TREX: Spatially distributed model to assess watershed contaminant transport and fate

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1. Introduction

Unmanaged contaminant releases from upland sources, their transport across the land surface, and delivery to stream networks can have adverse water quality and ecological impacts. High resolution tools are needed to assess chemical transport and fate at the watershed scale to formulate effective management plans that address chemical impacts. The need for high resolution is driven by the fact that contaminant occurrence and transport conditions are often highly heterogeneous and can differ significantly across small spatial and temporal scales.

The transport of metals from mine wastes is representative of a large class of water quality problems that can be readily assessed using high resolution watershed models. Environmental impairments attributable to contaminants from inactive and abandoned mines are widespread. Across the western U.S., contaminants associated with acid mine drainage are estimated to affect more than 500,000 ac of land and several thousand miles of streams and other surface waters (IMCC, 2007).
1992; USEPA, 1996). The scale of this problem is so extensive that not all areas of contaminated sites can be rehabilitated. Consequently, priorities must be established to maximize remediation that can be achieved with limited resources. Spatially distributed watershed models can be used to evaluate site conditions, assess how contaminated areas contribute to overall site impairments, and develop remediation strategies that prioritize areas for cleanup. Such tools are particularly useful in the context of sites managed by the U.S. Environmental Protection Agency (USEPA) Superfund program. In addition to addressing metal impacts, models that integrate water, soils, and chemicals can be used to investigate other multimedia environmental problems, including: flash-floods (England et al., 2007); Total Maximum Daily Loads (TMDLs); and fire-related flood, sediment, and water quality studies.

2. Research objectives

The objectives of this research were to: (1) develop and describe the algorithms of a spatially distributed model to simulate chemical transport and fate at the watershed scale; and (2) demonstrate model potential by a screening-level application to the California Gulch mine waste-contaminated watershed. To meet these objectives, the Two-dimensional, Runoff, Erosion, and Export (TREX) watershed model was developed. TREX is a fully distributed, physically-based numerical model to simulate chemical transport and fate at the watershed scale. In addition to hydrology and sediment transport, TREX simulates chemical partitioning and phase distribution, advection, erosion, deposition, and dissolved phase infiltration in surface water, soil, and sediment. Floodplain interactions are also simulated and include the bi-directional exchange of water, sediment, and chemicals both to and from floodplain areas of the overland plane and stream channels.

3. Model development

Key milestones in the development of fully distributed, physically-based watershed models include CASC2D (Julien and Saghaian, 1991; Julien et al., 1995; Johnson et al., 2000; Ogden and Julien, 2002; Julien and Rojas, 2002), GSSHA (Downer and Ogden, 2004), and the SHE series of models (Abbott et al., 1986; Wicks and Bathurst, 1996; Ewen et al., 2000). The starting point for TREX development was CASC2D. The basic CASC2D framework is an event-based model that simulates overland flow, surface soil erosion and deposition, channel flow and sediment transport through stream channels. As part of TREX development, the hydrologic and sediment transport components of CASC2D were expanded to support the addition of chemical transport features. Chemical transport and fate components were formulated based on those in the WASP/IPX series of stream water quality models (Ambrose et al., 1993; Velleux et al., 2001) to create a fully distributed model to simulate chemical transport and fate at the watershed scale. A review of key hydrologic, sediment transport, and chemical transport processes is informative to illustrate the physics behind the model. A conceptual diagram of model processes is presented in Fig. 1. More detailed descriptions of all processes in TREX are presented by Velleux (2005) and Velleux et al. (2006a).

3.1. Hydrologic submodel

The hydrologic processes in the model are: (1) rainfall, interception, and surface storage; (2) infiltration and transmission loss; and (3) overland and channel flow. The model state variables are water depth in the overland plane and stream channels. Rainfall can be uniform or distributed in both time and space and can also be specified using several grid-based formats to facilitate radar rainfall data use. When spatially distributed rainfall is simulated, areal rainfall estimates are interpolated from point rain gage data using an inverse distance weighting approach. Interception and surface storage are simulated as equivalent depths.

Infiltration and transmission loss rates are simulated using the Green and Ampt (1911) relationship (Li et al., 1976; Abdullrazzak and Morel-Seytoux, 1983; Freyberg, 1983; Julien, 2002):

\[ f = K_h \left( 1 + \frac{(H_u + H_i)}{F} (1 - S_i) \right) \]

where: \( f \) = infiltration or transmission loss rate [L/T]; \( K_h \) = effective hydraulic conductivity [L/T]; \( H_u \) = hydrostatic pressure head (ponded water depth) [L]; \( H_i \) = capillary pressure (suction) head at the wetting front [L]; \( S_i \) = effective soil or sediment porosity = \( \phi - \theta \) [dimensionless]; \( \phi \) = total soil or sediment porosity [dimensionless]; \( \theta \) = residual moisture content [dimensionless]; \( S_i \) = effective saturation [dimensionless]; and \( F \) = cumulative water depth (depth to wetting front) [L]. For infiltration on the overland plane, the hydrostatic pressure head of ponded water (\( H_u \)) is neglected.

Overland flow is two-dimensional and simulated using the diffusive wave approximation. Flow occurs when the water depth exceeds the storage depth and the friction slope is not zero (Julien et al., 1995; Julien, 2002):

\[ \frac{\partial h}{\partial t} + \frac{\partial q_x}{\partial x} + \frac{\partial q_y}{\partial y} = i_n - f + W = i_c \]

\[ q_x = x_h h^f \]

\[ q_y = y_h h^f \]

where: \( h \) = surface water depth [L]; \( q_x, q_y \) = unit discharge in the \( x \)- or \( y \)-direction = \( Q_x/B_x, Q_y/B_y \) [L^2/T]; \( Q_x, Q_y \) = flow in the \( x \)- or \( y \)-direction [L^2/T]; \( B_x, B_y \) = flow width in the \( x \)- or \( y \)-direction [L]; \( i_n \) = net precipitation rate (gross rainfall minus interception) [L/T]; \( W \) = flow point source (unit discharge) [L^2/T]; \( i_c \) = excess precipitation rate [L/T]; \( S_h \) = resistance coefficient for flow in the \( x \)- or \( y \)-direction = \( \frac{S_h}{x^2/2} / \mu_T \); \( S_h \) = Manning roughness coefficient [T/L^1/3]; \( S_f \) = friction slope (energy grade line) in the \( x \)- or \( y \)-direction = \( S_{f,x} - df/dx, S_{f,y} - df/dy \) [dimensionless]; \( S_{f,x}, S_{f,y} \) = ground surface slope in the \( x \)- or \( y \)-direction [dimensionless]. To solve the resistance coefficient equations for \( S_h \) and \( S_f \), the absolute value of \( S_f \) is used and the sign of \( S_f \) indicates the flow direction.

Channel flow is one-dimensional and simulated using the diffusive wave approximation. Flow occurs when the water
depth exceeds the storage depth and the friction slope is not zero (Julien et al., 1995; Julien, 2002):

\[
\frac{\partial A_c}{\partial t} + \frac{\partial Q_x}{\partial x} = q_l + W \tag{4}
\]

\[
Q_x = \frac{1}{R_m} A_c R_h^{2/3} |S_f|^{1/2} \tag{5}
\]

where: \(A_c\) = cross-sectional area of flow \([L^2]\); \(Q\) = total discharge \([L^3/T]\); \(q_l\) = lateral unit flow (into or out of the channel) \([L^2/T]\); \(W\) = unit discharge from/to a point source/sink (including direct rainfall to the channel) \([L^2/T]\); \(R_h\) = hydraulic radius of flow = \(A_c/P_c\) \([L]\); \(P_c\) = wetted perimeter of channel \([L]\). To solve Eq. (5), the absolute value of \(S_f\) is used and the sign indicates the flow direction.

In floodplain areas, water and any transported constituents are transferred between the overland plane and channel network based on the difference in water surface elevations. Floodplain transfers are bi-directional. Water and transported constituents move into stream channels by overland flow and can return to the overland plane when water levels in the stream exceed bank height. Similarly, materials can be moved from the sediment bed and can be delivered to the land surface by floodwaters.

3.2. Sediment transport submodel

The sediment transport processes in the model are: (1) advection and dispersion; (2) erosion and deposition; and (3) bed elevation adjustment. All processes occur in both the overland plane and stream channel. The model state variables are solid concentrations in overland runoff, soil, stream flow, and sediments. Any number of particle size classes can be simulated. Advection is computed from flow and concentration. Erosion and deposition rates are calculated as a function of the hydraulic properties of the flow, the physical properties of the soils and sediments such as particle grain size, and surface characteristics such as slope.

For the overland plane in two-dimensions, the concentration of particles in a flow is expressed by sediment continuity (Julien, 1998):

\[
\frac{\partial C_s}{\partial t} + \frac{\partial q_{sx}}{\partial x} + \frac{\partial q_{sy}}{\partial y} = \frac{1}{R} (J_{es} - J_{ds}) + \hat{W}_s \tag{6}
\]

\[
q_{sx} = v_x C_s - R_s \frac{\partial C_s}{\partial x} \tag{7a}
\]

\[
q_{sy} = v_y C_s - R_s \frac{\partial C_s}{\partial y} \tag{7b}
\]
where: \( C_s \) = concentration of particles in the water column \([M/L^3]\); \( q_{es} \), \( q_{xy} \) = total sediment transport flux in the \( x \)- or \( y \)-direction \([M/L^2T]\); \( J_{es} \) = sediment erosion flux \([M/L^2T]\); \( J_{es} \) = sediment deposition flux \([M/L^2T]\); \( \dot{v}_x \) = advection (flow) velocity in the \( x \)- or \( y \)-direction \([L/T]\); \( v_a \), \( v_f \) = dispersion (mixing) coefficient in the \( x \)- or \( y \)-direction \([L^2/T]\).

Similarly, for the channel network in one-dimension (laterally and vertically averaged), the concentration of particles in a flow is also expressed by sediment continuity \( \text{(Julien, 1998)} \):

\[
\frac{\partial C_s}{\partial t} + \frac{\partial q_{es}}{\partial x} - \frac{1}{R_p}(J_{es} - J_{ds}) + \dot{\theta}_s. \tag{8}
\]

Definitions of terms for the channel advection-diffusion equation are identical to those defined for the overland plane. Dispersion in channels is expected to be larger than for overland flow. However, channel dispersion may still be negligible relative to channel advection during intense flows.

Erosion is expressed as a mass rate of particle removal from the bottom boundary over time, based on transport capacity:

\[
J_{es} = v_t C_{sb} \tag{9}
\]

\[
v_t = \begin{cases} 
  J_c - \frac{v_t C_s}{\rho} & \text{for } J_c > v_t C_s \\
  0 & \text{for } J_c \leq v_t C_s \tag{10}
\end{cases}
\]

where: \( v_t \) = resuspension (erosion) velocity \([L/T]\); \( C_{sb} \) = concentration of particles in the soil or sediment bed \([M/L^3]\); \( J_c \) = sediment transport capacity flux \([M/L^2T]\); \( v_a \) = advection (flow) velocity (in the \( x \)- or \( y \)-direction) \([L/T]\); and \( R_p \) = dispersion (mixing) coefficient in the \( x \)- or \( y \)-direction \([L^2/T]\).

A modified form of the Kilinc and Richardson \( \text{(1973)} \) relationship is used to compute sediment transport capacity for the overland plane \( \text{(Johnson et al., 2000; Julien and Rojas, 2002)} \) using Universal Soil Loss Equation \( \text{(USLE)} \) \( \text{(Wischmeier and Smith, 1978)} \) parameters and an explicit erosion threshold:

\[
q_t = 1.542 \times 10^6(q - q_e)^{2.035}S_f^{0.66}KCP \tag{11}
\]

\[
J_c = \frac{q_t}{B_e} \tag{12}
\]

where: \( q_t \) = total sediment transport capacity \( \text{(kg/m s)} \) \([M/L^2T]\); \( q \) = unit flow of water \([L^2/T]\); \( q_e \) = critical unit flow for erosion (of the aggregate soil matrix) \([L^2/T]\); \( S_f \) = friction slope \([\text{dimensionless}]\); \( K \) = USLE soil erodibility factor; \( C \) = USLE soil cover factor; \( P \) = USLE soil management practice factor; and \( B_e \) = width of eroding surface in flow direction \([L]\). The erosion rate estimated for the aggregate soil and is apportioned for particle type simulated according to the fractional abundance of each particle in the soil matrix (grain size distribution) and the particle dimensionless diameter \( \dot{d}_p \).

The Engelund and Hansen \( \text{(1967)} \) relationship, modified to include an explicit erosion threshold, is used to estimate the total load sediment transport capacity for channels:

\[
C_w = 0.05 \left( \frac{G}{G - 1} \right) \left( \frac{v_a - v_c}{(G - 1)g_d} \right)^{1.63} \left( \frac{R_p S_f}{(G - 1)g_d} \right)^{0.5} \tag{13}
\]

\[
J_c = v_t C_{sb} \frac{C_w}{A_c} \tag{14}
\]

where: \( C_w \) = concentration of particles by weight at transport capacity \([\text{dimensionless}]\); \( G \) = particle-specific gravity \([\text{dimensionless}]\); \( v_a \) = advection (flow) velocity (in the down-gradient direction) \([L/T]\); \( \dot{v}_f \) = critical velocity for erosion \([L/T]\); \( S \) = friction slope \([\text{dimensionless}]\); \( g \) = gravitation acceleration \([L/T^2]\); \( d_p \) = particle diameter \([L]\); and \( C_s \) = concentration of particles in the water column at transport capacity \([M/L^3]\) = \( 10^5 C_w(G + (1 - G)C_w) \) for \( C_w \) in \( g/m^3 \).

Deposition is influenced by many factors including particle density, diameter, and shape, as well as fluid turbulence and is

<table>
<thead>
<tr>
<th>Feature</th>
<th>CASC2D</th>
<th>TREX</th>
</tr>
</thead>
<tbody>
<tr>
<td>General model controls</td>
<td>One time step</td>
<td>Variable time step based on flow</td>
</tr>
<tr>
<td>Time step</td>
<td>( \Delta t )</td>
<td>One time step</td>
</tr>
<tr>
<td>Hydrologic submodel</td>
<td>Dry start assumed</td>
<td>User specified wet or dry start</td>
</tr>
<tr>
<td>Initial water depth</td>
<td>Rojas (2002)</td>
<td>Any number of outlets and downstream boundary conditions</td>
</tr>
<tr>
<td>Outlets and downstream boundary conditions</td>
<td>One outlet, assumed normal depth</td>
<td>Enhanced to compute flooding from water surface elevations</td>
</tr>
<tr>
<td>Floodplain interaction</td>
<td>Nascent features</td>
<td>Channel connections in all eight raster grid directions</td>
</tr>
<tr>
<td>Channel topology: orientation</td>
<td>Limited to four ( N-S ) or ( E-W ) directions</td>
<td>Converging and diverging branches with 2–7 connecting branches</td>
</tr>
<tr>
<td>Channel topology: branching</td>
<td>Converging branches only, limited to two branches upstream</td>
<td>Overland plane and channels</td>
</tr>
<tr>
<td>Point sources/sinks</td>
<td>None</td>
<td>Overland plane and channels</td>
</tr>
<tr>
<td>Sediment transport submodel</td>
<td>Limited to three</td>
<td>Unlimited</td>
</tr>
<tr>
<td>Number of particle types</td>
<td>None</td>
<td>When floodplain submerged</td>
</tr>
<tr>
<td>Floodplain sediment transport</td>
<td>None</td>
<td>Aggradation or degradation</td>
</tr>
<tr>
<td>Channel erosion</td>
<td>Channel aggradation only</td>
<td>Overland plane and channels</td>
</tr>
<tr>
<td>Point sources/sinks</td>
<td>None</td>
<td>Three-phase partitioning</td>
</tr>
<tr>
<td>Chemical transport and fate submodel</td>
<td>None</td>
<td>Overland plane and channels</td>
</tr>
<tr>
<td>Number of chemical types</td>
<td>None</td>
<td>Unlimited</td>
</tr>
<tr>
<td>Chemical transport and fate</td>
<td>None</td>
<td>Three-phase partitioning</td>
</tr>
<tr>
<td>Point sources/sinks</td>
<td>None</td>
<td>Overland plane and channels</td>
</tr>
</tbody>
</table>
expressed as the mass rate of particle removal from the water column by gravity over time:

\[ J_{ds} = u_{se} C_s = P_{dep} v_s C_s \]  \hspace{1cm} (15)

where: \( u_{se} \) = effective settling (deposition) velocity \([L/T]\); \( v_s \) = quiescent settling velocity \([L/T]\); and \( P_{dep} \) = probability of deposition \([\text{dimensionless}]\). \( P_{dep} \) is computed as described by Gessler (1967) (non-cohesive particles) and Krone (1962) or Partheniades (1992) (cohesive particles).

The rise or fall of the bed surface is expressed by sediment continuity (Exner, 1925). Neglecting bed consolidation and compaction processes, and assuming that only vertical transport processes (erosion and deposition) occur, sediment continuity for the change in elevation of the soil or sediment bed surface is expressed as:

\[ \frac{dz}{dt} = u_{se} C_s - v_{sab} \]  \hspace{1cm} (16)

where: \( z \) = elevation of soil surface or sediment bed \([L]\); \( \rho_b \) = bulk density of soil or bed sediments \([M/L^3]\); and \( C_{sb} \) = concentration of particles in the soil or sediment bed \([M/L^3]\).

### 3.3. Chemical transport and fate submodel

The chemical transport and fate processes in the model include: (1) chemical partitioning and phase distribution; (2) advection–diffusion; (3) erosion; (4) deposition; (5) infiltration and transmission loss; and (6) mass transfer and transformation processes (chemical reactions). The model state variables are chemical concentrations in overland runoff, soil, stream flow, and sediments. Any number of chemicals can be simulated.

Metals and many other chemicals partition between dissolved, bound (complexed with dissolved organic compounds), and particulate phases (sorbed to particles). Chemical transport and interactions depend on chemical phase. The partition (or distribution) coefficient of a chemical is defined as the ratio of the chemical concentration in particulate form to the dissolved phase concentration. Similarly, the binding coefficient is defined as the ratio of the chemical concentration in bound form to the dissolved phase concentration. Partitioning and binding can be simulated on a solids concentration or organic carbon normalized basis (Thomann and Mueller, 1987). Particle-dependent partitioning is simulated as described by DiToro (1985). Assuming local equilibrium, the chemical phase distribution is simulated as (Thomann and Mueller, 1987; Chapra, 1997):

\[ f_d = \frac{1}{1 + D_{oc} K_b + \sum_{n=1}^{N} m_n K_{pn}} \]  \hspace{1cm} (17)

\[ f_b = \frac{D_{oc} K_b}{1 + D_{oc} K_b + \sum_{n=1}^{N} m_n K_{pn}} \]  \hspace{1cm} (18)

\[ f_{pn} = \frac{m_n K_{pn}}{1 + D_{oc} K_b + \sum_{n=1}^{N} m_n K_{pn}} \]  \hspace{1cm} (19)

where: \( f_d \) = fraction of chemical in the dissolved phase \([\text{dimensionless}]\); \( f_b \) = fraction of chemical in the bound phase \([\text{dimensionless}]\); \( f_{pn} \) = fraction of chemical in the particulate phase

---

Notes: OU = Operable Unit; AVIRIS = Airborne Visible-Infrared Imaging Spectrometer

Fig. 2 - California Gulch watershed: mine-waste distribution and monitoring stations.
Table 2 – California Gulch representative metal concentrations by media for each operable unit (OU)

<table>
<thead>
<tr>
<th>OU</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>Investigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Yak Tunnel</td>
<td>Malta Gulch</td>
<td>Arkansas Valley Smelter</td>
<td>Upper California Gulch</td>
<td>Smelter Sites</td>
<td>Stay Horse Gulch and Starr Ditch</td>
<td>Apache Tailings</td>
<td>Colorado Zinc-Lead Tailings</td>
<td>Leadville Soils</td>
<td>Oregon Gulch Tailings</td>
<td>Arkansas River Floodplain</td>
<td>Surface Water and Sediments</td>
<td></td>
</tr>
<tr>
<td>Waste rock (mg/kg)</td>
<td>( \text{Cd} )</td>
<td>60</td>
<td>60</td>
<td>108</td>
<td>25</td>
<td>USEPA (1987a,b,c), WWC (1993a)</td>
<td>( \text{Cu} )</td>
<td>332</td>
<td>206</td>
<td>782</td>
<td>59</td>
<td>( \text{Zn} )</td>
<td>11,100</td>
</tr>
<tr>
<td>Slag (mg/kg)</td>
<td>( \text{Cd} )</td>
<td>31</td>
<td>15</td>
<td>26</td>
<td>15</td>
<td>65</td>
<td>4</td>
<td>USEPA (1987a,b,c), Walsh (1992), CDM (1994)</td>
<td>( \text{Cu} )</td>
<td>110</td>
<td>250</td>
<td>206</td>
<td>247</td>
</tr>
</tbody>
</table>
associated with particle \( n \) [dimensionless]; \( K_b \) = binding coefficient \([L^3/M]\); \( K_{pn} \) = partition coefficient of chemical to particle \( n \) \([L^3/M]\); \( D_{oc} \) = concentration of dissolved organic compounds (or other binding agents) \([M/L^3]\); \( m_n \) = concentration of particle \( n \) \([M/L^3]\); and \( n \) = index for each particle type simulated = 1, 2, 3, etc. Note that the fractions of the total chemical mass in each phase sums to unity: \( f_{d} + f_{b} + \sum_{n} f_{pn} = 1 \).

Advection and dispersion transport all chemical phases (i.e. the total chemical). Erosion and deposition transport particulate phases. Infiltration transports dissolved and bound phases. Analogous to sediment transport, for the overland plane in two dimensions the concentration of a chemical in a flow is expressed by chemical continuity:

\[
\frac{\partial C_c}{\partial t} + \frac{\partial q_{cx}}{\partial x} + \frac{\partial q_{cy}}{\partial y} = \frac{1}{h} J_{ec} - J_{dc} - J_{ic} + \dot{W}_c \tag{20}
\]

\[
q_{cx} = v_x C_c - R_x \frac{\partial C_c}{\partial x} \tag{21a}
\]

\[
q_{cy} = v_y C_c - R_y \frac{\partial C_c}{\partial y} \tag{21b}
\]

where: \( C_c \) = total chemical concentration in the water column \([M/L^3]\); \( q_{cx}, q_{cy} \) = total chemical transport flux in the \( x \)- or \( y \)-direction \([M/L^2T]\); \( J_{ec} \) = chemical erosion flux \([M/L^2T]\); \( J_{dc} \) = chemical deposition flux \([M/L^2T]\); \( J_{ic} \) = chemical infiltration flux \([M/L^2T]\); and \( \dot{W}_c \) = volumetric chemical point source/sink flux \([M/L^3T]\).

Similarly, for the channel network in one dimension, the concentration of a chemical in a flow is also expressed by chemical continuity:

\[
\frac{\partial C_c}{\partial t} + \frac{\partial q_{cx}}{\partial x} = \frac{1}{h} J_{ec} - J_{dc} - J_{ic} + \dot{W}_c. \tag{22}
\]

Chemical erosion and deposition are directly coupled to corresponding transport fluxes for particles as (Thomann and Mueller, 1987):

\[
J_{ec} = \sum_{n=1}^{N} v_n f_{phn} C_{cb} \tag{23}
\]
where: $v_i$ = resuspension velocity of particle $n$ [L/T]; $v_{se}$ = effective settling velocity of particle $n$ [L/T]; $f_{ph}$ = fraction of total chemical in particulate phase associated with particle $n$ in the water column [dimensionless]; $f_{phb}$ = fraction of total chemical in particulate phase associated with particle $n$ in the soil/sediment bed [dimensionless]; $C_t$ = total chemical concentration in the water column [M/L^3]; and $C_{so} =$ total chemical concentration in the soil or sediment bed [M/L^3].

Chemical infiltration is coupled to the water infiltration or transmission loss flux as:

$$J_{dc} = \sum_{i=1}^{N} u_{in} f_{ph} C_t$$  \hspace{1cm} (24)

where: $v_i$ = infiltration or transmission loss rate of water [L/T]. Dissolved and bound phase chemicals are subject to advection and other processes (e.g. retardation) during subsurface transport. For clarity, note that $v_i$ in Eq. (25) was defined as $f$ in Eq. (1).

Chemicals may also be subject to other mass transfer and transformation processes such as biodegradation, hydrolysis, oxidation, photolysis, and volatilization, and dissolution. The present model development focuses on chemical partitioning. Addition of capabilities to simulate these other chemical processes is the subject of ongoing development efforts as described by Johnson and Zhang (2006).

3.4. TREX features and implementation

A comparative overview of TREX features is presented in Table 1. A useful enhancement is the addition of point sources and sinks for flow, solids, and chemicals. Groundwater interactions with the land surface or streams could be represented as a series of time-variable point sources and sinks. This feature allows TREX to be externally coupled with groundwater flow and solute transport models such as MODFLOW (Harbaugh et al., 2000), HST3D (Kipp, 1997), and MT3DMS (Zheng and Wang, 1999). Beyond these enhancements, TREX is fully distributed and designed to be compatible with data from raster geographic information system (GIS) sources. Data describing elevation, soil types, land use, and contaminant distributions can be processed in a GIS and used as model inputs. Model outputs are also designed for post-processing with a GIS.

4. Screening-level model application: California Gulch watershed

To demonstrate the potential for using TREX to simulate chemical transport at the watershed scale, a screening-level application to the California Gulch watershed was developed. At this site, environmental impacts attributable to mine wastes include surface and groundwater contamination from acid drainage (low pH), elevated metal concentrations on the land surface and in-stream channels (water column and sediment bed), and ecological impairments (USEPA, 1987a,b,c; Walsh, 1992; WWC, 1993a,b,c,d; Walsh, 1993; CDM, 1994). Due to their toxicity to wildlife, metals of particular concern are copper (Cu), cadmium (Cd), and zinc (Zn) (Clements et al., 2002). In response to rainfall and subsequent drainage, metals released from the gulch harm water quality and degrade aquatic habitat, particularly near the confluence with the Arkansas River (USEPA, 1987a; Techlaw, 2001).

4.1. Site description and characterization

California Gulch is part of a historical mining district located near Leadville, Colorado (USA). The site is in the headwaters of the Arkansas River basin and covers an area of 30 km². Approximately 2000 waste piles exist across the site (USEPA, 1987a). The watershed includes upper and lower reaches of California Gulch (CG), Stray Horse Gulch, Starr Ditch (SD), and several smaller drainages. Monitoring stations at CG-1, SD-3, CG-4, and CG-6 are shown in Fig. 2. Elevations in the watershed range from 2900 to 3650 m (9500 to 12,000 ft) and the average slope is 12.6%. The stream through upper California Gulch is narrow, steep and ephemeral. The stream meanders through lower California Gulch with a milder slope and perennial flow from ephemeral drainages. The Yak

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrologic variables</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_s$ (m/s)</td>
<td>$1.5 \times 10^{-6}$</td>
<td>Sandy loams</td>
</tr>
<tr>
<td></td>
<td>$1.5 \times 10^{-6}$ to $1.5 \times 10^{-5}$</td>
<td>Gravelly sandy loams</td>
</tr>
<tr>
<td></td>
<td>$1.5 \times 10^{-5}$ to $1.5 \times 10^{-4}$</td>
<td>Diggings and tailings</td>
</tr>
<tr>
<td></td>
<td>$0.5 \times 10^{-7}$</td>
<td>Channel bed</td>
</tr>
<tr>
<td>Manning $n$</td>
<td>0.45</td>
<td>Forest</td>
</tr>
<tr>
<td></td>
<td>0.30 to 0.45</td>
<td>Shrub and grassland</td>
</tr>
<tr>
<td></td>
<td>0.15</td>
<td>Bare rock/sand</td>
</tr>
<tr>
<td></td>
<td>0.05 to 0.15</td>
<td>Urban/commercial</td>
</tr>
<tr>
<td></td>
<td>0.08 to 0.18</td>
<td>Channel bed</td>
</tr>
<tr>
<td>Sediment transport variables</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean diameter (mm)</td>
<td>256</td>
<td>Boulder</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>Cobble</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>Gravel</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>Sand</td>
</tr>
<tr>
<td></td>
<td>0.031</td>
<td>Silt</td>
</tr>
<tr>
<td></td>
<td>0.002</td>
<td>Clay</td>
</tr>
<tr>
<td>Settling speed (mm/s)</td>
<td>1919</td>
<td>Boulder</td>
</tr>
<tr>
<td></td>
<td>1357</td>
<td>Cobble</td>
</tr>
<tr>
<td></td>
<td>479</td>
<td>Gravel</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>Sand</td>
</tr>
<tr>
<td></td>
<td>0.88</td>
<td>Silt</td>
</tr>
<tr>
<td></td>
<td>0.0034</td>
<td>Clay</td>
</tr>
<tr>
<td>$K$ (tons/ac)</td>
<td>0.05 to 0.28</td>
<td>Sandy loams</td>
</tr>
<tr>
<td></td>
<td>0.05 to 0.15</td>
<td>Gravelly sandy loams</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>Pits and dumps</td>
</tr>
<tr>
<td></td>
<td>0.02 to 0.64</td>
<td>Diggings and tailings</td>
</tr>
<tr>
<td>$C$</td>
<td>0.04 to 0.06</td>
<td>Forest</td>
</tr>
<tr>
<td></td>
<td>0.042 to 0.08</td>
<td>Shrub and grassland</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>Bare rock/sand</td>
</tr>
<tr>
<td></td>
<td>0.001 to 0.01</td>
<td>Urban/commercial</td>
</tr>
<tr>
<td>Chemical transport variables</td>
<td></td>
<td></td>
</tr>
<tr>
<td>log $K_i$</td>
<td>2.34</td>
<td>Cd</td>
</tr>
<tr>
<td></td>
<td>3.24</td>
<td>Cu</td>
</tr>
<tr>
<td></td>
<td>2.54</td>
<td>Zn</td>
</tr>
</tbody>
</table>
Tunnel mine water treatment works and Leadville wastewater treatment plant (WWTP) also contribute to surface drainage.

A database of field measurements collected as part of assessment and remediation efforts over the period 1984–2004 was compiled. To facilitate characterization, the site is divided into 12 operable units (OUs) shown in Fig. 2. Three basic types of mine waste are found at the site: waste rock, tailings, and slag. Metal concentrations in mine wastes were measured at representative locations (USEPA, 1987a,b,c; WCC, 1993a,b; MKC, 1992; Golder, 1997). Metal concentrations in soils were measured at thousands of locations (USEPA, 1987a,b,c; Walsh, 1992, 1993; CDM, 1994). Stream bed sediments were sampled at a limited number of locations (WCC 1993a,d). Typical metal concentrations are summarized by OU in Table 2. These measurements were further augmented by surface distributions of pyritic mineral decomposition products (pyrite, goethite, jarosite, and hematite) determined using the Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) (Swayze

<table>
<thead>
<tr>
<th>Site</th>
<th>Flow: June11-12, 2003</th>
<th>Flow: September 5-8, 2003</th>
</tr>
</thead>
<tbody>
<tr>
<td>CG-1</td>
<td><img src="image1" alt="Graph" /></td>
<td><img src="image2" alt="Graph" /></td>
</tr>
<tr>
<td>SD-3</td>
<td><img src="image3" alt="Graph" /></td>
<td><img src="image4" alt="Graph" /></td>
</tr>
<tr>
<td>CG-4</td>
<td><img src="image5" alt="Graph" /></td>
<td><img src="image6" alt="Graph" /></td>
</tr>
<tr>
<td>CG-6</td>
<td><img src="image7" alt="Graph" /></td>
<td><img src="image8" alt="Graph" /></td>
</tr>
</tbody>
</table>

Fig. 4 – Hydrologic calibration and validation results with uncertainty bounds.
et al., 2000). AVIRIS data are useful for identifying areas where chemicals from mine wastes have been transported over time (Fig. 2). The database includes digital elevation and land use data obtained from the U.S. Geological Survey (USGS) and soil survey information (USDA, 1975) including the Natural Resources Conservation Service (NRCS) Soil Survey Geographic (SSURGO) database (USDA, 1995). As part of site monitoring efforts, USEPA began to operate a series of automonitors in California Gulch starting in 2002. The automonitors measure stream flow (stage), precipitation, specific conductivity, water temperature, and pH. During 2002, data were collected at CG-1 and CG-6, initially at a 15-minute interval and later at a 10-minute interval. During 2003, precipitation and stream flow were measured at the CG-1, CG-4, and CG-6 monitoring stations (Fig. 2) at 10-minute intervals. Stream flow was also measured at the SD-3 monitoring station. These data were used to define watershed properties, forcing functions, boundary conditions, and initial conditions. The database also includes a limited number of total suspended solids (TSS) and metals concentration measurements as well as other surface water quality data collected at different times over the period 1984 to 2004 (WCC, 1993c; Golder, 1996; RMC, 2001, 2002; TTRMC, 2003; CMC, 2004). Although they do not define time series information for specific rainfall-runoff events, these water quality data define the range of expected sediment and chemical transport responses for the system when they are paired with flow measurements.

4.2. Model organization and parameterization

The site was simulated at a 30-meter by 30-meter grid scale to describe surface topography and the spatial distribution of mine wastes. Based on digital elevation data (Fig. 3), the watershed area was delineated with 34,022 cells for the overland plane and 25 links (reaches) totaling 1395 nodes for the channel network, defining a total stream length of approximately 42 km (including both perennial streams and intermittent drainages). The watershed outlet is the California Gulch confluence with the East Fork of the Arkansas River. Particle sizes on the land surface and in the stream bed range from clays to boulders and were simulated as six state variables (classes): boulders, cobbles, gravel, sand, silt, and clay. Three chemical state variables were simulated: Cd, Cu, and Zn.

Within the watershed, 14 soil associations occur. Soils within the City of Leadville urbanized area were further subdivided by land use, resulting in a total of 17 soil classes in the model (Fig. 3). The characteristics (Kh, Hc, K, porosity, grain size distribution etc.) of each soil class were defined based on values reported in the NRCS SSURGO database as well as texture using the methods of Rawls et al. (1983, 1993). Kh values were adjusted during calibration to achieve agreement between measured and simulated runoff. In the overland plane, the soil column was represented as two layers with a total thickness of 15 cm. The total soil layer thickness was selected based on review of NRCS soils data that indicates the uppermost soil horizons can be underlain by a layer of

<table>
<thead>
<tr>
<th>Date</th>
<th>Event</th>
<th>Station</th>
<th>Total volume (m³)</th>
<th>Peak flow (m³/s)</th>
<th>Time to peak (h)</th>
<th>NSEC</th>
<th>RMSE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 11-12, 2003</td>
<td>CG-1</td>
<td>491</td>
<td>430</td>
<td>–12.4</td>
<td>0.014</td>
<td>0.015</td>
<td>+9.4</td>
</tr>
<tr>
<td>SD-3</td>
<td>906</td>
<td>824</td>
<td>–9.1</td>
<td>0.042</td>
<td>0.061</td>
<td>+45.4</td>
<td>8.00</td>
</tr>
<tr>
<td>CG-4</td>
<td>2136</td>
<td>1701</td>
<td>–20.4</td>
<td>0.118</td>
<td>0.108</td>
<td>–8.6</td>
<td>8.33</td>
</tr>
<tr>
<td>CG-6</td>
<td>5606</td>
<td>6031</td>
<td>+7.6</td>
<td>0.098</td>
<td>0.114</td>
<td>+16.2</td>
<td>13.17</td>
</tr>
</tbody>
</table>
| All stations | +8.6 | +15.6 | –1.5 &ndash; | 128

* Notes: RPD=Relative Percent Difference; NSEC=Nash-Sutcliffe Efficiency Coefficient; RMSE=Root Mean Square Error.
Fig. 5 – Sediment and chemical transport calibration and validation results.
coarser material at a depth of 12 to 23 cm and further underlain by even coarser layers that contain a significant fraction of cobble and larger-sized material.

In the channel network, bed characteristics (porosity, grain size distribution etc.) were defined from field observations. The sediment bed was represented as two layers with a total thickness of 10 cm. This total sediment bed thickness was selected to permit at least some description of the limited extent of sediment availability from the stream bed. Samples collected from the gulch indicate that in some locations the channel bed has a relatively thin layer of finer sediment (sand and gravel) that overlie layers of much coarser material that includes large rock fragments or bed rock (hardpan).

Within the watershed, 13 land use classes occur (Fig. 3). The characteristics (roughness, rainfall interception depth, C, P, etc.) of each land use were defined based on descriptions in the USGS National Land Cover Database (NCLD). Surface roughness (Manning n) values were selected from tabulated values presented by Woolhiser et al. (1990) and USACE (1998). Interception depths were based on tabulated values presented by Wischmeier and Smith (1978) as summarized by Julien (1998).

Chemical concentrations and distributions in soil and sediment were estimated from site characterization and AVIRIS data. Two-phase partitioning was simulated, where the total concentration is the sum of the dissolved and particulate phases. Partition (distribution) coefficients for Cd, Cu, and Zn were defined as described by Sauvé et al. (2000, 2003) and Lu and Allen (2001). Chemical partitioning in surface water is sensitive to numerous environmental factors, including pH, which has been close to 6.0 in recent years (2001–2004).

### 4.3. Calibration and validation

A June 12–13, 2003 storm was used for calibration and a September 5–8, 2003 storm for validation. There was no precipitation for several days preceding either event, indicating that prevailing antecedent soil moisture conditions for the site were generally low. This is consistent with site-specific hydrologic analyses presented by SAI (1997). Flow records collected by USEPA in 2003 were used to calibrate the model. Discharges from the Leadville WWTP and stream inputs from groundwater were determined from flow records and were represented as flow point sources.

The calibration procedure focused on properly simulating runoff volume, peak flow, and the time to peak flow at the

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**Table 5 - Sediment and chemical transport model performance evaluation summary**

<table>
<thead>
<tr>
<th>Station</th>
<th>Variable</th>
<th>Measured concentration (mg/L)</th>
<th>Simulated concentration (mg/L)</th>
<th>Modeled period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Median (low–high)</td>
<td>Median (low–high)</td>
<td></td>
</tr>
<tr>
<td>CG-1</td>
<td>TSS</td>
<td>37.3 (1.0–386)</td>
<td>8.42 (3.77–11.9)</td>
<td>June 03</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>0.044 (0.011–1.82)</td>
<td>0.045 (0.007–0.055)</td>
<td>June 03</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.068 (0.001–0.077)</td>
<td>0.219 (0.111–0.225)</td>
<td>June 03</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>0.600 (0.098–15.1)</td>
<td>0.245 (0.019–0.435)</td>
<td>June 03</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>1.39 (0.208–31.7)</td>
<td>11.5 (2.33–13.1)</td>
<td>June 03</td>
</tr>
<tr>
<td>SD-3</td>
<td>TSS</td>
<td>40.4 (4.0–1680)</td>
<td>47.1 (6.92–293)</td>
<td>June 03</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>0.232 (0.005–0.772)</td>
<td>0.030 (0.016–0.033)</td>
<td>June 03</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>0.229 (0.017–12.9)</td>
<td>0.059 (0.042–0.095)</td>
<td>June 03</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>6.88 (0.031–78.0)</td>
<td>4.45 (2.67–5.00)</td>
<td>June 03</td>
</tr>
<tr>
<td>CG-4</td>
<td>TSS</td>
<td>30.0 (9.0–868)</td>
<td>13.6 (1.87–235)</td>
<td>June 03</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>0.139 (0.013–0.382)</td>
<td>0.057 (0.013–0.062)</td>
<td>June 03</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>0.476 (0.017–3.62)</td>
<td>0.225 (0.137–0.367)</td>
<td>June 03</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>37.3 (4.95–76.6)</td>
<td>12.3 (3.73–14.6)</td>
<td>June 03</td>
</tr>
<tr>
<td>CG-6</td>
<td>TSS</td>
<td>30.0 (1.0–446)</td>
<td>31.7 (11.7–82.6)</td>
<td>June 03</td>
</tr>
<tr>
<td></td>
<td>Cd</td>
<td>0.068 (0.005–0.282)</td>
<td>0.061 (&lt;0.001–0.069)</td>
<td>June 03</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>0.228 (0.011–2.56)</td>
<td>0.261 (0.006–0.336)</td>
<td>June 03</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>16.4 (1.10–57.7)</td>
<td>13.9 (0.074–15.3)</td>
<td>June 03</td>
</tr>
</tbody>
</table>

*Measurements were for the period 1984–2004. Low/high refer to the lowest/highest values measured in the field or simulated by the model.*
outlet (Station CG-6) and other monitoring stations (CG-1, CG-4, and SD-3). The model was then expected to yield reasonably good results in terms of runoff hydrographs, sediment transport in suspension and metals at the other internal station in the watershed. Model parameters subject to calibration were effective hydraulic conductivity ($K_h$), roughness ($n$), soil erodibility ($K_c$), land cover factor ($C$), and the chemical distribution (partition) coefficient ($K_d$). Calibrated parameter values are summarized in Table 3. With one exception, parameter values for the validation simulation were identical to those for calibration. The exception was that June storm $K_h$ values for two soil types that occur at elevations greater than 3350 m were 50% lower than values for the September storm to account for frozen soil conditions that existed as determined from snowpack monitoring data for California Gulch (Gerton, 2004), NRCS snowpack telemetry (SNOTEL) data from a nearby gage at an elevation of 3475 m, and air temperature data from the Lake County Airport weather station at an elevation of 3056 m.

Hydrologic submodel performance was evaluated by comparing model results and measurements for three metrics: total flow volume, peak flow discharge, and time to peak flow. Rainfall intensities, measured and simulated flow discharges at Stations CG-1, SD-3, CG-4, and CG-6 are presented in Fig. 4 for both the calibration and validation events. Hydrologic submodel uncertainty limits are also presented in Fig. 4. These limits were determined from upper and lower bound combinations for $K_h$ (+100%, −33%) and Manning $n$ (+100%, −50%) using a logic tree approach (Mishra, 2001). Performance evaluations for these simulations are presented in Table 4.

Solids and chemical transport submodel performance was evaluated by comparing model results with measurements as functions of flow discharge. Measured and simulated TSS, Cd, Cu, and Zn concentrations as functions of discharge at Stations CG-1, SD-3, CG-4, and CG-6 are presented in Fig. 5. Model performance for dissolved metals is similar to performance for total metals. TSS and metals show expected hysteresis patterns for their concentration-discharge rating curves that are typically caused by changes in flow acceleration during the rising and falling limbs of runoff hydrographs. Similar behavior has been observed for overland and channel flow in other systems (House and Warwick, 1998; Seeger et al., 2004; Bowes et al., 2005). Performance evaluations for these simulations are presented in Table 5. Additional results detailing solids and chemical transport submodel uncertainty limits are presented in Velleux (2005). Model results for a 1-in-100-year storm event, associated bounding calculations, and estimates of toxic impacts are also presented in Velleux (2005) and Velleux et al. (2006b).

5. Discussion

High quality data were available to construct and evaluate the hydrologic components of the California Gulch application. TREX model parameterization for the calibration event in June shows that flow volumes, peak flows, and times to peak were all accurately simulated at the outlet and at internal gauging stations. The total flow volume relative percent difference (RPD) was −8.6%, the peak flow RPD was +15.6%, and the time to peak RPD was −1.5%. The average Nash-Sutcliffe Efficiency Coefficient (NSEC) was 0.64 and Root Mean Square Error (RMSE) was 34.6%. For the validation event, simulated hydrographs generally had the proper overall shape with an average total flow volume RPD of +11.3%. However, differences in the scale and timing of peak flows resulted in lower NSEC and higher RMSE values.

In-stream data to evaluate sediment and chemical transport components of model application to California Gulch are less complete but nonetheless typical of the extent of data that might be available for a high mountain, mine-waste-contaminated watershed. In general, TSS and metal concentrations for the two rainfall events in 2003 are in the range of measurements for the period 1984 to 2004. This is encouraging because the model was able to simultaneously reproduce the hydrographs and concentration ranges for four different constituents (TSS, Cd, Cu, and Zn) at four locations. Each metal has a different spatial distribution on the land surface and in the stream bed. Good agreement with field measurements for metals transport is an indication of successful sediment transport simulation because metals transport is particle mediated.

It is worth noting that substantial remediation efforts to minimize erosion of mine wastes from the land surface were completed between 1984 and 2004. In particular, the Apache Tailings area (OU 7) and Starr Ditch (the stream between Stray Horse Gulch and California Gulch) have undergone extensive remediation. Consequently, the tendency of simulated metal concentrations for these storm events in 2003 to be near the low range of measurements at SD-3 and CG-4 may be a reflection of the impact of remediation near those monitoring stations. It is also worth noting that the model calibration and validation effort represent a screening-level application intended to demonstrate the basic operation and utility of TREX chemical transport components rather than an exhaustive exploration of the site-specific characteristics of California Gulch. Model evaluation at other mine-waste sites with more extensive water quality data, particularly time series data, is warranted.

TREX was developed as a tool to assess potential remediation efforts of metals contaminants at mine-waste sites. Two key features of this model are: (i) the ability to represent the horizontal and vertical distributions of site features and contaminants; and (ii) to integrate water, soils and chemicals into a single model framework. In the context of California Gulch, the model was used to examine impacts associated with the contemporary distribution of wastes across a Superfund site. TREX could also be used to evaluate environmental management alternatives for a site where remediation has not yet begun to assess potential changes in spatial distributions of site characteristics. Similarly, TREX could also be used to examine operational considerations of waste placement at active mine sites.

6. Conclusions

TREX is a spatially distributed numerical model to assess the watershed transport and fate of contaminants. This model simulates event hydrology, sediment transport, and chemical transport and fate processes including: (1) chemical erosion, advection, and deposition; (2) chemical partitioning and phase distribution; and (3) chemical infiltration and redistribution.
Model functionality was demonstrated by a screening-level application to the California Gulch watershed. Using a database of observations for the period 1984–2004, site hydrology, sediment transport, and chemical transport and fate were simulated for two events. The model reproduced measured flow volumes, peak flows, and times to peak for these events. Average relative percent differences for flow volume estimates were $-8.6\%$ for the calibration event and $+11.3\%$ for the validation event. The model also reproduced measured ranges of TSS and total metal concentrations.

Acknowledgments

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