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# Simulation of Metals Transport and Toxicity at a Mine-Impacted Watershed: California Gulch, Colorado

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The transport and toxicity of metals at the California Gulch, Colorado mine-impacted watershed were simulated with a spatially distributed watershed model. Using a database of observations for the period 1984−2004, hydrology, sediment transport, and metals transport were simulated for a June 2003 calibration event and a September 2003 validation event. Simulated flow volumes were within approximately 10% of observed conditions. Observed ranges of total suspended solids, cadmium, copper, and zinc concentrations were also successfully simulated. The model was then used to simulate the potential impacts of a 1-in-100-year rainfall event. Driven by large flows and corresponding soil and sediment erosion for the 1-in-100-year event, estimated solids and metals export from the watershed is 10 000 metric tons for solids, 215 kg for Cu, 520 kg for Cu, and 15 300 kg for Zn. As expressed by the cumulative criterion unit (CCU) index, metals concentrations far exceed toxic effects thresholds, suggesting a high probability of toxic effects downstream of the gulch. More detailed Zn source analyses suggest that much of the Zn exported from the gulch originates from slag piles adjacent to the lower gulch floodplain and an old mining site located near the head of the lower gulch.

## Introduction

California Gulch is part of a historical mining district located near Leadville, Colorado. Mining and related activities such as ore milling and smelting began in the gulch in 1859 (*1*). One legacy of these activities is extensive contamination of the watershed by a variety of mining wastes including waste rock, tailings, and slag. Approximately 2,000 waste piles exist across the site (*1*−*6*). Environmental impacts attributable to these wastes include surface water and groundwater contamination from acid rock drainage, elevated metals concentrations on the land surface and in stream sediments, and ecological impairments (*2*−*10*). Metals of particular concern due to their toxicity to aquatic organisms are cadmium (Cd), copper (Cu), and zinc (Zn) (*11*). In response to rainfall, surface erosion, and subsequent transport, metals are exported from the gulch and harm water quality and habitat in downstream areas, particularly at the confluence with the Arkansas River (*2*, *12*). Efforts to remediate the gulch began in 1983 when the U.S. Environmental Protection Agency (USEPA) placed the site on the National Priority List for the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) (Superfund) (*2*).

The objectives of this research were to (1) calibrate and validate a watershed model to simulate the transport and fate of metals at California Gulch, and (2) demonstrate how the model can be used to assess the extent that individual contaminated areas contribute to overall impairments. To meet these objectives, the *T*wo-dimensional, *R*unoff, *E*rosion, and *E*xport (TREX) watershed model (*13*) was applied to California Gulch. Runoff, sediment transport, and metals transport were simulated using TREX for a June, 2003 calibration event and a September, 2003 validation event. Once calibrated and validated, the model was used to simulate metals transport and toxicity, and the contributions of different source areas for a 1-in-100-year, 2-hour-duration design storm.

## Methods

**Site Description and Characterization.** The site covers an area of approximately 30 km$^2$ and lies within the headwaters of the Arkansas River basin (Figure 1). The California Gulch watershed includes the upper and lower reaches of California Gulch, Stray Horse Gulch, and several smaller drainages. The locations of the most extensive waste rock piles, fluvial tailings, and slag piles are shown. These mine wastes are widely distributed across the site. Stream monitoring stations at CG-1, SD-3, CG-4, and CG-6 are shown. Through upper California Gulch, the stream is narrow, high slope, and ephemeral. In its lower reaches, the stream meanders, has a milder slope, and is perennial, receiving water from ephemeral drainages, the Yak Tunnel mine water treatment works, the Leadville wastewater treatment plant, and recharge from the shallow alluvial aquifer that underlies the stream.

A database of field observations collected as part of characterization and remediation efforts over the period 1984−2004 was compiled. Within the watershed, three basic types of mine waste exist: waste rock, tailings, and slag. Metals concentrations in mine wastes were measured during numerous sampling efforts (*2*−*4*, *14*−*15*). In addition, metals concentrations in soils were measured at thousands of locations across the site (*2*, *7*−*10*). Stream sediments were also sampled (*5*−*6*). Typical metals concentrations are summarized in Table 1. These field measurements were further augmented by surface distributions of pyrite mineral decomposition products (pyrite, goethite, jarosite, and hematite) determined using the Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) (*16*). AVIRIS data are useful for identifying areas where chemicals from mine wastes have been transported over time. The database includes suspended solids and metals concentrations as well as other surface water quality data (*5*, *17*−*21*). The database also includes digital elevation and land use data obtained from the U.S. Geological Survey (USGS) and soil survey information (*22*) including the Natural Resources Conservation Service (NRCS) SSURGO database (*23*). During 2003, rainfall and streamflow data were collected at the CG-1, CG-4, and CG-6 monitoring stations at a 10-minute interval. Flow data were also collected at the SD-3 monitoring station at a 10-minute interval.

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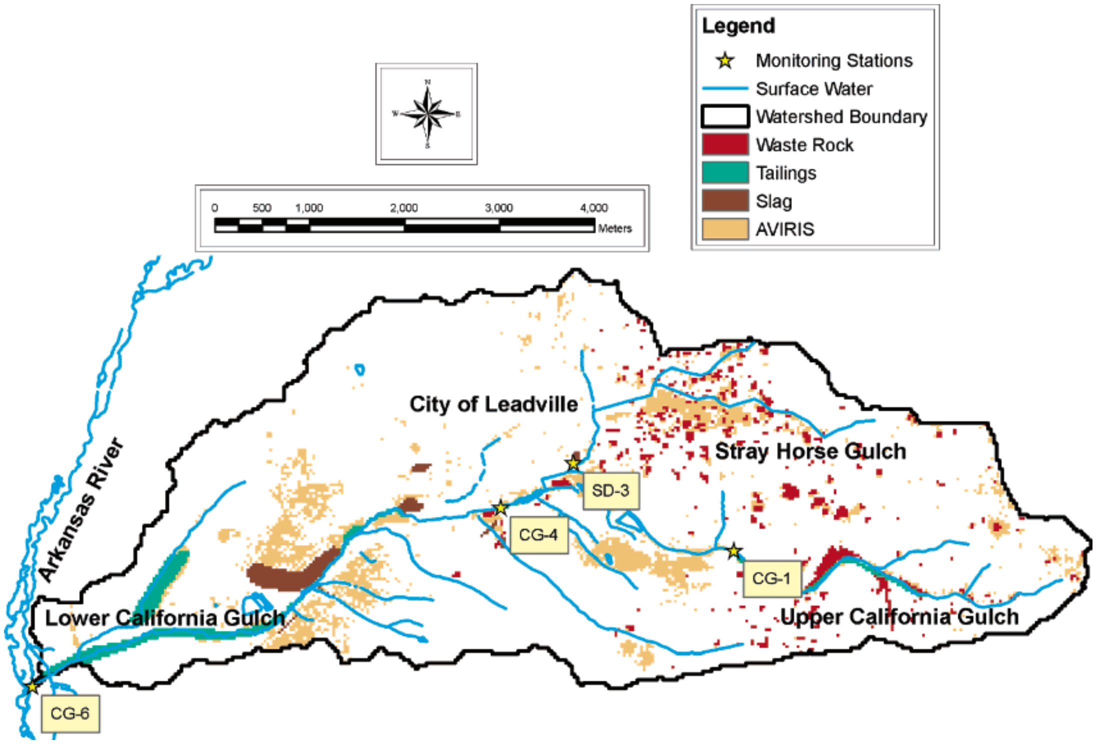


**FIGURE 1. California Gulch Watershed: waste distribution and monitoring stations.**

**TABLE 1. California Gulch Metals Concentrations**

| material | typical concentration range (mg/kg) cadmium | copper | zinc | investigation |
|---|---|---|---|---|
| waste rock | 25–108 | 59–782 | 4,040–14,200 | USEPA (*2, 7*)<br>WWC (*3*) |
| tailings | 12–61 | 160–826 | 859–12,200 | USEPA (*2, 7*)<br>WWC (*4*)<br>Golder (*16*) |
| slag | 5 | 570 | 66,000 | USEPA (*2, 7*)<br>MKC (*15*) |
| disturbed soils | 4–65 | 110–250 | 573–4,568 | USEPA (*2, 7*)<br>Walsh (*8*)<br>CDM (*10*) |
| undisturbed soils | 15 | 159 | 590 | USEPA (*2, 7*)<br>Walsh (*8, 9*)<br>CDM (*10*) |
| sediments | 2–438 | 84–1,260 | 200–7,500 | WWC (*5, 6*)<br>Golder (*18*) |

**TREX Watershed Model.** TREX is a fully distributed, physically based numerical model to simulate chemical transport and fate at the watershed scale. TREX has three major submodels: hydrology, sediment transport, and chemical transport. The hydrologic submodel is driven by rainfall and includes processes for infiltration, overland flow, channel flow, and transmission loss. Key parameters include hydraulic conductivity ($K_h$), and surface roughness (Manning $n$). The sediment transport submodel is driven by overland and channel flows and includes processes for erosion and deposition. Key parameters include grain size, erosion threshold (e.g., critical shear stress), soil erosivity ($K$), land cover factor ($C$), porosity, and grain size distribution. The chemical transport submodel is driven by flow and sediment transport and includes processes for chemical partitioning, erosion, deposition, and dissolved phase infiltration. Key parameters include the distribution (partition) coefficient ($K_d$) and the initial distribution of chemicals in soil and sediment. A detailed description of TREX model development is presented in the Supporting Information (SI). A conceptual diagram of the chemical model processes in the TREX California Gulch application is presented in Figure 2.

The toxicity of a mixture of metals is expressed by the cumulative criterion unit (CCU) index (*11, 24–25*). The CCU is the ratio of dissolved recoverable metals concentration to a hardness-adjusted water quality criterion, summed for all metals in the mixture. Water quality criterion continuous concentrations (*26*) are used to represent chronic effects. CCU values less than 1.0 correspond to a no-observed-effects level and values greater than 10 correspond to a high probability of effects (*11*).

**Model Organization and Parameterization.** The site was simulated at a 30-meter by 30-meter grid scale to resolve surface topography and the spatial distribution of mine wastes. Based on digital elevation data, the watershed area was delineated as 34,002 cells for the overland plane and 25 links (reaches) totaling 1395 nodes for the channel network. The watershed outlet is the California Gulch confluence with the Arkansas River. Particles range in size from clays to boulders and were simulated as six state variables: boulders,

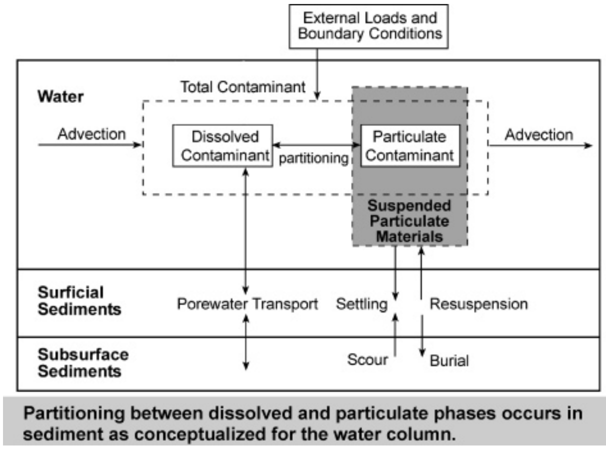


**FIGURE 2. Generalized conceptual model framework for chemical processes.**

cobbles, gravel, sand, silt, and clay. Three chemical state variables were simulated: Cd, Cu, and Zn.

Within the watershed, 14 soil associations and 13 land use classes occur. In the City of Leadville urbanized area, soils were further subdivided by land use resulting in a total of 17 soil types in the model. Soil characteristics ($K_h$, $K$, porosity, grain size, etc.) were defined by values reported in the SSURGO database (*23*) as well as texture using the methods described by Rawls et al. (*27*–*28*). 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 indicate the uppermost soil horizons are underlain by a layer of coarser material at a depth of 12–23 cm and further underlain by even coarser layers that contain a significant fraction of cobble and larger-sized material. Land use characteristics were defined based on descriptions in the USGS National Land Cover Database. Surface roughness values were selected from tabulated values presented by Woolhiser et al. (*29*) and USACE (*30*). Interception depths were based on tabulated values presented by Linsley et al. (*31*) and Woolhiser et al. (*29*). Land cover factors were selected based on values presented by Wischmeier and Smith (*32*) as summarized by Julien (*33*).

In the channel network, bed characteristics were defined from field observations. The sediment bed is non-cohesive and 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 streambed. Bed samples collected from the gulch indicate that in some locations the channel bed has a thin layer of finer sediment (sand and gravel) that overlies layers of much coarser material that includes large rock fragments or bedrock (hardpan).

Metals concentrations in soil, sediment, and mine waste were defined 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 selected as described by Sauvé et al. (*34*–*35*) and Lu and Allen (*36*). Chemical partitioning is sensitive to several environmental factors, the most significant of which is pH. California Gulch surface water pH is highly variable and has been observed to range from less than 3 to more than 8. Over this range, partition coefficients (log $K_d$) for Cd, Cu, and Zn vary by more than a factor of 3. A representative surface water pH of 6.0 determined from recent field observations was used to account for the pH dependence of partition coefficients, with log $K_d$ values in the range presented by Sauvé et al. (*34*). Metals toxicity is strongly influenced by hardness. Hardness in the gulch ranges from 58 to 1330 mg/L and averages approximately 400 mg/L. Hardness-adjusted water quality criterion continuous concentrations for dissolved Cd, Cu, and Zn are 0.58, 55, and 382 $\mu$g/L, respectively.

**TABLE 2. Summary of Calibrated Model Parameter Values for California Gulch**

| parameter | range | description |
|---|---|---|
| $K_h$ (m/s) | $1.5 \times 10^{-6}$ | sandy loams |
| | $1.5 \times 10^{-6}$–$2.0 \times 10^{-6}$ | gravelly sandy loams |
| | $1.5 \times 10^{-6}$–$2.8 \times 10^{-6}$ | pits and dumps |
| | $1.0 \times 10^{-6}$–$1.5 \times 10^{-6}$ | diggings and tailings |
| | 0–$5.0 \times 10^{-7}$ | channel bed |
| K (tons/acre) | 0.05–0.28 | sandy loams |
| | 0.05–0.15 | gravelly sandy loams |
| | 0.02 | pits and dumps |
| | 0.02–0.64 | diggings and tailings |
| Manning $n$ | 0.45 | forest |
| | 0.30–0.45 | shrub and grassland |
| | 0.15 | bare rock/sand |
| | 0.05–0.15 | urban/commercial |
| | 0.08–0.18 | channel bed |
| C | 0.4–0.6 | forest |
| | 0.042–0.08 | shrub and grassland |
| | 0.2 | bare rock/sand |
| | 0.001–0.01 | urban/commercial |
| log $K_d$ (L/kg) | 2.34 | Cd |
| | 3.24 | Cu |
| | 2.54 | Zn |

## Results

**Model Calibration and Validation.** A June 12–13, 2003 storm was used for calibration and a September 5–8, 2003 storm was used for validation. The events simulated were selected from the precipitation record based on rainfall volume, intensity, and duration. The pattern of rainfall for the validation event is significantly different from that of the calibration event as needed to test the reliability of the model parameterization. There was no precipitation for several days preceding either event. The model parameters subject to calibration were hydraulic conductivity, surface roughness, soil erosivity, land cover factor, and chemical distribution coefficients. Calibrated model parameter values are summarized in Table 2. With one exception, parameter values for the validation simulation were identical to those for calibration. The exception was that during the June storm hydraulic conductivity values for soil types at the highest elevations (>3350 m) in the watershed were decreased by 50% to account for frozen soil conditions as determined from NRCS SNOTEL data from a nearby gage at an elevation of 3475 m.

Rainfall, flow, total suspended solids (TSS), and total Zn concentrations at CG-1, SD-3, CG-4, and CG-6 for the calibration and validation events are presented in Figure 3. Results for Zn are representative of results for Cd and Cu. Model performance for dissolved metals is similar to performance for total metals. Hydrologic submodel performance was evaluated by comparing the relative percent difference (RPD) between model results and observations for three metrics: (1) total flow volume; (2) peak flow; and (3) time to peak flow. Summaries of hydrologic performance evaluations are presented in Table 3. Note that TSS and metals concentration data were collected over the period 1984 to 2004. No concentration data are paired in time with the specific events simulated or any other events for which both rainfall and flow data exist. In the absence of comparable time series data, sediment and chemical transport submodel performance was evaluated by comparing the range of model results to the range of observations as functions of flow. Summaries of sediment and chemical transport performance evaluations are presented in Table 4. TSS and metals show

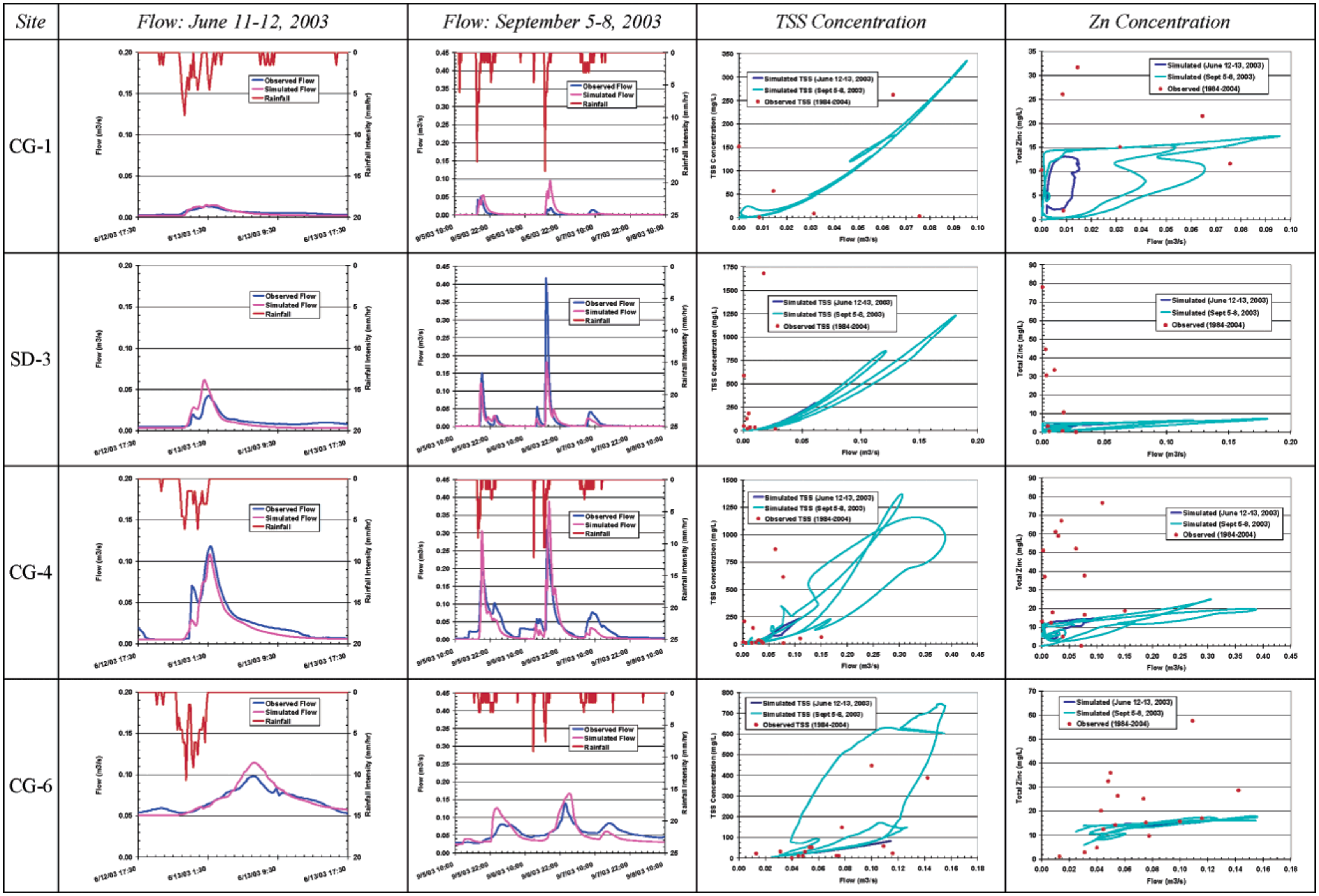


FIGURE 3. Hydrologic, sediment transport, and chemical transport calibration and validation results.

**TABLE 3. Hydrologic Model Performance Evaluation Summary**

| | | metric | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | total volume ($m^3$) | | | peak flow ($m^3$/s) | | | time to peak (hrs) | | |
| event | station | observed | simulated | RPD[a] (%) | observed | simulated | RPD[a] (%) | observed | simulated | RPD[a] (%) |
| June | CG-1 | 491 | 430 | −12.4 | 0.014 | 0.015 | +9.4 | 7.83 | 7.82 | −0.2 |
| | SD-3 | 906 | 824 | −9.1 | 0.042 | 0.061 | +45.4 | 8.00 | 7.58 | −5.2 |
| | CG-4 | 2136 | 1701 | −20.4 | 0.118 | 0.108 | −8.6 | 8.33 | 8.20 | −1.6 |
| | CG-6 | 5606 | 6031 | +7.6 | 0.098 | 0.114 | +16.2 | 13.17 | 13.30 | +1.0 |
| | all stations | | | −8.6 | | | +15.6 | | | −1.5 |
| September | CG-1: 1st peak | 737 | 1541 | +109 | 0.051 | 0.055 | +8.9 | 9.00 | 9.80 | +8.9 |
| | 2nd peak | | | | 0.020 | 0.095 | +382 | 8.83 | 8.65 | −2.1 |
| | 3rd peak | | | | 0.014 | 0.003 | −78.3 | 3.33 | 5.45 | +63.5 |
| | SD-3: 1st peak | 3570 | 2371 | −33.6 | 0.150 | 0.122 | −18.7 | 9.17 | 8.85 | −3.4 |
| | 2nd peak | | | | 0.412 | 0.181 | −56.6 | 7.16 | 7.40 | +3.3 |
| | 3rd peak | | | | 0.041 | 0.023 | −43.3 | 2.33 | 1.60 | −31.4 |
| | CG-4: 1st peak | 9571 | 7138 | −25.4 | 0.188 | 0.306 | +62.5 | 9.33 | 9.15 | −2.0 |
| | 2nd peak | | | | 0.308 | 0.388 | +25.8 | 7.50 | 8.25 | +10.0 |
| | 3rd peak | | | | 0.077 | 0.033 | −56.9 | 3.00 | 2.75 | −8.3 |
| | CG-6: 1st peak | 14997 | 14276 | −4.8 | 0.082 | 0.127 | +55.9 | 16.00 | 14.35 | −10.3 |
| | 2nd peak | | | | 0.140 | 0.167 | +19.0 | 13.83 | 15.20 | −9.9 |
| | 3rd peak | | | | 0.084 | 0.060 | −27.6 | 8.83 | 7.95 | −10.0 |
| | all stations: 1st peak | | | +11.3 | | | +27.1 | | | −1.7 |
| | 2nd peak | | | | | | +92.5 | | | +5.3 |
| | 3rd peak | | | | | | −51.5 | | | +3.4 |

[a] RPD = relative percent difference.

**TABLE 4. Sediment and Chemical Transport Model Performance Evaluation Summary**

| | | observed concentration (mg/L) | | | simulated concentration (mg/L) | | | |
|---|---|---|---|---|---|---|---|---|
| station | variable | low | median | high | low | median | high | modeled period |
| CG-1 | TSS | 1.0 | 37.3 | 386 | 3.77 | 8.42 | 11.9 | June 03 |
| | | | | | 3.52 | 49.3 | 335 | Sept 03 |
| | Cd | 0.011 | 0.044 | 1.82 | 0.007 | 0.045 | 0.055 | June 03 |
| | | | | | 0.001 | 0.068 | 0.077 | Sept 03 |
| | Cu | 0.098 | 0.600 | 15.1 | 0.111 | 0.219 | 0.225 | June 03 |
| | | | | | 0.019 | 0.245 | 0.435 | Sept 03 |
| | Zn | 0.208 | 1.39 | 31.7 | 2.33 | 11.5 | 13.1 | June 03 |
| | | | | | 0.343 | 14.5 | 17.4 | Sept 03 |
| SD-3 | TSS | 4.0 | 40.4 | 1680 | 6.92 | 47.1 | 293 | June 03 |
| | | | | | 4.01 | 30.1 | 1231 | Sept 03 |
| | Cd | 0.005 | 0.232 | 0.772 | 0.016 | 0.030 | 0.033 | June 03 |
| | | | | | 0.002 | 0.028 | 0.042 | Sept 03 |
| | Cu | 0.017 | 0.229 | 12.9 | 0.042 | 0.059 | 0.095 | June 03 |
| | | | | | 0.014 | 0.056 | 0.235 | Sept 03 |
| | Zn | 0.031 | 6.88 | 78.0 | 2.67 | 4.45 | 5.00 | June 03 |
| | | | | | 0.324 | 4.38 | 7.23 | Sept 03 |
| CG-4 | TSS | 9.0 | 30.0 | 868 | 1.87 | 13.6 | 233 | June 03 |
| | | | | | 1.62 | 26.9 | 1370 | Sept 03 |
| | Cd | 0.013 | 0.139 | 0.382 | 0013 | 0.057 | 0.062 | June 03 |
| | | | | | 0.002 | 0.050 | 0.095 | Sept 03 |
| | Cu | 0.017 | 0.476 | 3.62 | 0.137 | 0.225 | 0.367 | June 03 |
| | | | | | 0.026 | 0.209 | 1.09 | Sept 03 |
| | Zn | 4.95 | 37.3 | 76.6 | 3.73 | 12.3 | 14.6 | June 03 |
| | | | | | 0.380 | 11.2 | 25.0 | Sept 03 |
| CG-6 | TSS | 1.0 | 30.0 | 446 | 11.7 | 31.7 | 82.6 | June 03 |
| | | | | | 4.47 | 27.2 | 747 | Sept 03 |
| | Cd | 0.005 | 0.068 | 0.282 | < 0.001 | 0.061 | 0.069 | June 03 |
| | | | | | < 0.001 | 0.044 | 0.076 | Sept 03 |
| | Cu | 0.011 | 0.228 | 2.56 | 0006 | 0.261 | 0.336 | June 03 |
| | | | | | 0.002 | 0.240 | 0.542 | Sept 03 |
| | Zn | 1.10 | 16.4 | 57.7 | 0.074 | 13.9 | 15.3 | June 03 |
| | | | | | 0.034 | 11.2 | 17.8 | Sept 03 |

the expected patterns of concentration-discharge loop hysteresis that is typically caused by changes in flow acceleration over time (rising vs falling limbs of the hydrograph) and has been observed for overland and channel flow in other systems (*37*–*39*).

With respect to hydrology, model performance for calibration was quite good. The flow volume, peak flow, and time to peak are all accurately simulated. The total flow volume RPD was −8.6%, the peak flow RPD was +15.6%, and the time to peak RPD was −1.5%. Although less strong than the calibration, the overall model performance for validation was also good. In particular, the total flow volume RPD across all stations for the September event was +11.3%.

With respect to sediment transport, TSS concentrations for both simulations were well within the range of observations and considered to be satisfactory. In general, the minimum, median, and maximum values observed were reproduced. However, in some instances the model has a low bias where simulated TSS is less than observed. This low bias may be attributable to uncertainty in the initial grain size distribution of solids in the sediment bed or erosion thresholds.

With respect to chemical transport, metals concentrations for both simulations were also within the range of observations and considered to be satisfactory. In general, the minimum and median values observed were reproduced, although results for Zn and Cd were more accurate than those for Cu. In comparison to maximum values, the model has a low bias as simulated metals are typically less than observed. As noted for TSS, this low bias may be attributable to uncertainty in the initial grain size distribution of solids in the sediment bed as well as uncertainty in initial sediment metals concentrations. However, some of the variability in metals concentrations at low flow may reflect spatial and temporal variations in surface water−groundwater interactions. At several locations across the gulch the stream bed intersects the phreatic surface and metals in groundwater can enter the stream. For simplicity, metals concentrations in stream base flow were neglected because, in terms of mass, metals input from groundwater is expected to be a very small component of the overall mass balance during the events simulated.

**Model Application: 1-in-100-Year Design Storm Simulation and Source Identification.** The calibrated watershed model was used to simulate hydrology, sediment transport, and chemical transport and fate for the 1-in-100-year, 2-hour-duration design storm event. This design storm was selected because it is of a size typically considered informative for remediation planning purposes. Based on the analysis of SAI (*40*), this event was estimated to have an intensity of 22 mm/hour and was assumed to have a uniform distribution over the entire watershed. SAI (*40*) further found that the probability of very intense rainfall events is greatest when average soil moisture (unsaturated and snow-free) conditions are most common. For all parameters other than rainfall, model setup for the 1-in-100-year design storm was identical to the September 2003 storm.

Water depths, TSS and Zn concentrations, and metals CCU index values across the watershed at different times during the 1-in-100-year event simulation are presented in Figure 4. At CG-6, the average flow was 4 $m^3/s$ and the peak flow was 22 $m^3/s$. This is within the range summarized by SAI (*40*). Driven by the large flows generated and corresponding soil and sediment erosion during the simulation, solids and metals export from the watershed is very large. At CG-6, TSS export was approximately 10 000 metric tons while exports for total Cd, Cu, and Zn were 215, 520, and 15 300 kg, respectively. As expressed by the CCU index, metals concentrations in water leaving the gulch far exceed potential toxic effects thresholds. However, it should be noted that this simple assessment only considers exposure magnitude. For a more realistic assessment it is necessary to also consider the exposure duration under the conditions at the impact site.

Net elevation change and net Zn mass accumulation for the 1-in-100-year event are presented in Figure 5. Regions of the greatest net elevation decrease (net erosion) generally correspond to the areas of the greatest metals loss. However, some mine waste types have extremely large metals concentrations (i.e., slag is 6.6% Zn by weight) so even a relatively small degree of erosion can cause a very large net loss of metals from a waste pile.

A check on model performance was made using dissolved Zn loads monitored during Spring 2003 and extrapolating to flow conditions for the 1-in-100-year event. During Spring 2003, the average dissolved Zn load at CG-6 was approximately 45 kg/day and ranged from 22 to 110 kg/day, while flows averaged 0.07 $m^3/s$ and ranged from 0.03 to 0.15 $m^3/s$ (*20*). This corresponds to a typical dissolved Zn concentration of 7.5 $g/m^3$. Assuming dissolved Zn concentrations stay constant as flow increases (to provide a lower bound estimate), the inferred dissolved Zn load for the 1-in-100-year event is 2600 kg/day at the average flow rate and 14 250 kg/day at peak flow. This compares well with the simulated dissolved Zn load of 9500 kg/day for the 1-in-100-year event.

The model results can be used to address questions of management interest to guide mine waste impact mitigation efforts by examining the load of material transported through different areas of the gulch. In-stream solids and metals loads passing CG-1 are typically twice as large as loads passing SD-3, suggesting that the upper gulch is a more significant contributor of material to the lower gulch than is Stray Horse Gulch. However, solids and metals loads exported from the lower gulch are larger than loads imported from the upstream channel network. This suggests floodwaters can erode wastes along channel margins in the lower gulch floodplain.

Using Zn as an example, further information was obtained by using the model to track metals transport from different source areas (Table 5). This analysis is based on a decomposition of the model solution using the principle of linear superposition and treating Zn from each source area as an independent state variable. At CG-6, 90% of the Zn exported to the Arkansas River originates from the lower gulch floodplain. Export from more distant source areas is more limited because flows are smaller (less erosion) and the potential for deposition is larger because transport distances are longer and slopes decrease in floodplain areas. However, because mining and ore processing activities did not occur directly in the lower gulch floodplain, the metals mass exported from this area must have originated from other areas over time. For Zn, mass import exceeded export and the inventory within the floodplain increased by 15 500 kg.

## Discussion

The Zn source analysis illustrates how the model can be used to assess the relative impacts that upstream source areas have on downstream water quality. Although the lower gulch floodplain contributes the majority of metals delivery to the Arkansas River, more distant sources contribute to the buildup of metals in the lower gulch floodplain. This imported mass would be available for export during future events, suggesting that a series of events can ultimately export metals from even very distant sources over time. With respect to managing site remediation, this suggests that there is a significant risk of lower gulch floodplain recontamination due to the potential for transport from upstream areas over time. More importantly, even though 2000 waste piles are scattered across the site, the results suggest that much of the Zn entering the lower gulch floodplain originates from two main areas: slag piles adjacent to the lower gulch floodplain and an old mining site located near the head of the lower gulch. The net transport from these two areas is large and can be seen as the areas of intense sediment and zinc net loss in Figure 5.

The physical setting of California Gulch is similar to other high mountain mine waste sites in the region so the results of these simulations can be generalized. Large, infrequent rainfall events can export substantial metals masses over short timeframes but also redistribute mine wastes across the landscape and place even larger metals masses into transient storage in stream networks and adjacent floodplains. Smaller, more frequent events do not mobilize as much material from the land surface but can transport considerable material already within stream networks. Although not assessed in the present simulations, snowmelt

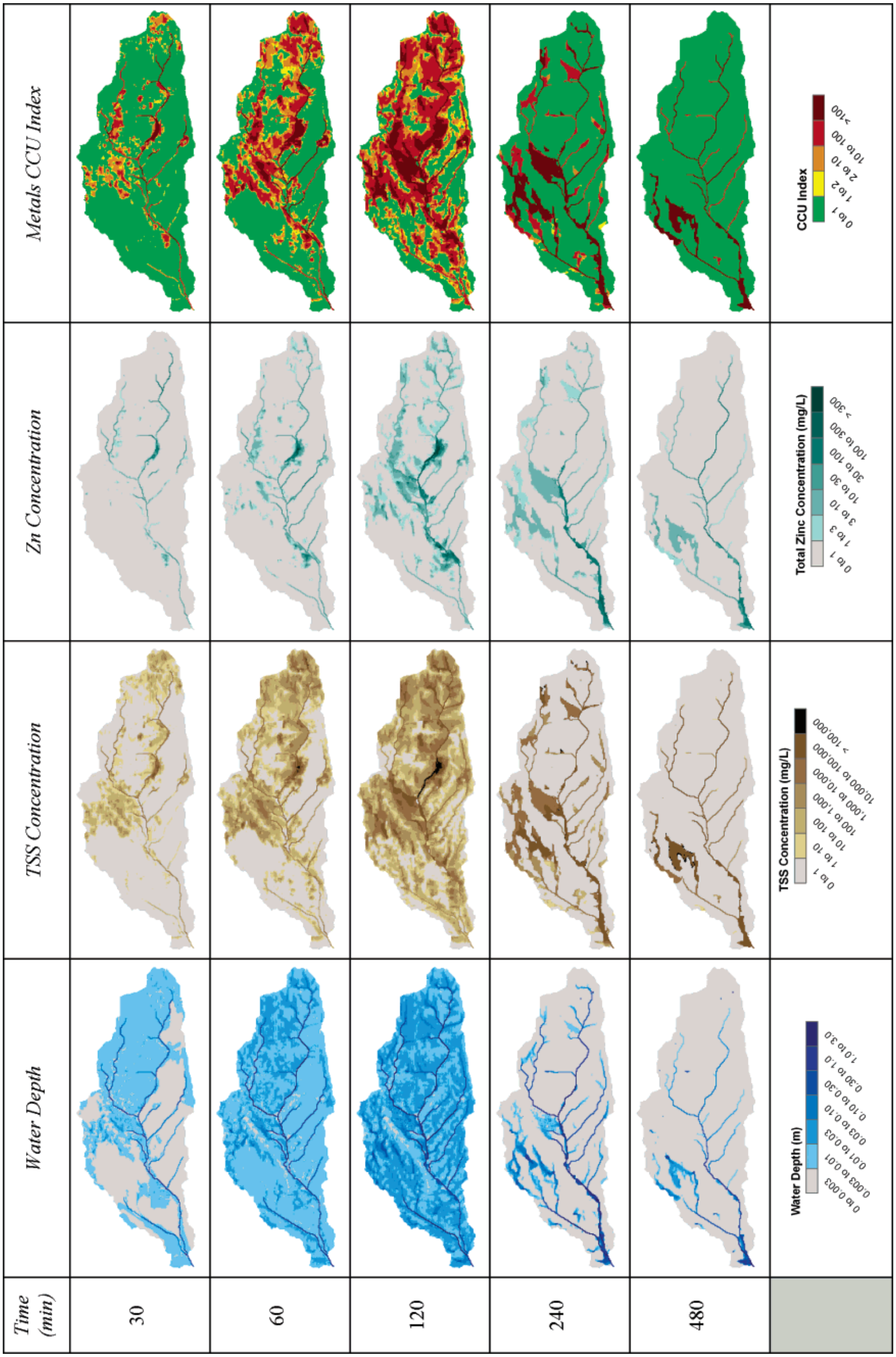


**FIGURE 4. Simulated 1-in-100-year event water depths, TSS and Zn concentrations, and metals toxicity CCUs.**

can also be a significant component of annual hydrology, leading to extended periods of more continuous metals transport in addition to pulse inputs from discrete storm events.

Future research is expected to focus on (1) snow hydrology and snowmelt-driven sediment and metals transport; (2) contaminant hydrogeology and surface water−groundwater interactions; and (3) continuous simulation capabilities.

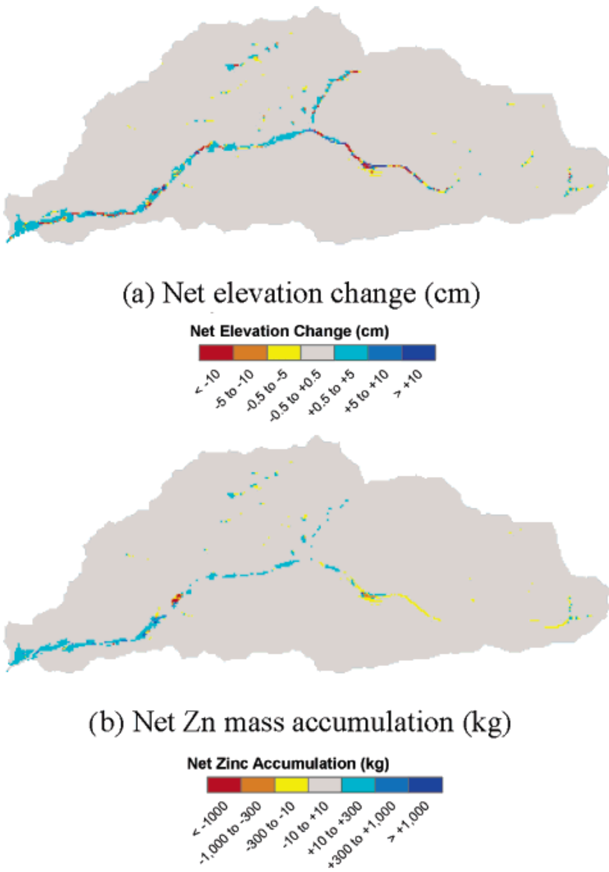


**FIGURE 5. Simulated net elevation change and net accumulation of Zn mass.**

**TABLE 5. Estimated Zn Import and Export for Chemical Source Tracking Example[a]**

| source area | SHG | UCG | LCG | LCGFP | total |
|---|---|---|---|---|---|
| import (kg) | 100 | 7,530 | 25,170 | N/A | 32,800 |
| export (kg) | 3 | 57 | 1,440 | 13,800 | 15,300 |

[a] SHG = Stray Horse Gulch; UCG = upper California Gulch; LCG = lower California Gulch excluding floodplain; LCGFP = lower California Gulch floodplain; Import = mass entering LCGFP area from upstream areas; Export = mass leaving LCGFP and delivered to the Arkansas River.

While improvements to the TREX model framework can be made, further improvements to the model application to California Gulch are dependent on acquisition of streamwater quality data paired in time with the conditions simulated. To date, site characterization efforts have focused on mine wastes on the land surface and contaminated soils to meet Superfund project goals while less effort has been devoted to storm event water quality and sediment monitoring.

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## Supporting Information Available

Details of TREX watershed model development and formulation. This information is available free of charge via the Internet at http://pubs.acs.org.

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