DEVELOPMENT OF A DISTRIBUTED WATERSHED CONTAMINANT TRANSPORT, TRANSFORMATION AND FATE (CTT&F) SUB-MODULE FOR MILITARY INSTALLATIONS

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1. INTRODUCTION

Many U.S. Department of Defense (DoD) installations contain soil, sediment, surface water, and groundwater environments contaminated with explosives and energetics (Brannon and Myers, 1997). Both TNT and RDX are widely used explosives. Human exposure can occur by drinking contaminated water, breathing contaminated air, or coming in contact with contaminated soil. Risk assessments should adequately link a contaminant source, transmission pathways, and exposure potential. Meanwhile, compliance with water quality regulations is becoming increasingly important at military installations. Ecosystem management to provide for sustained and future sustainable mission capacity remains the DoD policy for military installations. The ecosystem management expectation can only be met 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. These installations should be provided with immediately usable and effective models that can be implemented for compliance with water quality regulations as well as long-term watershed planning and management. Modeling as part of watershed management to meet water quality goals is not new but most current models were developed and tested two decades ago. Watershed models are largely confined to lumped and semi-distributed surface water simulation. 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.

To meet this need a physically based, distributed source Contaminant Transport, Transformation and Fate (CTT&F) sub-module was developed by the U.S. Army Engineer Research and Development Center, to simulate point and non-point sources across a watershed. The model operates on a cell by cell basis. Soil types, land uses, and other hydrologic characteristics can be varied spatially among cells. Potential chemicals are routed through the cells from the watershed divide to the outlet. The distributed, process-oriented structure of the model can be used for identifying critical source areas of non-point sources within the watershed, and can give insight on both the persistence and fate of explosives. The expectation is that a model of this type is able to quantify transport and transformation of multiple contaminants and can facilitate the assessment of the fate of distributed sources and lead to better management of the watershed environment for military installations. CTT&F can be linked to any distributed hydrologic model, assuming the hydrologic model provides the required flow and sediment transport fluxes. The ability of the model to simulate explosives in watersheds is demonstrated by a test case study in the laboratory environment.

2. GOVERNING EQUATIONS

To simulate the chemical transport processes in watersheds, it is necessary to estimate beforehand the hydrological variables. The hydrological variables required to drive CTT&F can be calculated using any distributed model capable of producing a reasonable simulation of the flow and sediment transport fields in the watershed. As presented in the SHETRAN model (Ewen, et al., 2000), the basic model components include hydrology, erosion, and sediment and chemical transport. The calculations for each process at any time level are independent and information is carried forward from the hydrology sub-module to the sediment transport sub-module to the chemical transport sub-module in order to generate a solution.

2.1 Hydrology and flow sub-module

Considerable advances have been made in physically based distributed hydrologic modeling

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watershed in the past few years. There are several grid-based, distributed models to simulate watershed 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 hydrometeorological inputs (Downer and Ogden, 2004). GSSHA is a reformulation and enhancement of the CASC2D model and encompasses the full hydrologic cycle.

The governing equations for water flow with the GSSHA or similar distributed models are based primarily on the Saint-Venant equations of continuity and momentum. Overland flow is routed in two orthogonal directions (x and y) in each grid cell during each time step. Once water enters a "channel" grid cell, then the volume of water is added to the channel system and routed to the watershed outlet. The 2D continuity equation for gradually-varied flow over a plane is:

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

where h = surface water depth [L]; q_x, q_y = unit discharges in the x- or y-direction [L^2/T]; and i_e = excess precipitation rate [L/T].

The diffusive wave approximation of the Saint-Venant equations have found wide application in many areas and are well established for modeling a variety of watershed hydrologic processes. The 2D diffusive wave momentum equations are described as:

$$S_{fx}=S_{0x}-\frac{\partial h}{\partial x}, \qquad S_{fy}=S_{0y}-\frac{\partial h}{\partial y} \qquad (2)$$

where S_{fx}, S_{fy} = friction slope in the x- or y-direction; and S_{0x}, S_{0x} = ground surface slope in the x- or y-direction.

2.2 Erosion and sediment transport sub-module

Sediment erosion and transport processes take place both on the land surface and within the channel network. Sediment erosion and transport are potentially very important processes at the watershed scale. Excess sediment can affect water quality directly. Sediment transport also influences chemical transport and fate. Many chemicals sorb strongly to sediment and thus undergo settling, scour, and sedimentation. Sorption also affects a chemical's mass transfer and transformation rates. Both sediment transport rates and concentrations must be simulated in most toxic chemical studies. For the overland plane in 2D, the concentration of sediment particles in a flow is governed by conservation of mass (sediment continuity) (Julien, 1998):

$$\frac{\partial C_s}{dt}+\frac{\partial q_{tx}}{\partial x}+\frac{\partial q_{ty}}{\partial y}=J_e-J_d+W_s \qquad (3)$$

where C_s = concentration of sediment particles in the flow [M/L^3]; q_{tx}, q_{ty} = total sediment transport areal flux in the x- or y-direction [M/L^2T]; J_e = sediment erosion volumetric flux [M/L^3T]; J_d = sediment deposition volumetric flux [M/L^3T]; and W_s = sediment point source/sink volumetric flux [M/L^3T].

The governing equations for the channel flow routing process are similar to those for overland flow, the flow and suspended sediment transport in channels is described by the 1-D equation.

2.3 Chemical transport, transformation and fate sub-module

The CTT&F sub-module includes all possible physical and biochemical processes taking place in the watershed. Physical transport mechanisms affect the spatial variability of chemical mass throughout the watershed. Partitioning and biochemical reactions, meanwhile, determine the distribution of chemical mass among different phases and thereby affect the amount of mass available for transport. In consideration of these important processes, the governing equations for chemicals are established over a differential control volume through which the fluid is flowing. A basic principle of contaminant transport models is the conservation of mass. Mathematically modeling for chemical transport involves the simultaneous solution of governing equations of both water flow and upper sediment. The soil sediment bed plays an important role in the transport of contaminants. Particles and associated chemicals in the surficial sediments may enter deeper sediment layers by burial or be returned to the water columns by scour. An overview of the processes included in CTT&F is presented in Fig. 1.

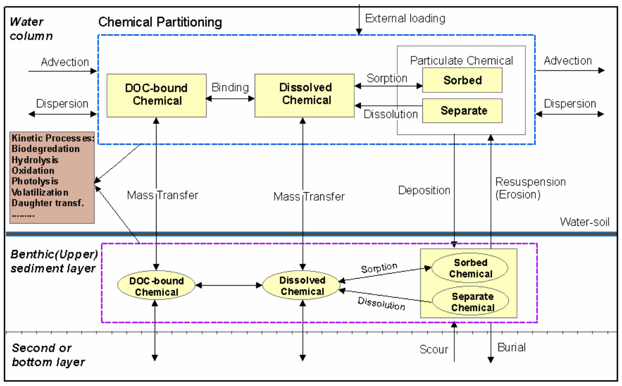


Fig. 1. Schematic chart of the key processes of CTT&F sub-module

2.3.1 Chemical partitioning and distribution

CTT&F incorporates “four phase partitioning”, where a contaminant may partition between solid particles, sediments, DOC, and water. Pure solid chemicals are assumed to be a separate phase and are modeled as reactive solid particles. Equilibrium partitioning between the truly dissolved (aqueous), particle-sorbed, and DOC-bound phases is assumed. The equilibrium partition coefficient can be used to describe the fraction of the total chemical that is associated with each phase. The concentration of the chemical in truly dissolved, bound, and particulate phases then can be calculated by:

$$C_d = f_d C_T, \quad C_b = f_b C_T, \quad C_p = \sum f_{pn} C_T \qquad (4)$$

$$f_b = \frac{k_b C_{DOC}}{1 + k_b C_{DOC} + \sum k_{pn} C_{pn}} \qquad (5a)$$

$$f_{p_n} = \frac{k_{pn} C_{pn}}{1 + k_b C_{DOC} + \sum k_{pn} C_{pn}} \qquad (5b)$$

$$f_d = 1 - f_b - \sum f_{pn} \qquad (5c)$$

where C_d = dissolved phase chemical concentration [M/L^3]; C_b = bound phase chemical concentration [M/L^3]; C_p = particulate phase chemical concentration [M/L^3]; C_T = total chemical concentration of the dissolved, DOC bound and sorbed phases [M/L^3]; f_d = fraction of the total chemical in the dissolved phase; f_b = fraction of the total chemical in the bound phase; f_{p_n} = fraction of the total chemical in the particulate phase associated with particle “*n*”; k_b = equilibrium binding coefficient [L^3/M]; C_{DOC} = concentration of DOC [M/L^3]; k_{pn} = particle-dependent partition coefficient [L^3/M]; and C_{pn} = concentration of particle “*n*” [M/L^3].

2.3.2 Chemical Transport

Overland transport of chemicals is vital for quantifying a distributed source. The transport processes that are included in the overland flow in CTT&F are advection, dispersion, infiltration, erosion and deposition, and mass transfer between overland flow and the upper soil. Consideration of these important processes leads to the 2D advection-dispersion equation (ADE). The governing equations for the total chemical concentration in the overland flow and upper soil layer, respectively, can be written as follows (Johnson and Zhang, 2006).

Overland flow:

$$\frac{\partial (hC_T^r)}{\partial t} + \frac{\partial (q_x C_T^r)}{\partial x} + \frac{\partial (q_y C_T^r)}{\partial y} - \frac{\partial}{\partial x}\left(hD_x \frac{\partial C_T^r}{\partial x} \right) - \frac{\partial}{\partial y}\left(hD_y \frac{\partial C_T^r}{\partial y} \right) = -J_{df} + J_{dm} + J_{pe} - J_{pd} + \sum S_k \qquad (6)$$

Upper soil layer:

$$\frac{\partial (zC_{T2}^r)}{\partial t} = J_{df} - J_{dm} - J_{pe} + J_{pd} + \sum S_k \qquad (7)$$

where C_T^r = total chemical concentration in the overland flow [M/L^3]; C_{T2}^r = total chemical concentration in the upper soil layer [M/L^3]; z = depth of the upper soil layer [L]; D_x, D_y = chemical dispersion coefficient in the x- or y-direction [L^2/T]; J_{df} = dissolved chemical infiltration flux [M/L^2/T]; J_{dm} = dissolved chemical mass transfer flux between surface water and upper soil layer [M/L^2/T]; J_{pe} = sorbed chemical erosion flux [M/L^2/T]; J_{pd} = sorbed chemical deposition flux [M/L^2/T]; and ΣS_k = total biochemical transformation flux, positive indicates a source, negative a sink [M/L^3/T].

Similarly, two conceptual areas are defined within the channel: the main channel and the bed sediment. Internal transport processes of a chemical occur in the channel are advective and dispersive movement, sedimentation, resuspension, and mass transfer between bulk water and benthic sediments. Consideration of these important mechanisms leads to the familiar 1D ADE. The governing equations for the total chemical concentration in the channel flow and benthic sediment, respectively, can be written as follows (Johnson and Zhang, 2006).

Channel flow:

$$\frac{\partial C_T^w}{\partial t} + \frac{Q_x}{A}\frac{\partial C_T^w}{\partial x} - \frac{1}{A}\frac{\partial}{\partial x}\left(AD_x \frac{\partial C_T^w}{\partial x} \right) = \frac{q_l}{A}\left(C_T^r - C_T^w \right) + \frac{1}{h}\left(J_{pe} - J_{pd} - J_{dt} \right) + J_{dd} + \sum S_k \qquad (8)$$

Bed sediments:

$$\frac{\partial (z_m C_{T2}^w)}{\partial t} = -J_{pe} + J_{pd} - J_{dd} + \sum S_k \qquad (9)$$

where C_T^w = total chemical concentration in the channel flow [M/L^3]; C_{T2}^w = total chemical concentration in the bed sediments [M/L^3]; Q_x = flow in the channel direction [L^3/T]; J_{dt} = dissolved chemical transmission loss flux [M/L^{2}T]; and J_{dd} = pore water diffusion flux of dissolved chemicals [M/L^3/T].

Beyond partitioning and mass transport processes, transformation of explosives has been observed as summarized by Townsend and Myers (1996) and their fate is potentially influenced by a number of biochemical transformation processes that include, but are not limited to, biodegradation, hydrolysis, oxidation, photolysis, volatilization. These processes may not be operative in all environmental settings. Some chemicals 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 chemical of interest and environmental settings. The chemicals may be independent or they may be linked with reaction yields, such as a parent compound-daughter product sequence. CTT&F allows the simulation of a variety of biochemical processes that may affect chemicals, which were adapted, in part, from the WASP (Ambrose, et al., 1993) and IPX (Velleux, et al., 2000) water quality models because biochemical transformation mechanisms and their interrelations are poorly understood for explosive compounds. The transport equations described above must be supplemented by the following biochemical process fluxes as source or sink terms.

2.3.3 Biodegradation of chemicals

CTT&F simulates biodegradation as a first-order kinetics process, 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 can be combined into a single decay coefficient.

$$\frac{\partial C_T}{dt} = k_{bio} C_T \tag{10}$$

where k_{bio} = overall biodegradation rate [1/T].

2.3.4 Hydrolysis of Chemicals

Hydrolysis is a reaction in which cleavage of a molecular bond of the chemical and formation of a new bond with either the hydrogen or the hydroxyl component of a water molecule occurs. Hydrolysis by specific acid, neutral, or base-catalyzed pathways is considered for the various species and phases of each chemical. The total rate of hydrolysis transformation of a chemical is computed by CTT&F as the sum of three contributing processes.

$$k_{hyd} = \sum_j \left(k_{aj} \left[H^+ \right] + k_{nj} + k_{bj} \left[OH^- \right] \right) f_j \tag{11}$$

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

2.3.5 Oxidation of Chemicals

Oxidation is modeled by CTT&F as a general second-order process for the various species and phases of each chemical. Oxidation reactions are computed from the chemical input data and the total environmental concentrations of reactive oxidizing species.

$$k_{oxi} = [RO_2] \sum_j k_{oj} f_j \tag{12}$$

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

2.3.6 Photolysis of chemicals

Photolysis or photodegradation is the transformation of a chemical due to absorption of light energy. The first order rate coefficient for photolysis is calculated by CTT&F from the absorption rate and the quantum yield for chemical in each phase.

$$k_{pht} = \sum_j k_{aj} \phi_j f_j \tag{13}$$

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

2.3.7 User-defined extra reaction of chemicals

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

$$k_{urd} = [E] \sum_j k_{ej} f_j \tag{14}$$

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

2.3.8 Dissolution of solid phase chemicals

Explosives associated compounds are commonly present as crystalline solids (McGrath (1995). Dissolution of solid phase chemicals into water is a primary mechanism by which solid chemical contamination spreads through. Once dissolved, the chemicals are available for transport or other biochemical transformation processes. For explosive chemical compounds dissolution rates have not been widely studied. In CTT&F, the first-order approximation of the dissolution process is used to describe explosive dissolution rate (Cussler, 1997):

$$\frac{\partial VC_s}{dt} = k_{dsl} \alpha \left[S - \left(f_d + f_b \right) C_T \right] \tag{15}$$

where C_s = solid phase chemical concentration [M/L^3]; k_{dsl} = the dissolution mass transfer coefficient

[L/T]; α = area available for mass transfer between the solid and liquid [L^2]; and S = aqueous solubility of the chemical [M/L^3].

2.3.9 Transformations and daughter products

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

$$J_{kji} = \sum_j \sum_k k_{kj} C_j Y_{kji} \tag{16}$$

where J_{kji} = production of chemical "i" from chemical "j" undergoing reaction "k" [$M/L^3/T$]; K_{kj} = effective rate coefficient for chemical "j" reaction "k" [1/T]; and Y_{kji} = yield coefficients for production of chemical "i" from chemical "j" undergoing reaction "k" [M/M].

2.3.10 Numerical solutions

The coupled set of CTT&F differential equations is solved by numerical techniques, which uses a finite difference (FD) control volume solution scheme. A watershed system is discretized into a mesh of square grids, the locations of which are described in terms of rows, columns, and layers. 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. By using a FD algorithm, solution of the model yields a general equation of the form:

$$C(x,y,t) = \left(Hydrologic\ \ Transport\right) + \left(Transformation\right) \tag{17}$$

3. MODEL TESTING AND VALIDATION

3.1 Experiment set-up

Given required data from field studies, CTT&F can be used to assess the fate of explosive compounds in watershed systems. Efforts to model RDX and TNT from Camp Shelby fire range watershed, Mississippi, the largest state-owned training site in the nation, are currently underway with the CTT&F sub-module. Unfortunately, reliable watershed field data is, up to now, unavailable. In order to validate the general performance of the model, the CTT&F sub-module was evaluated by means of a laboratory test case study of explosives transport and transformation in a laboratory. A laboratory experiment was conducted to simulate rainfall and overland flow associated with sediment and chemical transport. The experimental procedure was designed to mimic field conditions resulting from the direct action of rainwater on target distributed sources in military installations. The experiment plot was 9.0’x 7.5’. The bed slope of the plot was 2% and designed to collect runoff water and sediment from the plot. Two land covers were used as part of the experiments to simulate two different surface roughness: “disturbed” (unvegetated) and “undisturbed” (vegetated). The soils used in the experiment were obtained from the Camp Shelby military fire range. The chemical and physical properties of the soils before rainfall were analyzed by standard test methods. The rainfall was introduced through a rainfall simulator. Rainfall intensity for the overall plot area was ranged from 2.7 to 2.9 in/hr. The simulated rainfall event lasted 30 ± 60 ± 90 min. Runoff and sediment were collected at the downstream end of the plot and measured volumetrically. Runoff rates and volumes were determined by collecting runoff every minute of a 30 minute rainfall simulation and every minute after rainfall was discontinued until it was noted that runoff had ceased. The total suspended sediment (TSS) samples were collected every minute for the first 15 minutes of runoff, then every five minutes during the 30 minutes rainfall simulations and every minute afterward. To simulate the transport and transformation of RDX and TNT, a total of 500 g Comp B of varying sizes 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 chemical transport. Comp B, which has been widely used in munitions, is commonly present as crystalline solids and is a 60/39 mixture of RDX and TNT that contains 1% wax. TNT solubility is greater than RDX. The chemical reaction and transport caused by each rainfall event were measured by collecting samples. During each rainfall event, 4- liter runoff samples were collected every 5 minutes for chemical analysis of explosives; their concentrations were determined. This test case primarily explores the dissolution and overland transport capabilities of CTT&F.

The experiment plot was modeled using a domain consisting of 30 grid cells, the size of the grid was 1.5 ft by 1.5 ft. The time interval for the simulation was 0.5 sec. 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 actual average explosive compound concentrations for three Comp B samples. Other values for the relevant parameters, as showed in Table 2 were adopted from Lever et al. (2005) and McGrath (1995), but ultimately they were adjusted by trial-and-error to reproduce the measured concentrations of RDX and TNT from the experiment. Many transformation processes affecting explosives are active primarily in the aqueous phase and therefore may be limited by dissolution kinetics.

This study gives the results in predicted solid persistence and multi-phase chemical loading from solids into aqueous solution for TNT and RDX.

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

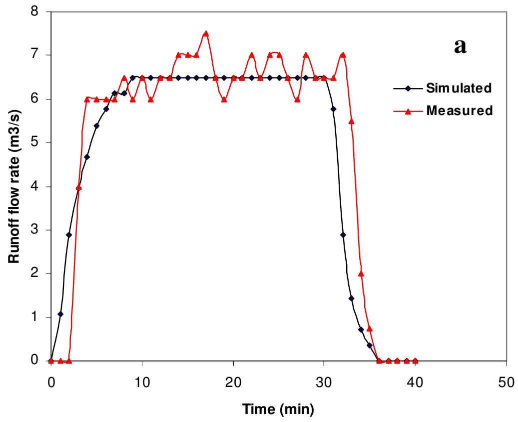
Parameter	Comp B	RDX	TNT
Aqueous solubility (g/cm^3)	-	4.6×10^{-5}[a]	1.3×10^{-4}[a]
Diffusion coefficient(cm^2/s)	-	2.2×10^{-6}[a]	6.7×10^{-6}[a]
Density (g/cm^3)	1.65[a]	1.82[b]	1.654[b]
1st transformation rate (1/hr)	-	$0 - 1.0 \times 10^{-1}$[b]	-

[a] from Lever et al. (2005)
[b] from McGrath (1995).

3.2 Results and discussion

Numerical results were obtained from running the CTT&F sub-module. In this experiment, overland flow causes erosion and dissolution of the solid Comp B, a fraction of which infiltrates into the soil while the remainder is transported downstream. Even though distributed observations for RDX and TNT concentrations were not measured in this study, we can infer and trace the migration of distributed RDX and TNT sources using the model.

In this study, the model was calibrated by comparing the simulated and measured surface runoff, sediment concentration, and chemical concentration such that the errors between simulated and measured values were minimum. The calibration results for this test case study using the selected model parameters are listed in Tables 4. 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. To describe the model goodness of fit to the overall hydrographs and pollutographs, the RMSEs (Root Mean Square Errors) were calculated and given in Tables 4. The R^2 and Nash-Sutcliffe Efficiency (NSE) criteria for assessing the efficiency of the model are also given in Tables 4. For surface runoff from both unvegetated and vegetated plots, the simulated values compared reasonably well with measurements. The event averaged percent errors of both simulated total surface discharges were less than 10% of its corresponding measured value. The RMSE and R^2 values between simulated and measured results for the unvegetated plot were 1.195 and 0.723, respectively. For the vegetated plot the RMSE and R^2 values between simulated and measured results were 0.641 and 0.944, respectively. The model did not fully capturing the initial wash-off of sediments, the event averaged percent error of simulated TSS concentration from both unvegetated and vegetated plots was 31.76% and 55.22%, respectively. The RMSE was considered to be high and the R^2 value was low. The model performance for suspended sediment concentration was strongly affected by the initial six samples collected, and the extremely high sediment concentrations were measured from these samples. Furthermore, 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, RMSE, R^2, and NSE values are greatly improved without the inclusion of the first six samples. For explosive compounds, simulated errors are very small (within 7%). The R^2 values between simulated and measured concentration results from the unvegetated plot were 0.995 and 0.997 for RDX and TNT, respectively. The R^2 values between simulated and measured results from the vegetated plot were 0.687 and 0.895 for RDX and TNT, respectively. Further, the model performed well consistently for two different data sets. 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 from (a) unvegetated plot and (b) vegetated plot are shown in Fig. 2 to 5, respectively. As can be observed, the agreement of model simulations and experimental results for the explosive compounds from the field is satisfactory thus showing that the CTT&F sub-module is able to capture the essence of explosive transport and transformation processes. Although not investigated in this study, the behavior, transport and ultimate fate of distributed sources in watersheds may be affected by other chemical reactions and related phenomena.



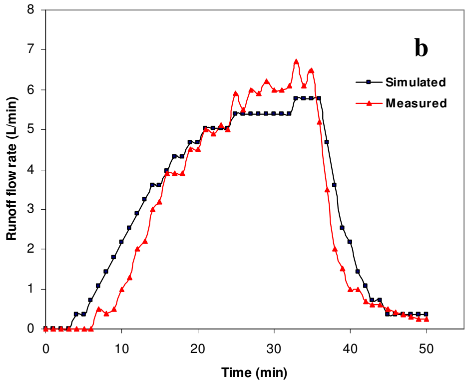


Fig. 2. Comparison of simulated and experiment results over time for surface runoff discharge

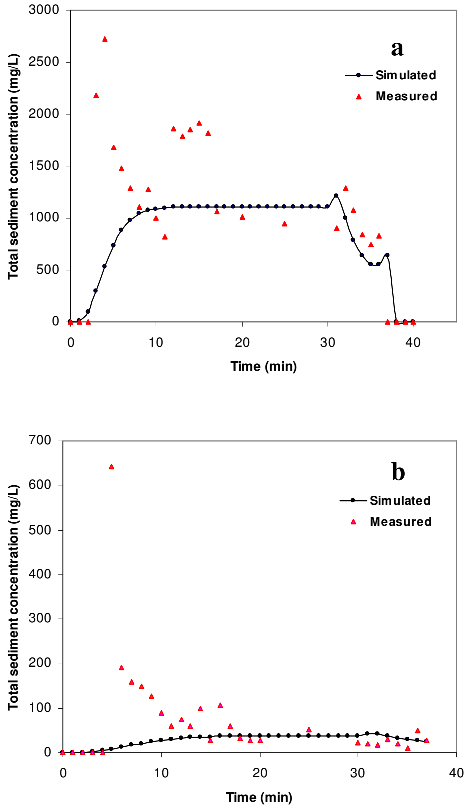
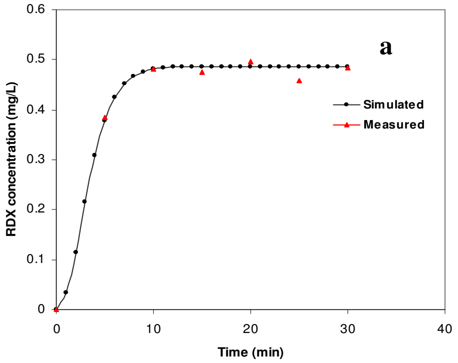


Fig. 3. Comparison of simulated and experiment results over time for TSS concentration in overland flow



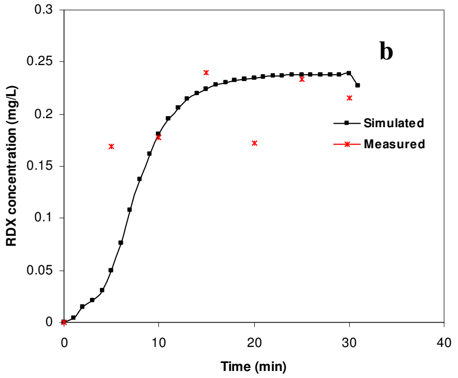


Fig. 4. Comparison of simulated and experiment results over time for RDX concentration in overland flow

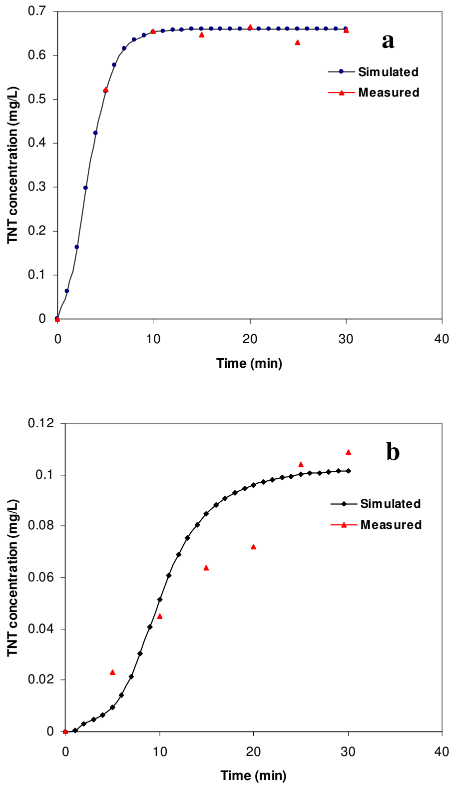


Fig. 5. Comparison of simulated and experiment results over time for TNT concentration in overland flow

4. SUMMARY AND CONCLUSIONS

A contaminant transport, transformation and fate sub-module, CTT&F, has been developed for simulating distributed sources in watersheds. CTT&F is able to simulate both surface runoff and channel processes of contaminants. The CTT&F equations are comprehensive, physically based, and fully compatible with various distributed hydrologic models which provides the required hydrological and sediment variables. The physical basis is important since it

Table 4. Comparison of simulated and measured hydrographs and pollutographs

Parameter	Simulated	Measured	Error (%)	R^2	RMSE	NSE
unvegetated plot						
Surface runoff (L/min)	189.72	201.75	5.96	0.723	1.195	0.685
Total suspended sediment (mg/L)	20917.60	30653.33	31.76	0.166	719.47	0.231
Dissolved RDX (mg/L)	2.805	2.782	0.84	0.995	0.012	0.994
Dissolved TNT (mg/L)	3.806	3.776	0.79	0.997	0.012	0.997
vegetated plot						
Surface runoff (L/min)	151.20	139.83	8.13	0.944	0.641	0.923
Total suspended sediment (mg/L)	726.02	2106.67	65.53	0.04	134.00	0.247
Dissolved RDX (mg/L)	1.155	1.207	4.32	0.687	0.052	0.532
Dissolved TNT (mg/L)	0.443	0.417	6.34	0.895	0.014	0.865

provides the link between the simulations and physical property measurements.. The model computes on a grid basis for considering spatially varied soils, land uses, and other hydrologic characteristics. CTT&F can quantify the changes in environmental conditions such as chemical loads, corresponding to various management scenarios, through physically meaningful parameters. CTT&F was tested to demonstrate its performance using an experiment plot. Comparisons between simulated and measured results have been described. The comparisons showed that the model was capable of simulating the explosive compounds from the field with reasonable accuracy. Overall comparisons were encouraging, and showed promise for the potential use of the CTT&F sub-module for studying the fate of distributed sources in watersheds. Further research and development will help to identify the dominant biochemical transformation processes, followed by better descriptions for the dominant processes and then better estimates of their parameter values for each variable supporting the model. The applicability of the model will be further validated and evaluated using more data sets.

ACKNOWLEDGMENTS

The work reported in this paper was supported by the Environmental Quality Technology Program of the U.S. Army Corps of Engineers. We acknowledge and appreciate the laboratory experiment work conducted by Ms. Cynthia Price and her team.

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

25th Army Science Conference
November 27-30, 2006
Orlando, Florida

Dr. Billy E. Johnson, ERDC-EL
Dr. Zhonglong Zhang, SpecPro Inc.

Environmental Quality and Installations

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Discussion Items

- Background
- GSSHA Model Components
- Current CTT&F Sub-model Features

  Joint Collaboration between Colorado State University and ERDC-EL
- Model Testing and Validation Studies
- Summary and Conclusions

Background

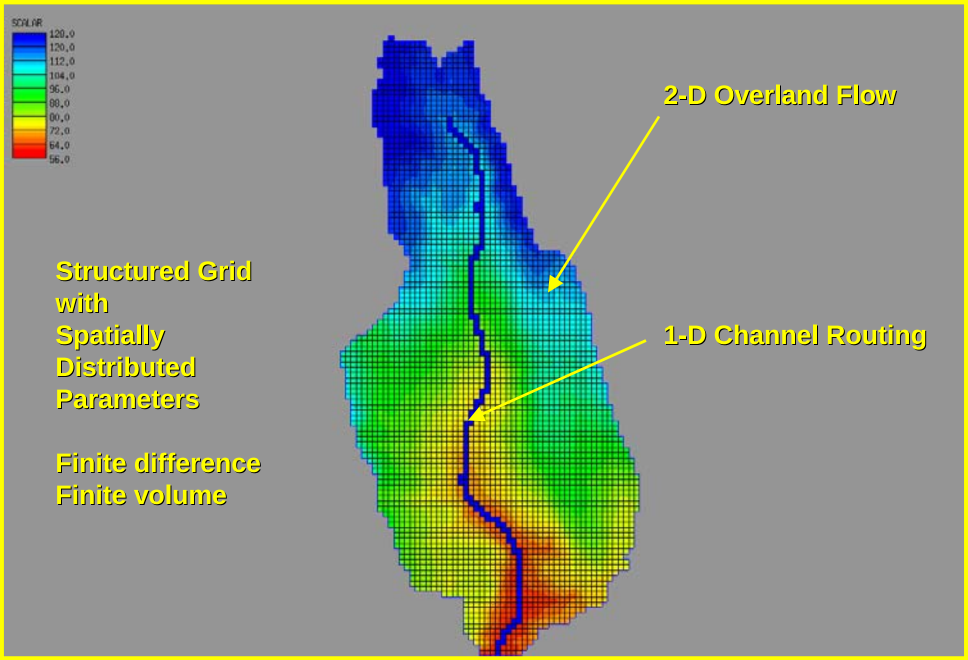
Many U.S. Military installations potentially contain soil, sediment, surface water, and groundwater environments contaminated with explosives and energetics.

The release of contaminants from military installations, transport across the land surface, and delivery to stream networks and ground water can have adverse water quality and ecological impacts. Compliance with water quality regulations is becoming increasingly important at military installations thus necessitating the development of usable and effective models for compliance as well as long-term watershed planning and management.

To meet this need, a physically based distributed sources Contaminant Transport, Transformation and Fate (CTT&F) sub-model was developed, for linkage with existing distributed watershed models, to simulate explosive compounds from both point and non-point sources across a watershed.

Gridded Surface Sub-surface Hydrologic Analysis (GSSHA) Model

- **Spatial distribution of precipitation**
- **2D Overland flow (Diffusive Wave)**
- **1D Channel flow (Diffusive Wave)**
- **Infiltration (Green-Ampt, Green-Ampt Redistribution, and Richard's Eq.)**
- **Evapo-transpiration (Penman-Monteith and Deardorff)**
- **2D/3D Lateral groundwater flow**
- **Surface water/Groundwater Interaction**
- **Snow accumulation and melting**
- **Overland and channel sediment transport**



2-D Overland Flow

1-D Channel Routing

Structured Grid with Spatially Distributed Parameters

Finite difference
Finite volume

Current CTT&F Sub-model's Features

- Spatial Grid Discretization
- Four Phases Partitioning:
  - *dissolved*
  - *bound to DOC (Dissolved Organic Carbon)*
  - *sorbed to sediment particles*
  - *separate solid particles*
- 2D Overland Flow Transport with Upper Soil Layer
- 1D Channel Flow Transport with Bed Sediments
- Seven Biochemical Transformation Processes:
  - *biodegradation*
  - *hydrolysis*
  - *oxidation*
  - *photolysis*
  - *dissolution of solid phase*
  - *user-defined extra reaction*
  - *transformations and daughter products*

Chemical Partitioning

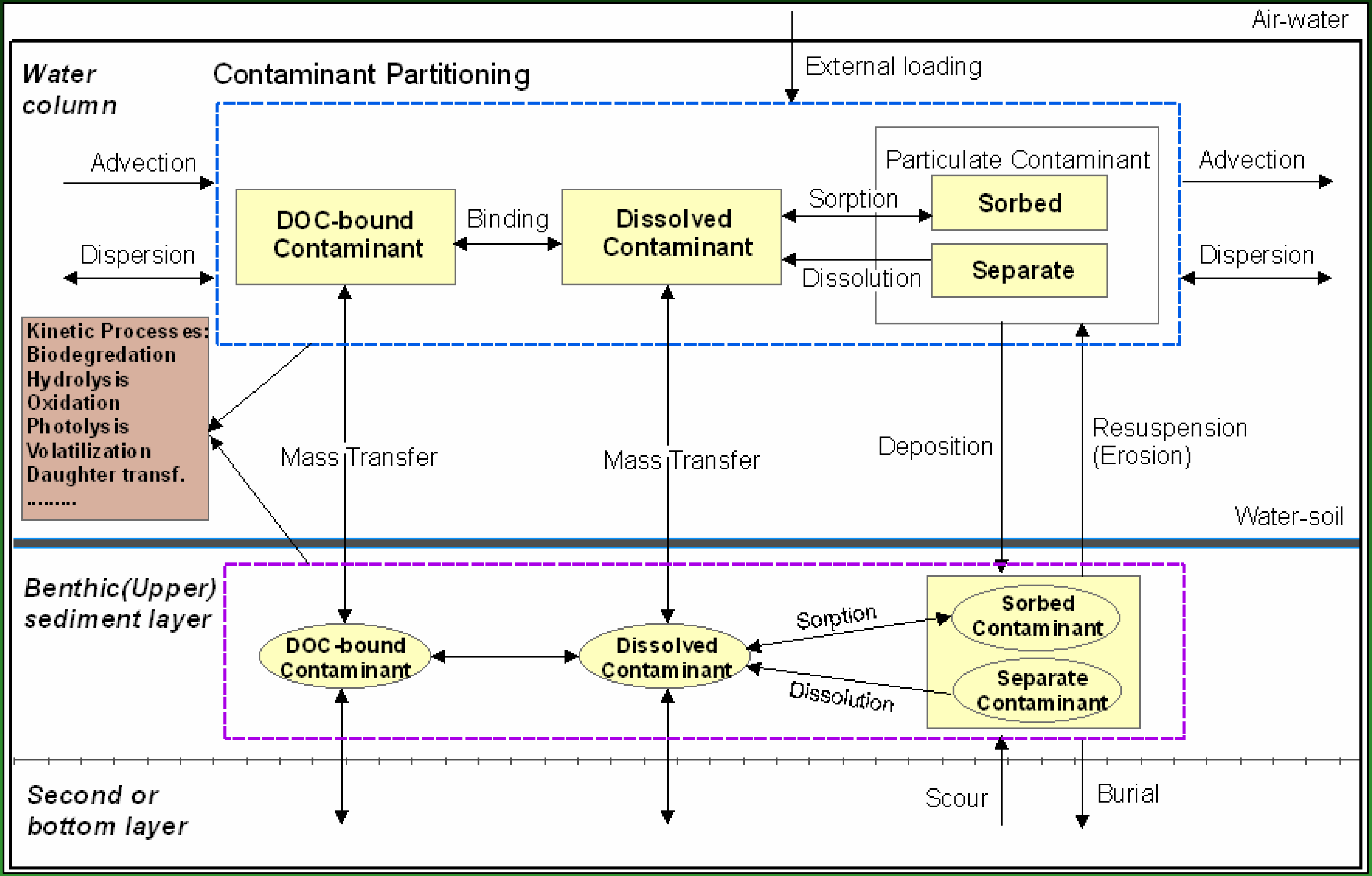
Environmental Quality and Installations

Equilibrium partitioning of contaminants among dissolved phase, sediment sorbed phase, and DOC bound phase.

$$C_d = f_d C_T \qquad C_b = f_b C_T \qquad C_p = \sum_{n=1}^{N} f_{pn} C_T$$

Fourth phase must account for the effect of "melting" of solids (dissolution). The explosive solid is modeled as a reactive particle.

Contaminant Transport and Transformation Processes



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Biochemical Transformation Processes

Biodegradation: is the process by which organic substances are broken down by other living organisms.

CTT&F simulates biodegradation as a first-order kinetics process.

$$\frac{\partial C_T}{dt} = k_{bio} C_T$$

Hydrolysis: is a reaction or process in which a molecule is split into two parts by reacting with a molecule of water, which has the chemical formula H_2O. The reactions are first order for the neutral chemical and second order for the acidic or basic forms of the chemical.

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

$$k_{hyd} = \sum_j \left(k_{a\,j} \left[H^+ \right] + k_{n\,j} + k_{b\,j} \left[OH^- \right] \right) f_j$$

Biochemical Transformation Processes

Oxidation: reactions include all chemical processes in which atoms have their oxidation number (oxidation state) changed. Oxidation describes the loss of an electron by a molecule, atom or ion.

Oxidation is modeled by CTT&F as a general second-order process for the various species and phases of each chemical.

$$k_{oxi} = [RO_2]\sum_j k_{oj} f_j$$

Photolysis: is a chemical reaction in which a chemical compound is broken down by photons (e.g. light).

The first order rate coefficient for photolysis is calculated by CTT&F from the absorption rate and the quantum yield for chemical in each phase

$$k_{pht} = \sum_j k_{aj}\phi_j f_j$$

Biochemical Transformation Processes

User-Defined Extra Reaction: An extra user-defined second-order reaction for the various phases of each chemical is included in CTT&F.

$$k_{urd} = [E]\sum_{j} k_{ej} f_j$$

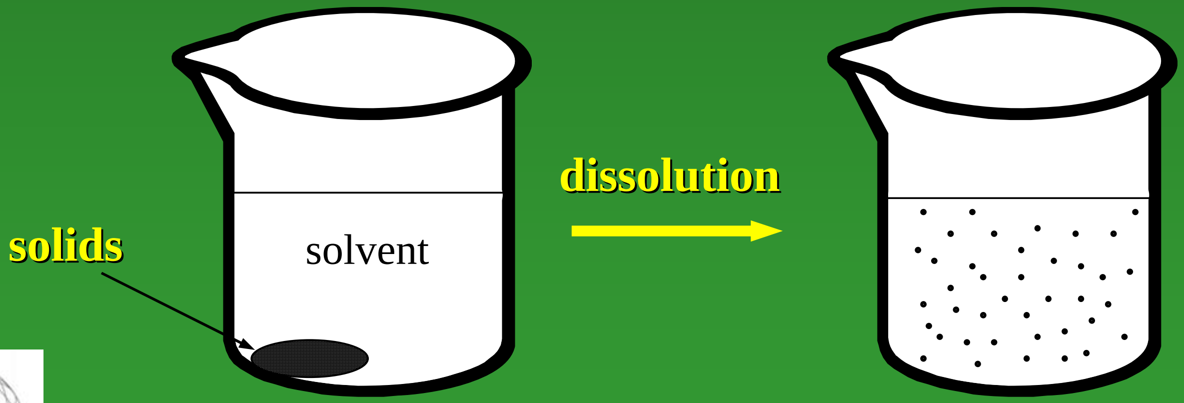
Transformations and Daughter Products: The contaminants simulated by CTT&F may be independent, or they may be linked with reaction yields, such as a parent compound-daughter product sequence.

$$J_{kji} = \sum_{j}\sum_{k} k_{kj} C_j Y_{kji}$$

Biochemical Transformation Processes

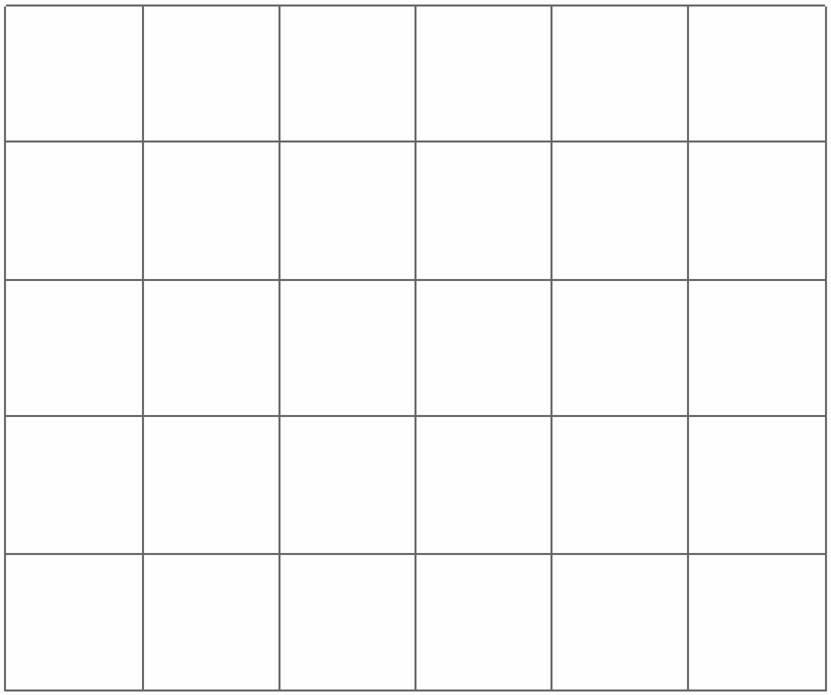
Dissolution of Solid Phase: Explosives associated compounds are commonly present as crystalline solids. Dissolution of solid phase contaminants into water is a primary mechanism by which solid contamination spreads through the system. Once dissolved, the contaminants are available for other transport or transformation processes. In CTT&F, the first-order kinetic process is used to describe the explosive dissolution rate:

$$\frac{\partial C_s}{dt} = k_{dsl}\alpha\left[S-\left(f_d+f_b\right)C_T\right]$$



Model Testing and Validation Studies

- The test plot was set-up as 9.0’x 7.5’. The bed slope of the plot was designed with 2% for collecting runoff water from the surface of the soil. The soils were obtained from Mississippi Camp Shelby military fire range. The rainfall (2.8 in/hr) was introduced through a rainfall simulator.
- Comp B is a 60/39 mixture of RDX and TNT. Comp B is commonly present as crystalline solids and were simulated by uniformly spreading over the land surface.
- Runoff, sediment and contaminant samples were collected at the downstream end of the plot and measured volumetrically.



Experiment Plot (7.5 x 9')

Model Testing and Validation Studies

Model parameters for RDX and TNT in water			
Parameter	**Comp B**	**RDX**	**TNT**
Aqueous solubility (25°C) *(g/cm^3)*	**--1.65[a]-**	**$4.6 \times 10^{-5,a}$**	**$1.3 \times 10^{-4,a}$**
Diffusion coefficient (25°C) (cm^2/s)		**$2.2 \times 10^{-6,a}$**	**$6.7 \times 10^{-6,a}$**
Density (g/cm^3)		**1.82[b]**	**1.654[b]**
1st order transformation rate (1/hr)		**$0 - 1.0 \times 10^{-1,b}$**	**-**

a. from Lever et al. (2005)

b. from McGrath (1995).

Lever, J.H., Taylor, S., Perovich, L., Bjella, K., Packer, B., 2005. "Dissolution of composition B detonation residuals." *Environ. Sci. Technol., 39(22): 8803 –8811.*

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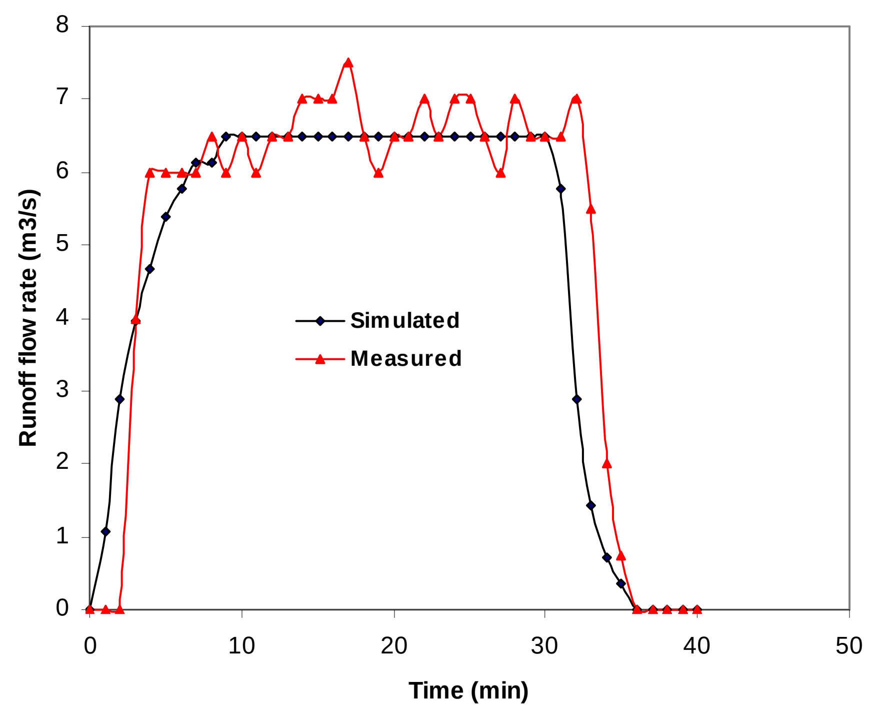
FY06 Model Development Activities

Test Plot Model Hydrology Results

Comparison of simulated and experiment results over time for surface runoff discharge.

Unvegetated



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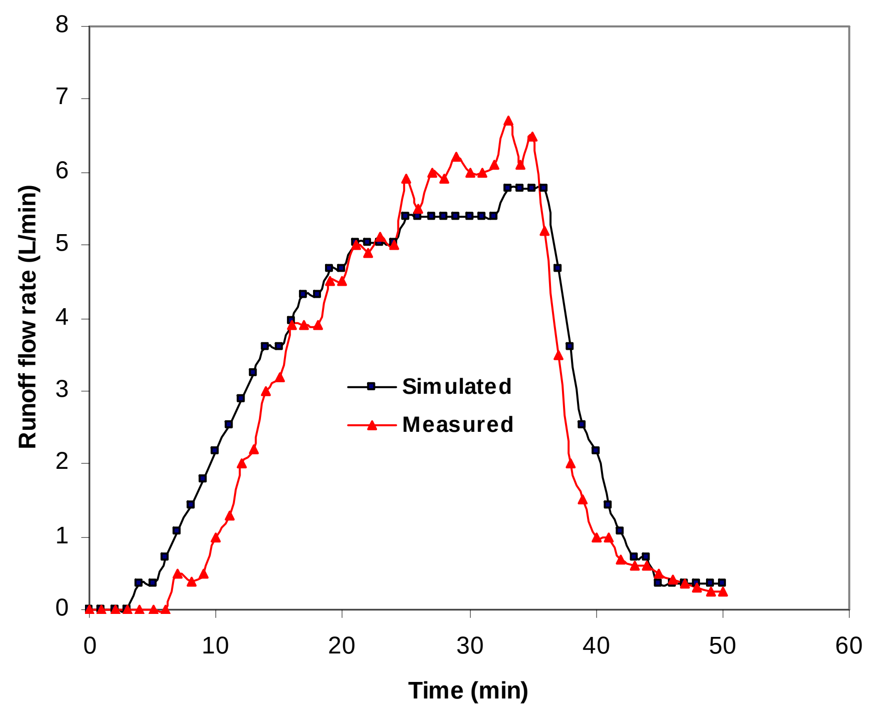


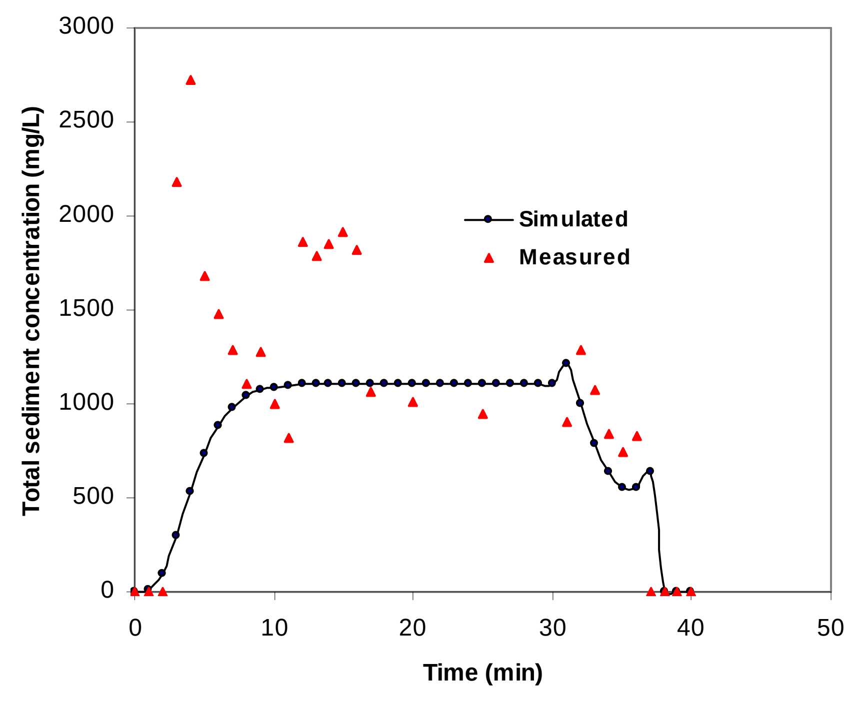
FY06 Model Development Activities

Test Plot Model Sediment Results

Environmental Quality and Installations

Comparison of simulated and experiment results over time for total suspended sediment concentration in overland flow.

Unvegetated



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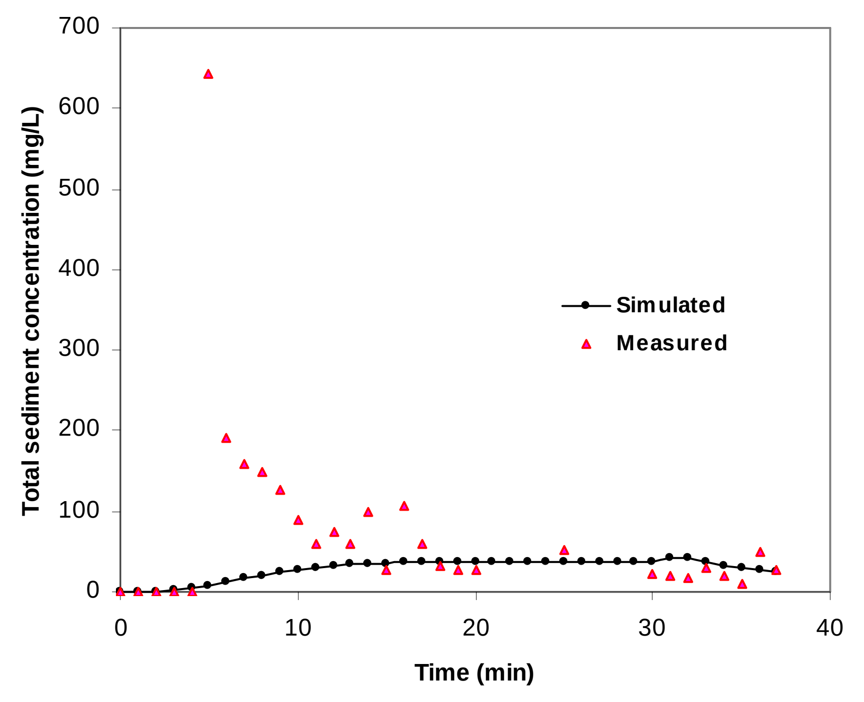

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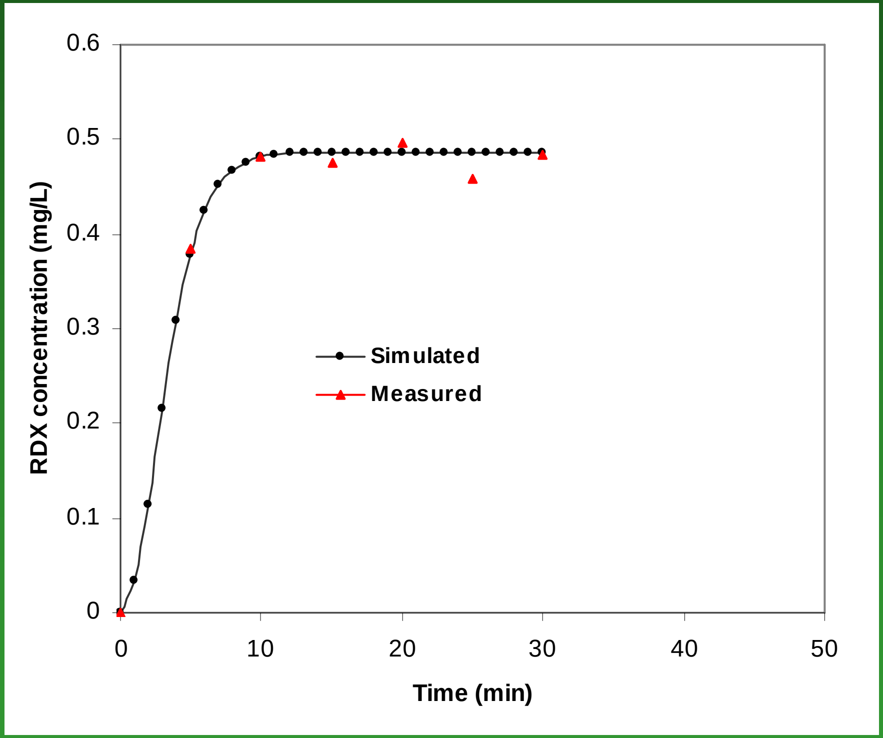
FY06 Model Development Activities

Test Plot Model Contaminant Results

Environmental Quality and Installations

Comparison of simulated and experiment results over time for dissolved RDX concentration in overland flow.

Unvegetated



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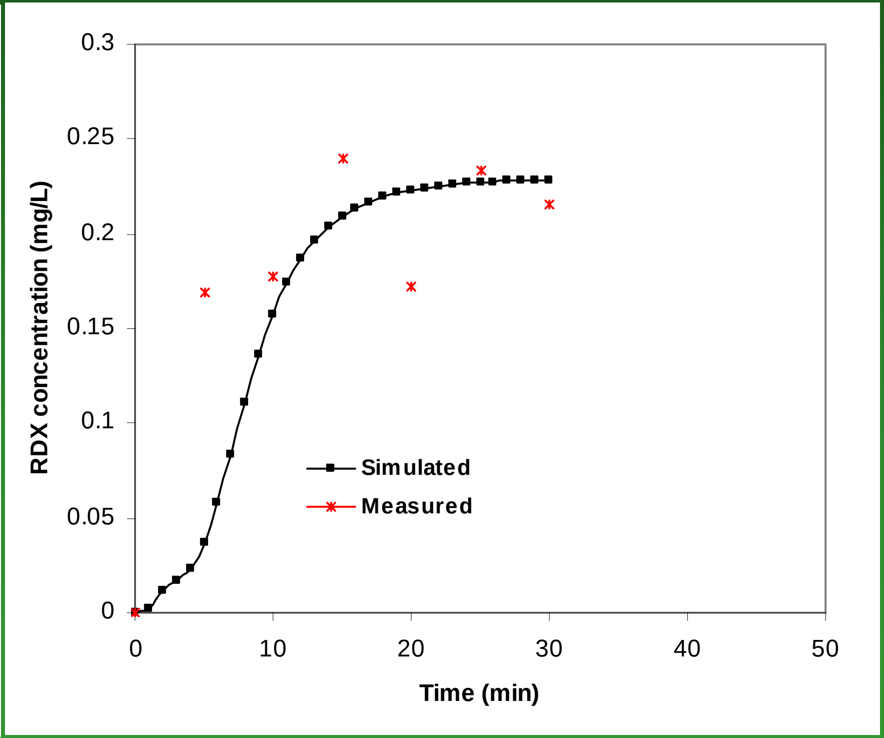
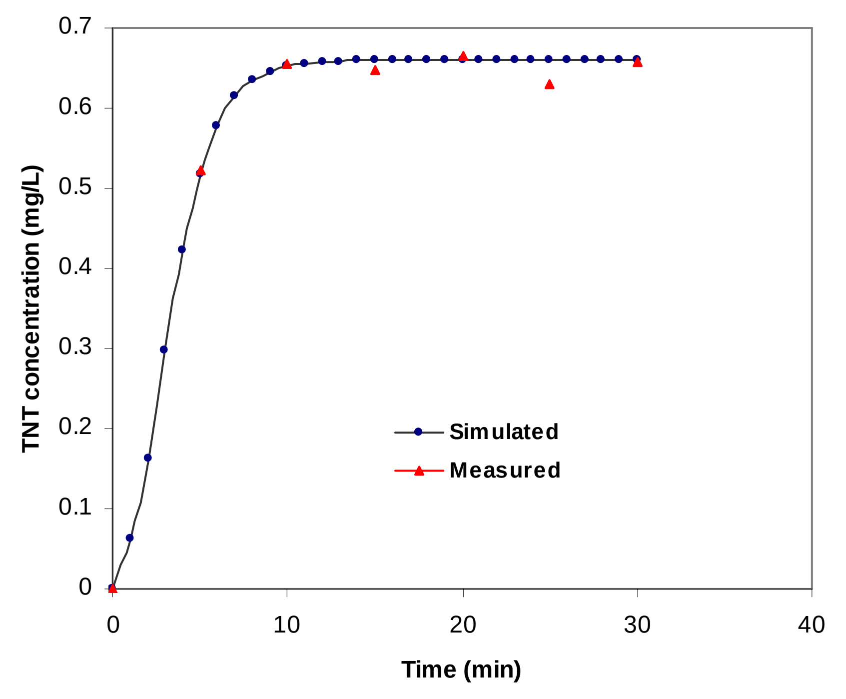


FY06 Model Development Activities

Test Plot Model Contaminant Results

Comparison of simulated and experiment results over time for dissolved TNT concentration in overland flow.

Unvegetated



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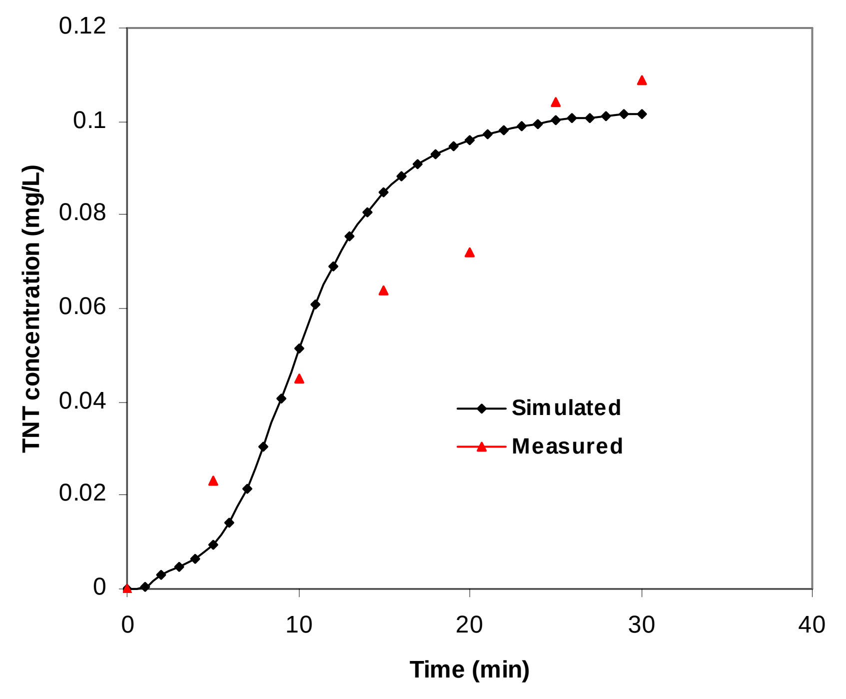
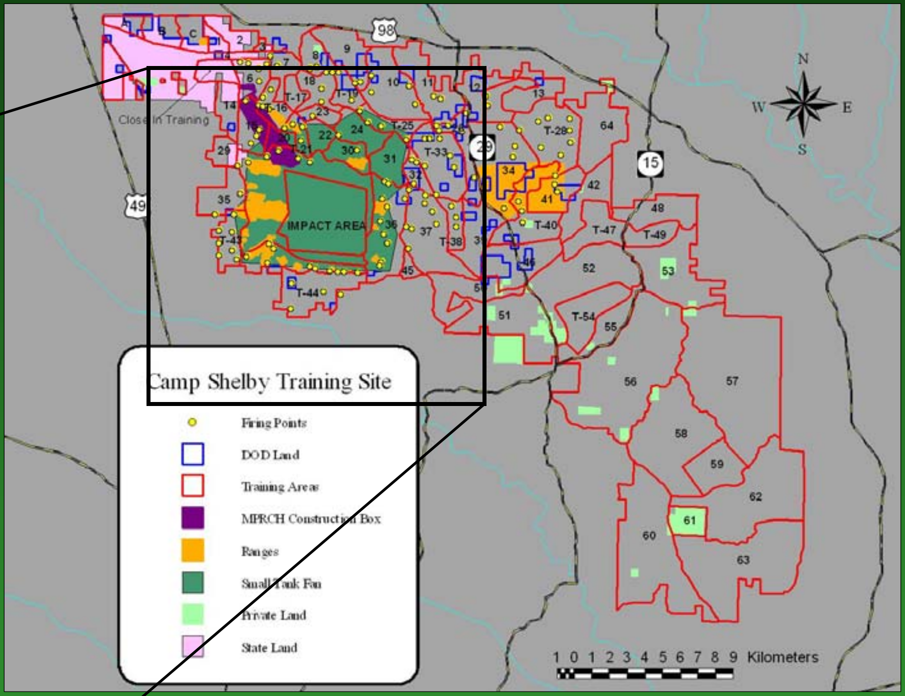


FY06 Model Development Activities

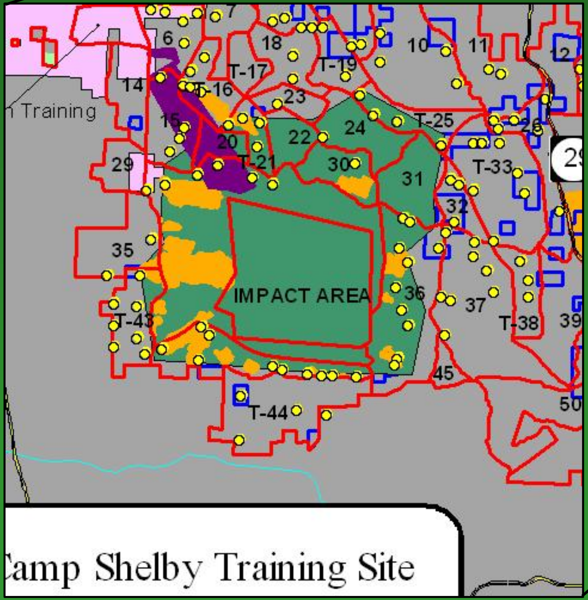
Environmental Quality and Installations

Watershed Validation Site

Camp Shelby Training Sites



Model Testing Site



FY06 Model Development Activities

Validation Site - Camp Shelby

- Camp Shelby, Mississippi, the largest state owned training site in the nation, has a long history of serving the country and is considered by many as “a national treasure.” During wartime, the camp's mission is to serve as a major, independent mobilization station of the U.S. Army Forces Command (FORSCOM). Camp Shelby

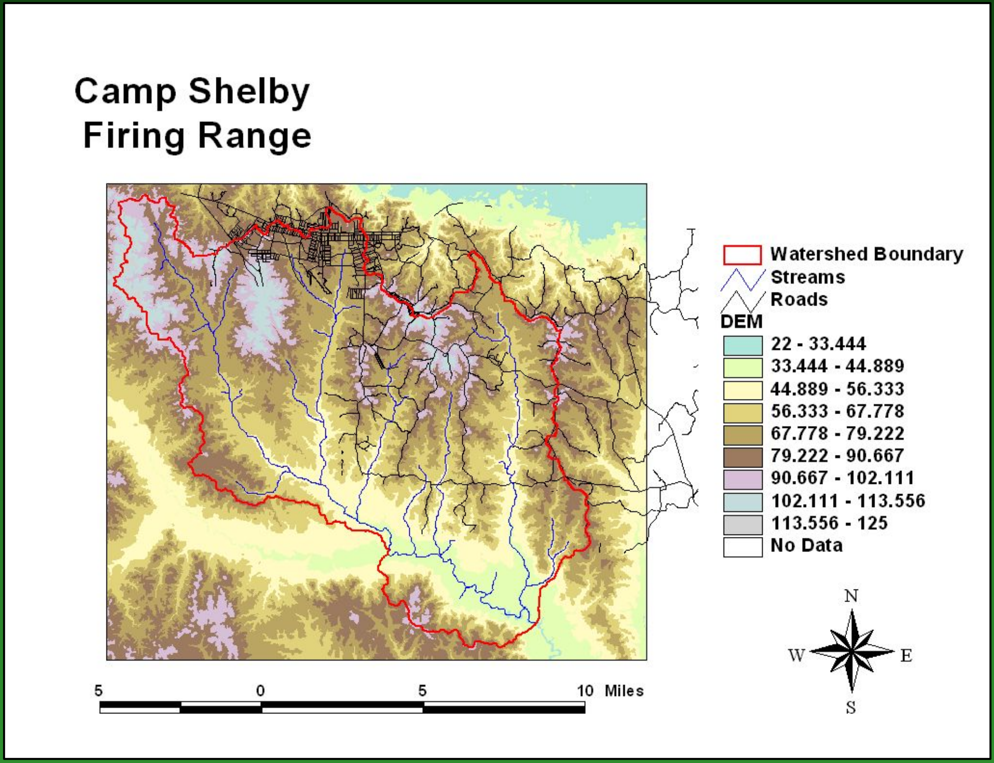
- Training Site is the largest reserve component training site, covering 136,000 acres, allowing up to battalion level maneuver training, excellent FA Firing Points, and a wide range of support facilities. This is the normal Annual Training location for National Guard and Reserve units located in Mississippi, Alabama, and Tennessee. However, units from across the country use its excellent assets to support a varity of missions.

- Watershed Area is approximately 112 square miles.

FY06 Model Development Activities

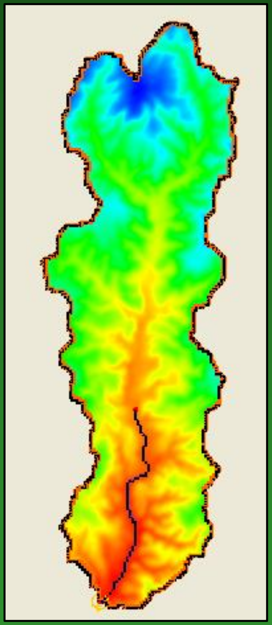
Environmental Quality and Installations

Validation Site - Camp Shelby



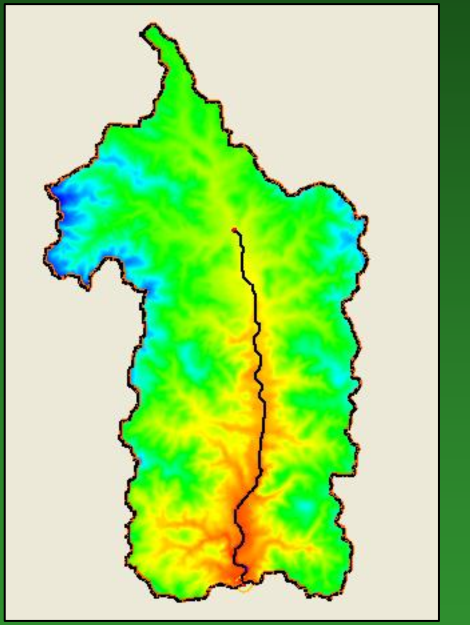
Drainage Area = 112 mi^2

Middle Creek



Drainage Area = 4.0 mi^2

Pearces Creek



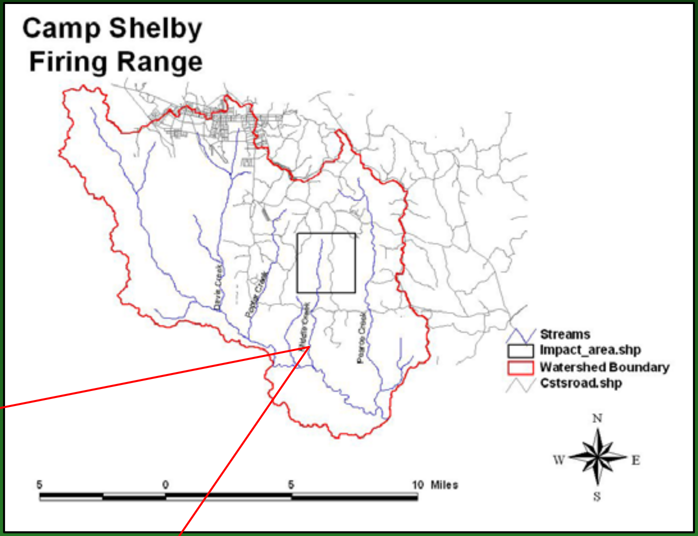
Drainage Area = 17.4 mi^2

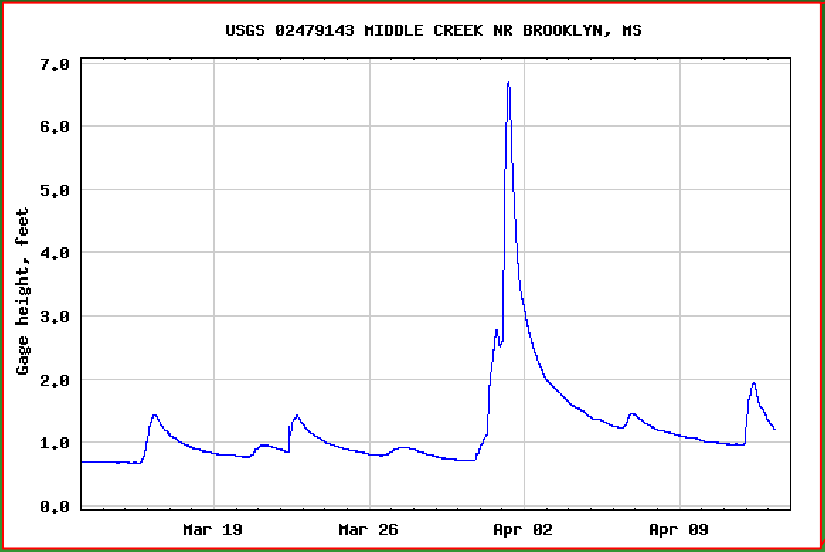
FY06 Model Development Activities

Environmental Quality and Installations

Camp Shelby Gage Data

Middle Creek (FY04)
Stage and Flow Data

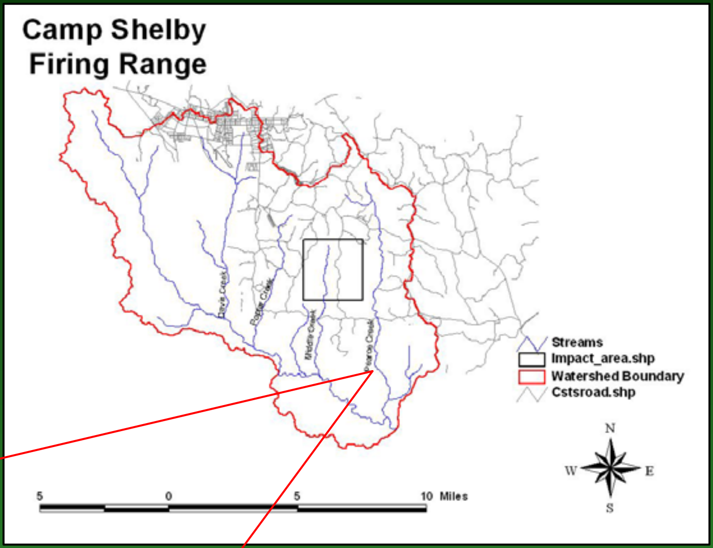


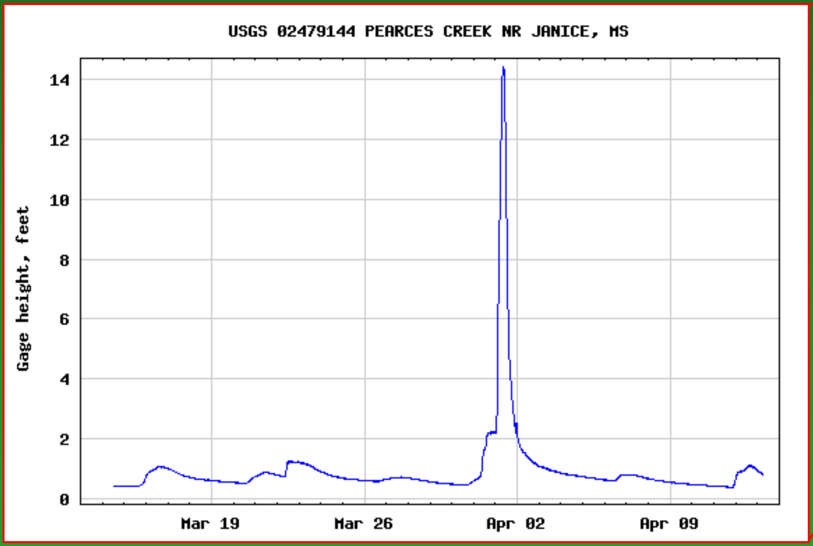


FY06 Model Development Activities

Camp Shelby Gage Data

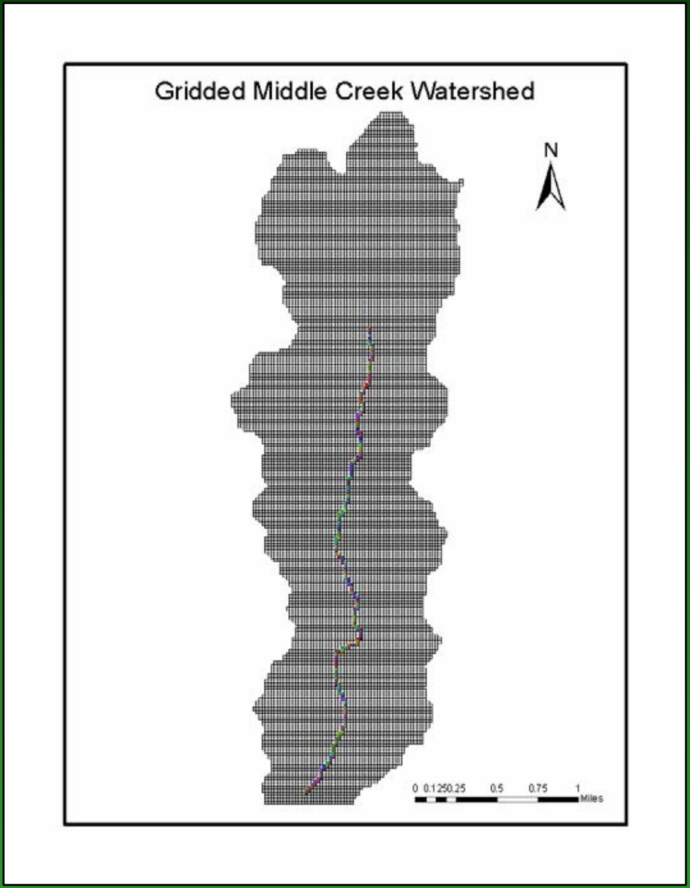
Pearces Creek (FY05)
Stage Data

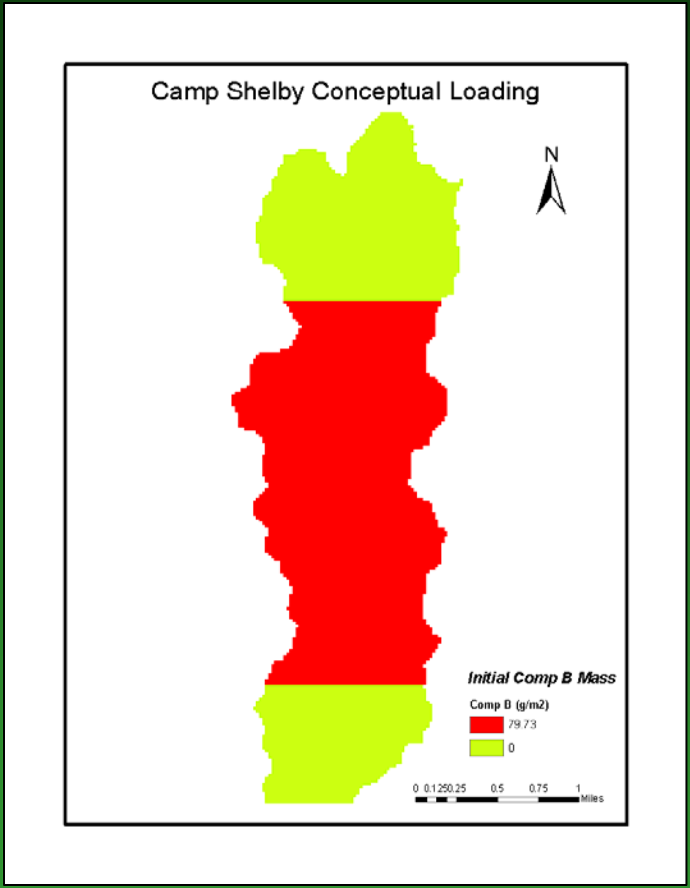




FY06 Model Development Activities

Middle Creek Model Development





Drainage Area = 4.0 mi^2

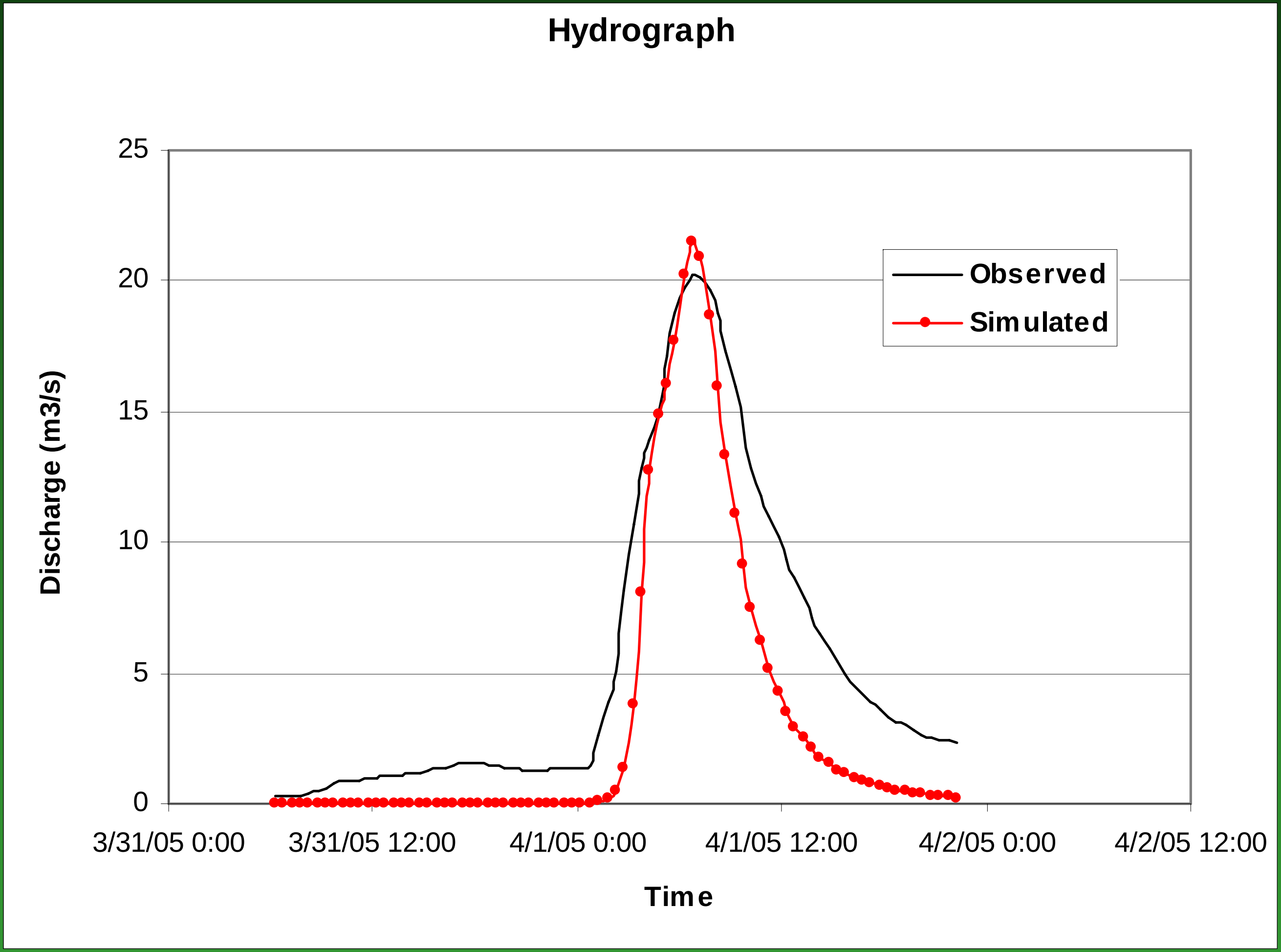
Grid Cell Resolution = 30 m

Rows = 228

Columns = 76

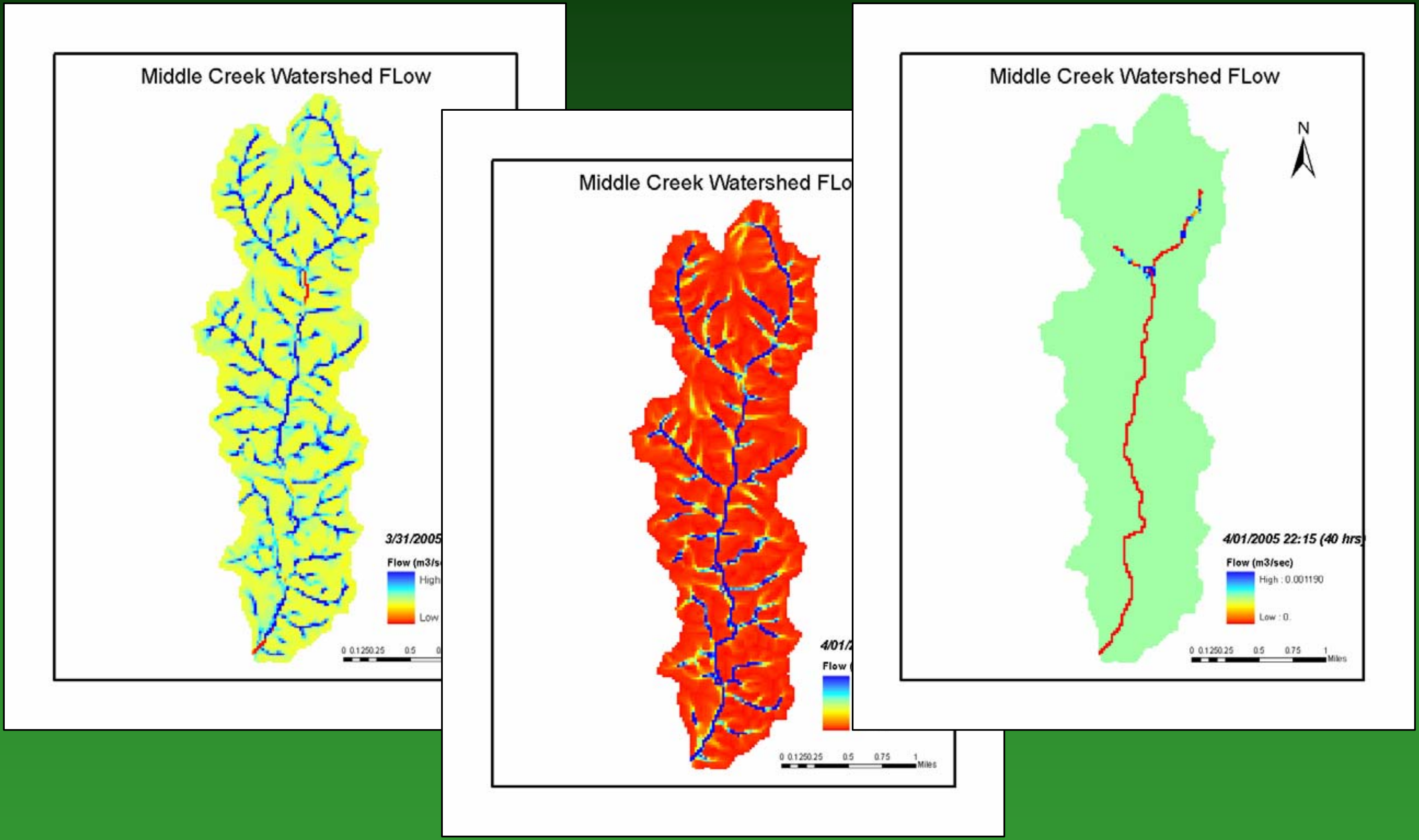
FY06 Model Development Activities

Middle Creek- Simulated Hydrograph



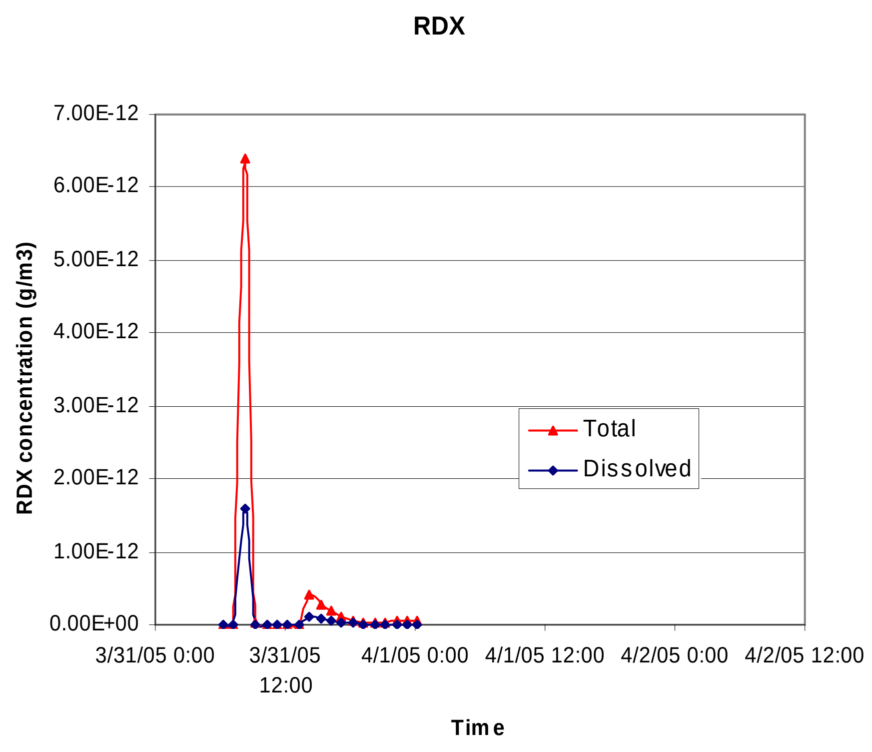
FY06 Model Development Activities

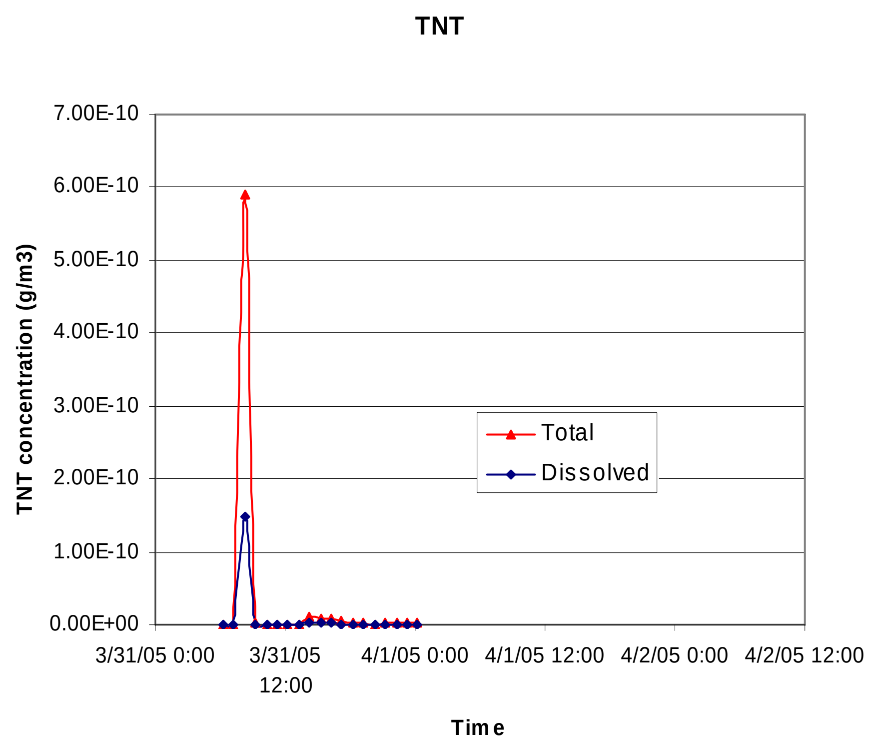
Middle Creek- Simulated Distributed Flow



FY06 Model Development Activities

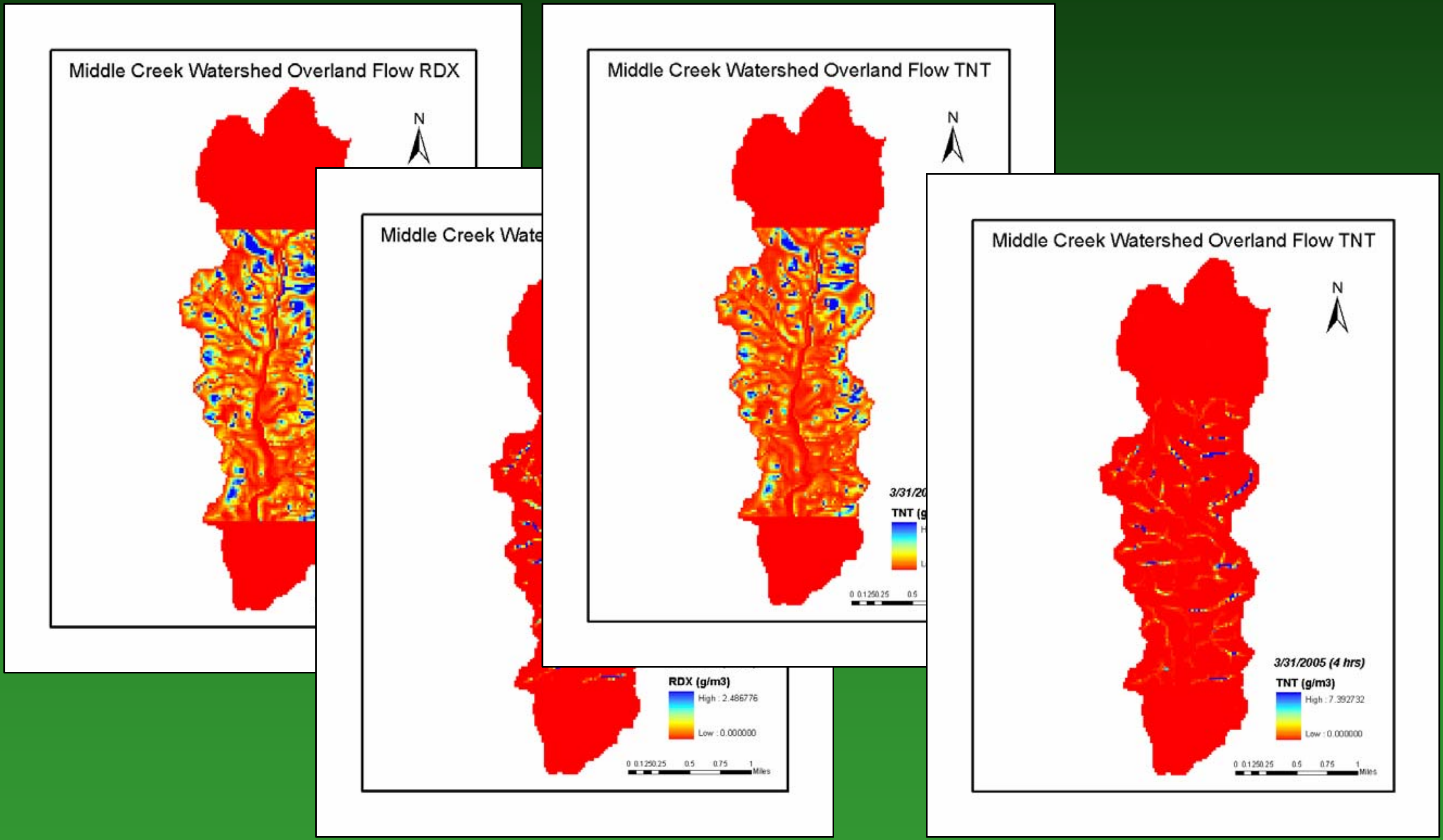
Middle Creek- Simulated Contaminants (RDX, TNT)





FY06 Model Development Activities

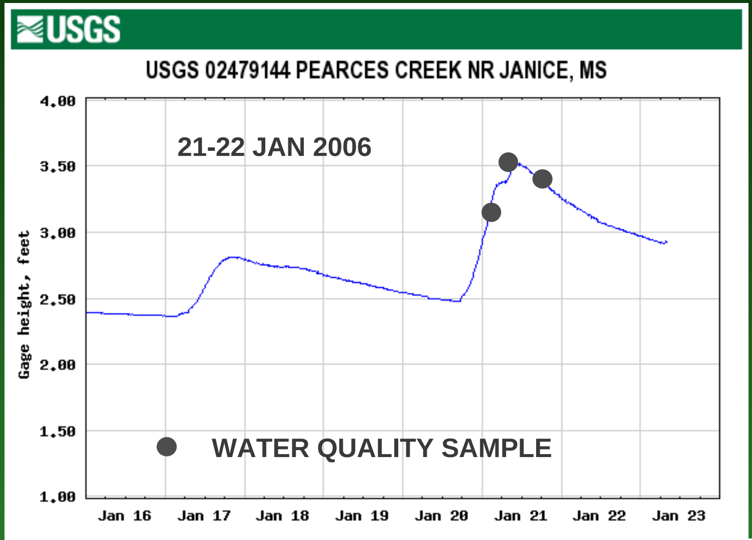
Middle Creek- Simulated Distributed Contaminants – RDX and TNT

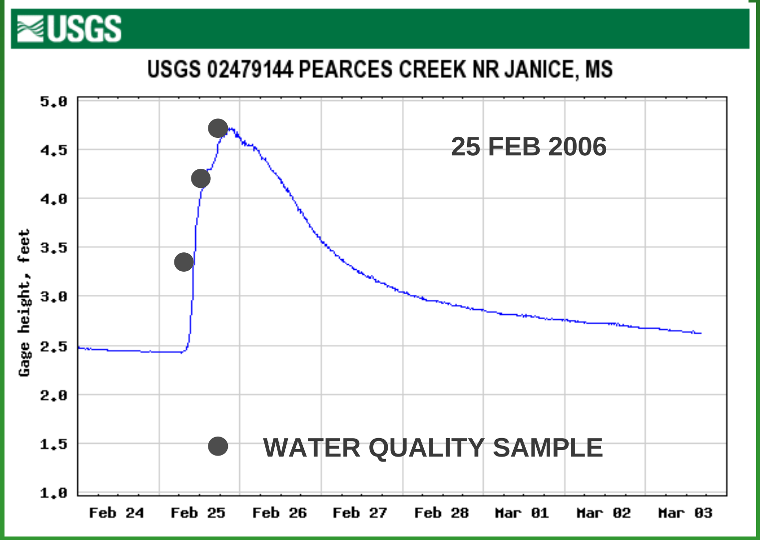


FY06 Model Development Activities

Model Validation – Pearces Creek Explosives Flux in Surface Water During Storm Events

- *Water quality samples collected during two storm events at two gauged streams that drain central impact area at Camp Shelby*
- *Storms represent two different discharge conditions – enable calculation of explosives flux*
- *Explosives (TNT, RDX) detected at parts per trillion level in samples from January storm event*





Summary and Conclusions

- A CTT&F sub-model has been developed based on the mass conservative form of the coupled system of 2D overland flow and 1D channel flow for watersheds. The CTT&F equations are comprehensive, physically based, and are compatible with the physically based (flow and sediment), distributed watershed hydrologic models.
- CTT&F works on a grid basis for considering spatially varied soils, land uses, and other hydrologic characteristics.
- CTT&F generates time series and spatial outputs over time.
- CTT&F was tested for RDX and TNT from a test plot in laboratory. The comparisons showed that RDX and TNT concentrations in overland flow can be simulated accurately.
- The applicability of the model needs to be further evaluated/validated using watershed scale data sets. The spatial concentrations of contaminants in the water and the benthic sediment need to be evaluated at the watershed scale.

In Support of Our Troop Training and Mission Goals!

Environmental Quality and Installations

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