and is a 60/39 mixture of RDX and TNT that contains 1 percent wax. This compound has been used in munitions since World War II for its high explosive yield.

The experimental plot domain consisted of 30 grid cells with a grid cell resolution of 1.5 ft by 1.5 ft. The computational time step for the model simulation was 0.5 sec, with an initial application of Comp B of 500 g assumed to be spread uniformly across the grid cells. The physical, chemical, and biological properties of RDX and TNT and their kinetic reaction rates required by the model were estimated by using the data collected from the experiment. Table 1 shows the observed average explosive compound concentrations for three Comp B samples. Other relevant parameters, shown in Table 2, Lever et al. (2005), and McGrath (1995), were evaluated but ultimately were adjusted by trial-and-error to reproduce the measured concentrations of RDX and TNT.

Table 1. Analysis for three Comp B particles.

Comp B	HMX mg/kg	RDX mg/kg	TNT mg/kg
1	59424	562798	350955
2	68039	637121	393580
3	71505	672170	422214

Table 2. Model parameters for RDX and TNT in water.

Parameter	Comp B	RDX	TNT
Aqueous solubility (25 °C) (g/cm ³)	-	4.6 x 10 ^{-5,a}	1.3 x 10 ^{-4,a}
Diffusion coefficient (25 °C) (cm ² /s)	-	2.2 x 10 ^{-6,a}	6.7 x 10 ^{-6,a}
Density (g/cm ³)	1.65 ^a	1.82 ^b	1.654 ^b
1 st order transformation rate (1/hr)	-	0 - 1.0 x 10 ^{-1,b}	-

^a From Lever et al. (2005).

^b From McGrath (1995).

Many transformation processes affecting explosives are active primarily in the aqueous phase (e.g., biotransformation) and therefore may be limited by dissolution kinetics. A quantitative understanding of the multiple controls on solubility and dissolution is necessary to predict contaminant loading rates to the surface water from contaminated soils. This study gives the results in predicted solid persistence and multi-phase contaminant loading from this solid into aqueous solution for TNT and RDX.

Model results and discussion

In this analysis, rainfall resulted in overland flow causing erosion and dissolution of the solid Comp B with a fraction of the rainfall infiltrating the soil. Even though distributed observations for RDX and TNT concentrations were not measured in this study, the model can be used to infer and trace the migration of distributed RDX and TNT sources. As expected, the onset of rainfall resulted in dissolution of the solid explosive, with infiltration and wash-off resulting in removal of the solid within a short period of time. The graphical representation of the spatial variation of dissolved contaminant 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 sub-surface area occurs. The model results can provide quantitative information on the amount of contaminant infiltrating into the sub-surface. These

results are important when investigating the loss of explosives due to the transport and transformation of distributed sources within a watershed.

In this study, the model was calibrated by comparing the simulated model results to measured surface runoff, sediment concentration, and contaminant concentration. The model parameters were adjusted so that the errors between simulated and measured values were minimized. Table 3 lists calibration results for this test case study.

Methods used to evaluate model performance included comparison of simulated and measured results through statistical analysis. The most fundamental approach to assessing model performance in terms of behavior is through visual inspection of the simulated and observed results. For describing the goodness of fit to the overall hydrographs and pollutographs, the RMSEs (Root Mean Square Errors) were calculated and given in Table 3. For surface runoff from both unvegetated and vegetated plots, the simulated values compared reasonably well with the plot measurements. The event-averaged percent error of simulated total surface discharge, for both roughness conditions, was less than 10 percent of its corresponding measured value. The RMSE value between simulated and measured results for the unvegetated plot and vegetated plot were 1.195 and 0.641, respectively.

Table 3. Comparison of simulated and measured hydrographs and pollutographs.

Parameter	Simulated	Measured	Error ^a (%)	RMSE ^b
Unvegetated Plot				
Surface runoff (L/min)	189.72	201.75	5.96	1.195
Total suspended sediment (mg/L)	20917.60	30653.33	31.76	719.47
Dissolved RDX (mg/L)	2.805	2.782	0.84	0.012
Dissolved TNT (mg/L)	3.806	3.776	0.79	0.012
Vegetated Plot				
Surface runoff (L/min)	151.20	39.83	8.13	0.641
Total suspended sediment (mg/L)	726.02	2106.67	65.53	134.00
Dissolved RDX (mg/L)	1.155	1.207	4.32	0.052
Dissolved TNT (mg/L)	0.443	0.417	6.34	0.014

$$^a \text{Error}(\%) = \frac{\sum_i \text{simulated value}_i - \sum_i \text{measured value}_i}{\sum_i \text{measured value}_i} \times 100$$

$$^b \text{RMSE} = \sqrt{\frac{1}{n} \sum_i (\text{simulated value}_i - \text{measured value}_i)^2}$$

In regard to sediment runoff, the model was not capable of capturing the initial wash-off of sediments. Thus, the event-averaged percent error of simulated TSS concentration from both unvegetated and vegetated plots was 31.76 and 55.22 percent, respectively. The model performance for TSS concentration was strongly affected by the six initial samples collected, and extremely high sediment concentrations were measured from these samples.

As the model simulation proceeded, the results showed that the model was capable of capturing the general trends of TSS concentration over time; the simulated values compared well with measured values after the initiation of the event. The Error and RMSE values were greatly improved without the inclusion of the first six samples. For explosive compounds, simulated errors are very small (within 7 percent). From the model output, one can see that the model performed well for the two datasets.

Comparisons of the overall shape of simulated and measured results over time for surface runoff discharge, TSS concentration, dissolved RDX and TNT concentrations in surface runoff are shown in Figures 7 to 10, respectively. As one can see, the agreement of model simulations and experimental results for the explosive compounds from the field is satisfactory, thus indicating that the physically based distributed CTT&F sub-model is able to capture explosive transport and transformation processes controlled by dissolution.

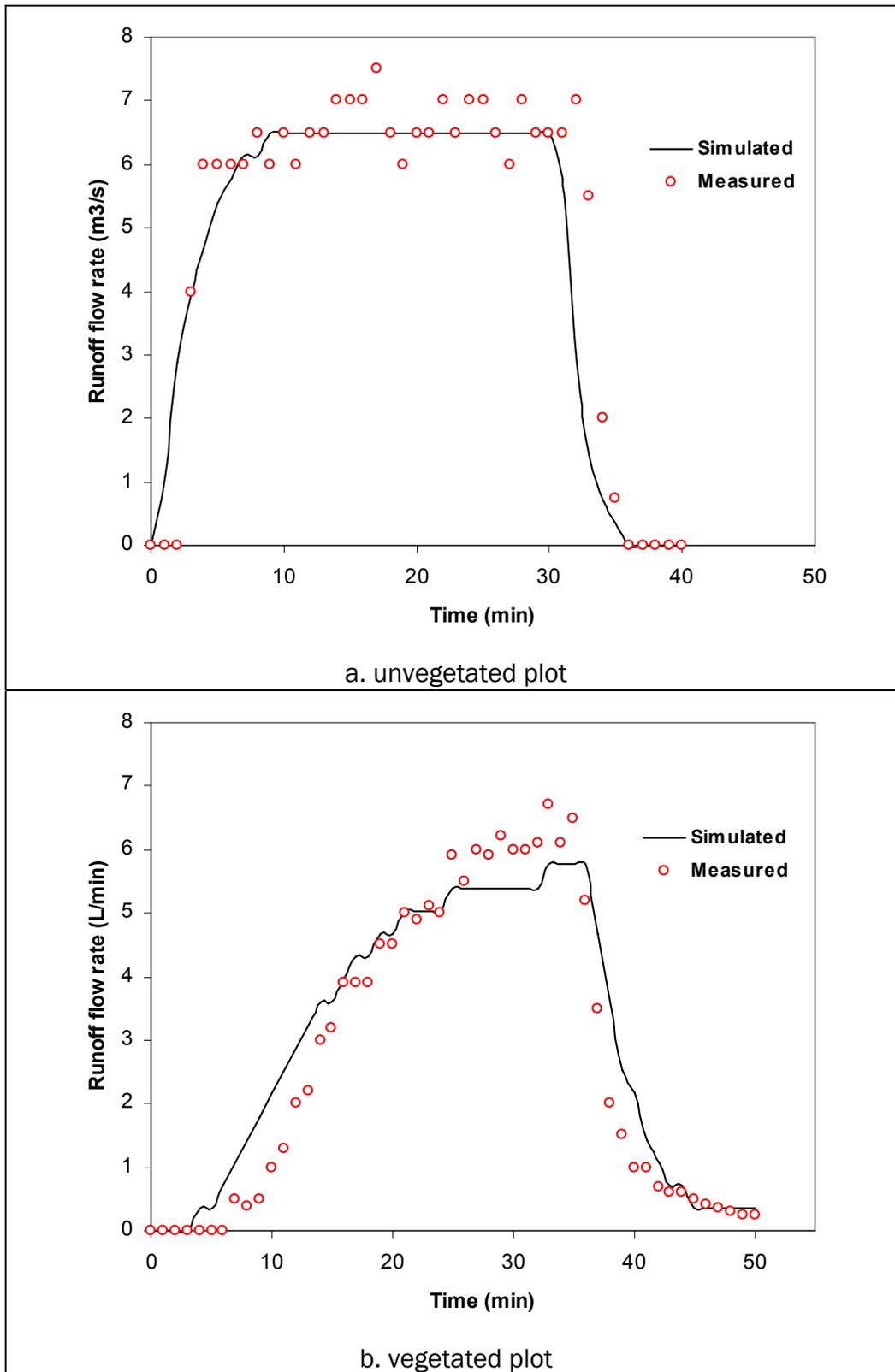


Figure 7. Comparison of simulated and experimental results over time for surface runoff discharge from unvegetated and vegetated plots.

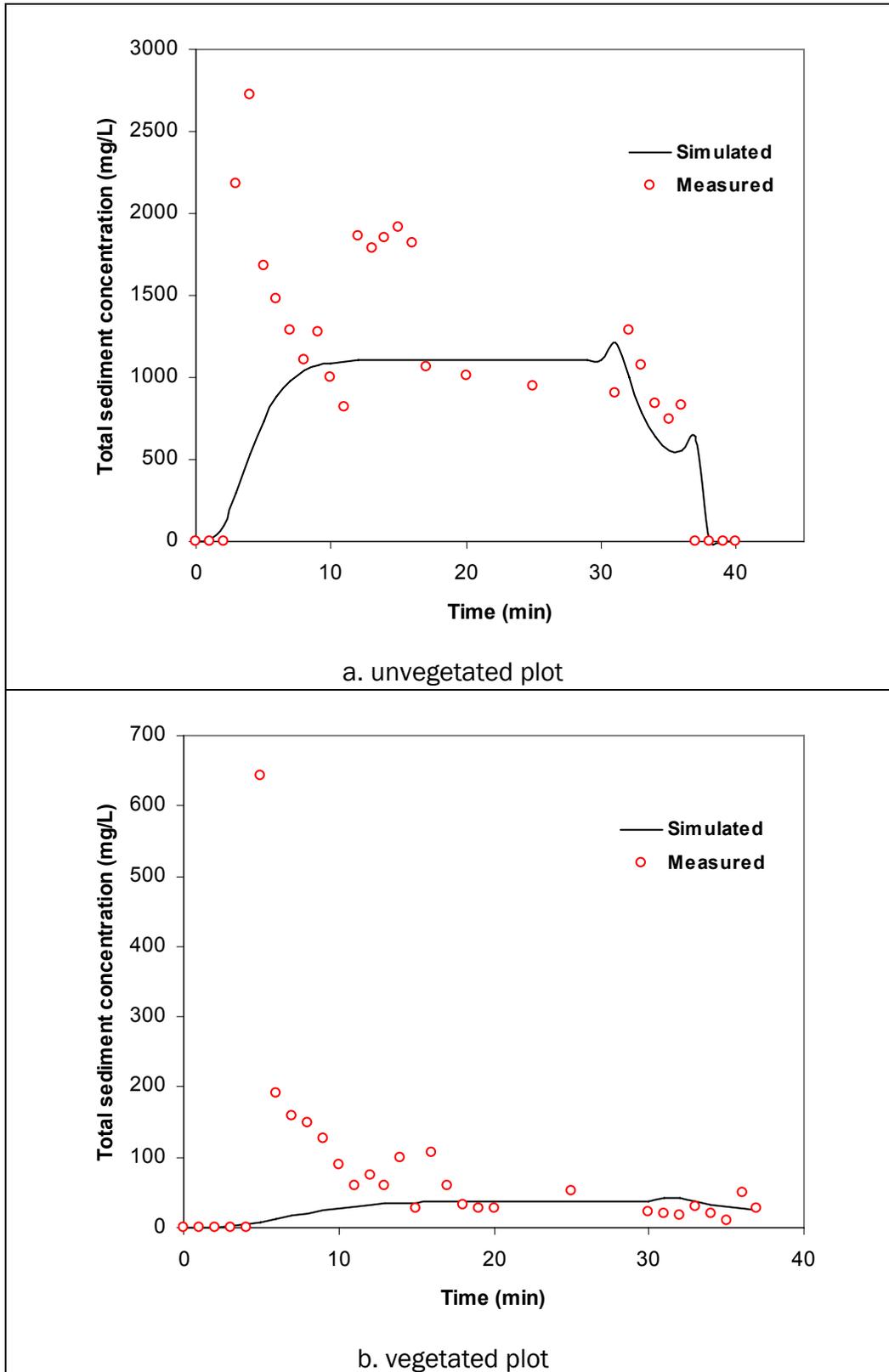


Figure 8. Comparison of simulated and experimental results over time for TSS concentration in overland flow from unvegetated and vegetated plots.

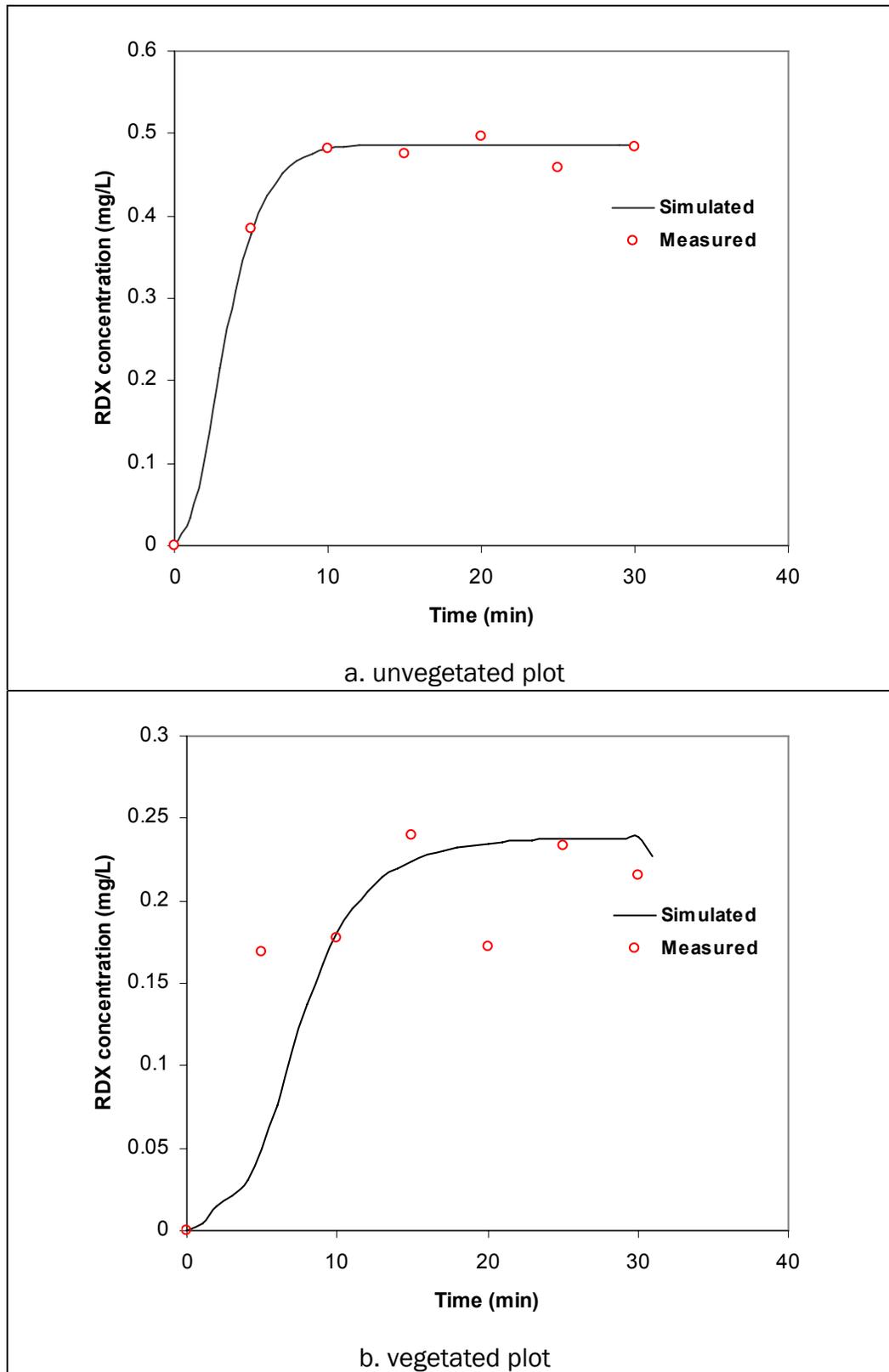


Figure 9. Comparison of simulated and experimental results over time for dissolved RDX concentration in overland flow from unvegetated and vegetated plots.

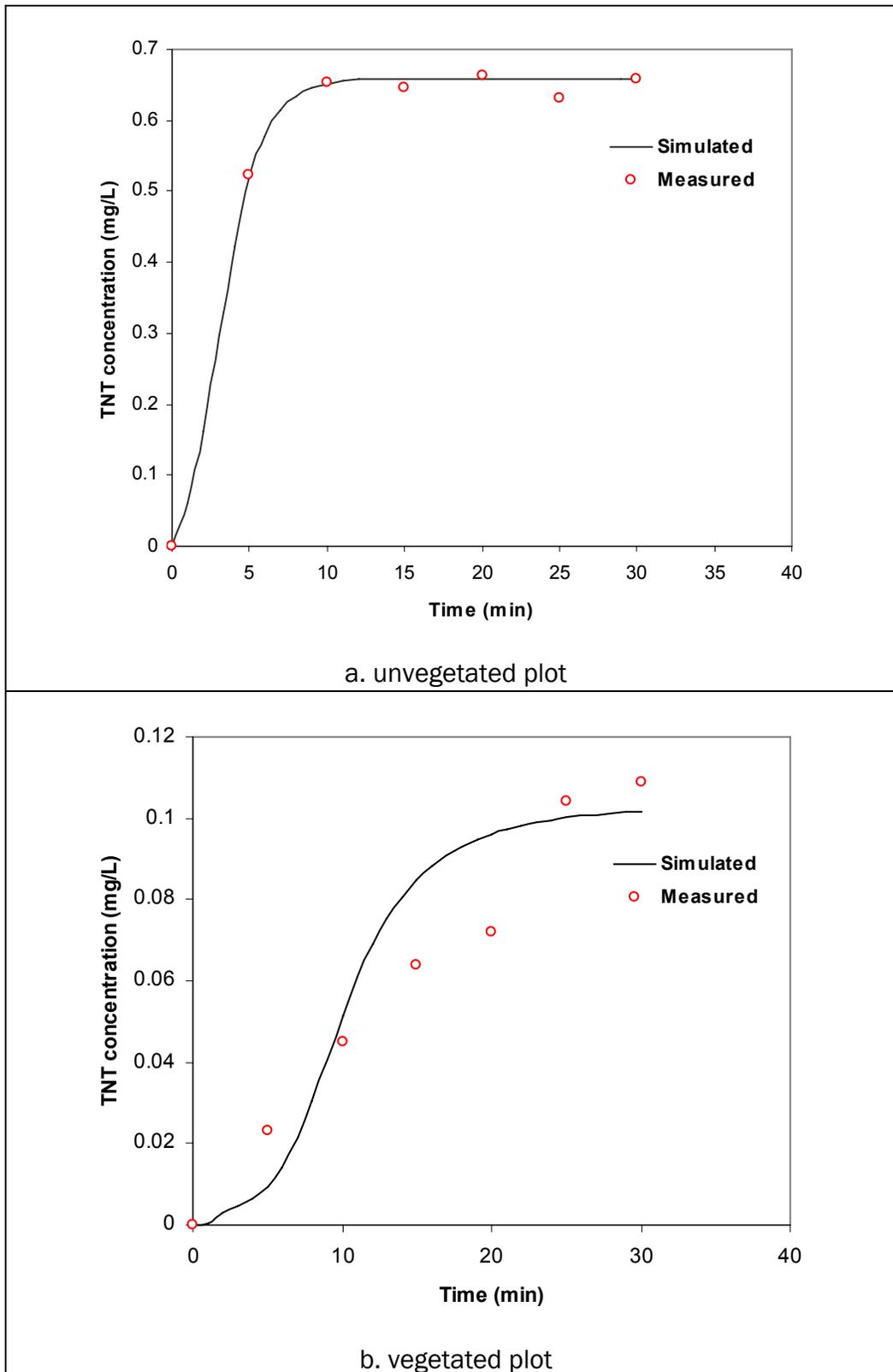


Figure 10. Comparison of simulated and experimental results over time for dissolved TNT concentration in overland flow from unvegetated and vegetated plots.

5 Conclusions and Recommendations

Conclusions

A contaminant transport, transformation, and fate sub-model, CTT&F, has been developed based on the mass conservative form of the coupled system of 2D overland flow and 1D channel flow for simulating distributed sources for watersheds. The sub-model works on a grid basis for considering spatially varied soils, land uses, and other hydrologic characteristics. The CTT&F equations described in the report are comprehensive, self-consistent, and fully compatible with the physically based, distributed watershed hydrologic models, which provide the required hydrological and sediment variables. Coupled with a distributed watershed model, CTT&F is able to simulate both surface runoff and channel processes of contaminants. The physical basis is important since it provides the link between simulations and physical property measurements. 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 evaluated for RDX and TNT using experimental data from a laboratory. Comparisons between simulated and measured results for hydrologic, sediment, and contaminant variables of the model have been described. The comparisons showed that RDX and TNT concentrations in overland flow can be simulated accurately. The ability to simulate spatially distributed concentrations, within a watershed scale, has not been evaluated due to a lack of field data at this time. As field data are collected, CTT&F will be evaluated for RDX and TNT at the Camp Shelby firing ranges.

Recommendations

The CTT&F sub-model framework is designed to be modular to allow future development and addition of expanded features. The following recommendations are made to further the development of the model.

The unsaturated zone is the portion of the sub-surface above-the-ground water table. Many constituents present in the surface water eventually find their way into the groundwater through the unsaturated zone. Contaminant transport and transformation processes in the unsaturated zone will

be incorporated into CTT&F and their development is currently in progress.

The algorithms describing the transformation processes used in CTT&F were adapted from surface water quality models because transformation reaction mechanisms and their interrelations are poorly understood for explosives. Translating these understanding and algorithms into quantitative mathematical process descriptors for explosives is impeded by the nature of the information available and will require additional process-level research. Additional research should be conducted with explosives in surface waters and subsurface soil environments to delineate transformation parameters and process descriptors. It is important to determine the transformation kinetics of individual compounds and those of explosive formulations as well. The CTT&F sub-model should be improved by incorporating better process descriptors of explosives in these environments.

Accurate modeling of explosive compounds is complicated by the need to select the correct transformation process description and then select the correct coefficient for each variable supporting the model. Although literature exists describing explosive transformations, far less data are available for transformation rates to be used in the modeling framework. Considerable research remains to be conducted to measure the values of these parameters in order to know the importance of these processes. Processes and parameterizations developed under idealized conditions at the laboratory scale are not likely to accurately depict the field-scale situation. Field-scale data collection is needed so that appropriate model parameters can be determined for calibration purposes.

Contaminant transformation and transport at sites contaminated with multiple explosive compounds will be challenging to simulate with a model. Each specific explosive formulation is expected to dissolve differently depending on composition and manufacturing processes. The interaction between different contaminants needs to be better understood, in some cases, in order to accurately model these scenarios.

Environmental conditions such as soil temperature, water temperature, and pH should be incorporated into the CTT&F sub-model in order to aid in the interpretation of data and to more accurately describe process descriptors such as dissolution kinetics, adsorption rates, biodegradation rates, hydrolysis rates, oxidation rates, photolysis rates, etc. Further

development is needed to add a series of spatially and temporally varying time functions to represent environmental conditions existing in the watershed environment, which can give insight on both the persistence of explosives as well as their fate processes.

Currently CTT&F does not have a plant dynamics capability. In future development efforts, attention needs to be given to contaminant uptake, by plant species and biomass generation from the plant communities. This capability will allow CTT&F to address phytoremediation scenarios.

The CTT&F equations need to be further validated directly against field data. Additional sets of validation studies are required to check the self-consistency and physical reasonableness of the CTT&F sub-model. It is critical to validate the model at the watershed scale in terms of data and modeling requirements. Past field-scale studies of explosives in military installations were generally not designed to examine which models provide the most robust, mechanistic description of contaminant transport and transformation processes. It is recommended that a research site be carefully chosen to validate a variety of contaminant processes of the CTT&F sub-model, and allow more rigorous evaluation of the robustness of alternative conceptual processes.

The potential for explosives contamination and the potential for exposure of environmental and human receptors resulting from various military activities cannot be assessed without accurate watershed models. Usable and effective watershed models can be implemented for installation compliance as well as long-term watershed planning and management.

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14. ABSTRACT One of the responsibilities of the U.S. military is to operate munitions test and live-fire training ranges. As a result of this testing and training, many explosives and their degradation products persist in the environment. Ecosystem management by military installations can be met only by providing the tools necessary to actively manage watersheds. Water quality and related aquatic ecosystems are major end-points and are insufficiently understood components of natural resource management. Numerical modeling, as part of watershed management, is not new. Considerable advances have been made in physically based distributed watershed hydrologic modeling in the past few years; however, few physically based, distributed models simulate contaminant transformation and transport processes. This report summarizes the development of overland and channel contaminant fate and transport modules for linkage with a variety of hydraulic and hydrologic modeling systems.					
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