JOURNAL OF THE AMERICAN WATER RESOURCES ASSOCIATION
DECEMBER AMERICAN WATER RESOURCES ASSOCIATION 2004

MODELING METALS TRANSPORT AND SEDIMENT/WATER INTERACTIONS IN A MINING IMPACTED MOUNTAIN STREAM[1]

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ABSTRACT: The U.S. Environmental Protection Agency (USEPA) Water Quality Analysis Simulation Program (WASP5) was used to model the transport and sediment/water interactions of metals under low flow, steady state conditions in Tenmile Creek, a mountain stream supplying drinking water to the City of Helena, Montana, impacted by numerous abandoned hard rock mines. The model was calibrated for base flow using data collected by USEPA and validated using data from the U.S. Geological Survey (USGS) for higher flows. It was used to assess metals loadings and losses, exceedances of Montana State water quality standards, metals interactions in stream water and bed sediment, uncertainty in fate and transport processes and model parameters, and effectiveness of remedial alternatives that include leaving contaminated sediment in the stream. Results indicated that during base flow, adits and point sources contribute significant metals loadings to the stream, but that shallow ground water and bed sediment also contribute metals in some key locations. Losses from the water column occur in some areas, primarily due to adsorption and precipitation onto bed sediments. Some uncertainty exists in the metal partition coefficients associated with sediment, significance of precipitation reactions, and in the specific locations of unidentified sources and losses of metals. Standards exceedances are widespread throughout the stream, but the model showed that remediation of point sources and mine waste near water courses can help improve water quality. Model results also indicate, however, that alteration of the water supply scheme and increasing base flow will probably be required to meet all water quality standards.
(KEY TERMS: metals; mining waste; modeling; watershed; water quality; transport; sediment.)

Caruso, Brian S., 2004. Modeling Metals Transport and Sediment/Water Interactions in a Mining Impacted Mountain Stream. Journal of the American Water Resources Association (JAWRA) 40(6):1603-1615.

INTRODUCTION

Many operational and historic abandoned hard rock metal mines in mountain watersheds in the western United States cause excess loadings of metals to aquatic systems and impair beneficial uses of streams, particularly aquatic life uses (USEPA, 1997; Caruso and Ward, 1998; Malmqvist and Hoffsten, 1999). The enhanced erosion and transport of particulate metals associated with sediment, tailings, and waste rock are common problems requiring investigation, some type of modeling for analysis and prediction, and mitigation (Nimick and Moore, 1991; Simons *et al.,* 1995). Metals interactions between bed sediment and water in these mountain streams play a critical role in metals fate and transport, impacts on water quality and aquatic biota, and the effectiveness of remediation efforts (Jenne and Zachara, 1987; Combest, 1991). Modeling metals transport and sediment/water interactions is often needed for mine reclamation and investigation and remediation of severely impacted mining areas, such as Superfund sites. In recent years, modeling is also required and performed for developing total maximum daily loads (TMDLs) and water quality restoration plans for mining-impacted streams under Clean Water Act requirements. Little information is available in the literature, however, on modeling metals transport in mining impacted watersheds, particularly the interactions of metals in bed sediment and water, and use of modeling for evaluating the effectiveness of remediation strategies. An understanding of watershed and reach scale processes derived as part of the modeling

[1]Paper No. 03035 of the *Journal of the American Water Resources Association* (JAWRA) (Copyright © 2004). **Discussions are open until June 1, 2005.**
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process is required for a range of purposes and regulatory requirements. Evaluation of the applicability, data requirements, advantages, and limitations of various modeling approaches, as well as the usefulness of information derived, is also often necessary.

The number and types of models available for these types of analyses are generally limited, and the goals, scope, and sophistication of the modeling and analysis required can vary widely (for examples see Sanden, 1991; Bouchard *et al.,* 1995; Whitehead and Jeffrey, 1995; Banwart and Malmstrom, 2001; Runkel and Kimball, 2002). Although several well known models are available and widely used for watershed and receiving water quality evaluation (including BASINS, HSPF, and QUAL2E), they are not capable of modeling most complex metals fate and transport processes. Researchers have generally applied other models to evaluate equilibrium metals species concentrations based on detailed pH and geochemical information, including MINTEQ (1997), (Pitt *et al.,* 1998; Runkel *et al.,* 1999), WATEQ (Williams and Smith, 2000), and PHREEQC (Tonkin *et al.,* 2002). These models, however, do not directly account for metals advective transport in streams. The USEPA's WASP is one of the few available models capable of modeling metals concentrations, loadings, and transport in receiving streams. Although the toxic subcomponent model of WASP was originally developed for organic chemicals, it is also useful for modeling metals fate and transport because it simulates advective transport as well as other important processes such as solute interactions between bed sediment and water and exchange between dissolved and particulate phases.

The Upper Tenmile Creek Watershed near Helena, Montana, is a good example of a mountain watershed severely impacted by hundreds of abandoned hardrock mines where application of a water quality and metals transport model such as WASP was needed for remedial planning and design. Tenmile Creek is a major drinking water supply for the city of Helena, and the entire watershed is a Superfund site. Constituents of concern in surface water and sediment include arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) (CDM, 2001a). The purpose of this study is evaluate metals transport and impacts in the Upper Tenmile Creek watershed and the influence of bed sediment on water column metals concentrations and loadings. This evaluation was performed using WASP to model fate and transport processes under low-flow, steady-state conditions. These conditions were modeled because monitoring results have shown that water column metals concentrations are typically highest during low flows in this stream, despite metal loadings to Tenmile Creek typically being greater during high flows. High flow conditions will be modeled as part of future studies. WASP Version 5 (WASP5) was used for this study because the current version of the model (WASP6) was not available and was still being debugged at the time of this work. The modeling performed as part of this study allows for the assessment of contaminant loadings and associated downstream water quality impacts under low flow conditions, transport and fate mechanisms in the watershed, and uncertainties in transport processes and in the model, including metals interactions between and sediment and water. It also assists in evaluation of water quality improvements that could be achieved by implementing potential mine waste cleanup options in the watershed.

SITE DESCRIPTION

The Upper Tenmile Creek Mining Area Superfund Site is located primarily in Lewis and Clark County, Montana (Figure 1). The watershed is 51 km^2 ranging in elevation from 1,335 to 2,485 m at the Continental Divide, with a stream length of approximately 17 km. The watershed is mountainous with high and sharp relief, and the geology, soils, and vegetation are typical of the Northern Rocky Mountains. The small town of Rimini is located approximately in the middle of the watershed. The area is rich in metal ore deposits with pyrite (FeS_2) and was mined for gold, lead, zinc, and copper between 1870 and the 1920s. There are currently hundreds of abandoned mines and tailings areas within the watershed with significant adverse impacts on water quality and aquatic ecosystems due to loadings of metals, sediment, and acidity (CDM, 2001a).

THE WASP5 MODEL

WASP5 is a surface water quality model developed by USEPA capable of simulating the fate and transport of solutes in up to three dimensions in the steady-state and dynamic mode (Ambrose *et al.,* 1993). The subcomponent toxics model, TOXI5, calculates solute (including metals) concentrations in segments (water column or benthic/stream bed) throughout a water body at each time step in a simulation period. Simulation includes interactions between the two compartments. The most important processes with regard to metals fate and transport include point source and nonpoint source water and contaminant loadings, including tributary loadings, inputs from and losses to ground water, and direct runoff; advection, dispersion and diffusion in the

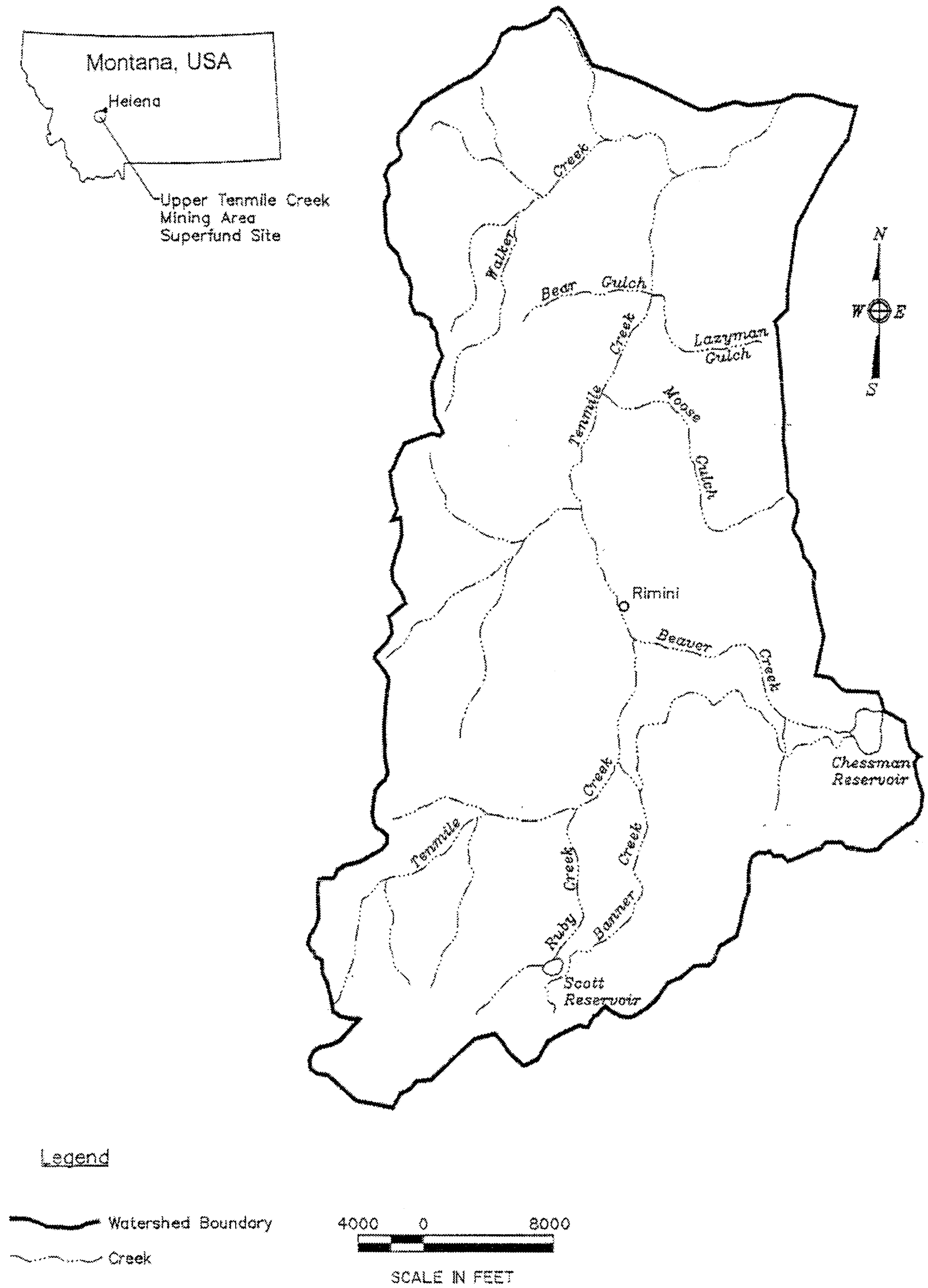


Figure 1. Location of Upper Tenmile Creek Watershed, Montana, USA.

channel; adsorption/desorption in association with sediment/particulates; precipitation/dissolution; and fluvial sediment transport and settling/scour of particulate metals (Figure 2). In Figure 2, Q is streamflow in the stream (modeled) segment. Q_{IN} is streamflow into the segment, and Q_{OUT} is streamflow out of the segment. NPS is nonpoint source pollution. Q_{NPS} is NPS flow into the stream. C_{NPS} is the metal concentration in Q_{NPS}. PS is point source pollution. M_{PS} is metal mass in PS flowing into the stream. T is a tributary. Q_T is flow of T or PS into the stream. C_T is metal concentration in Q_T. GW is ground water, and Q_{GW} is GW flow into or out of the stream. C_{GW} is metal concentration in Q_{GW}. C_D is dissolved metal concentration in the stream or bed pore water. C_P is particulate metal concentration in the stream or bed pore water. K_D is equilibrium partition coefficient. Hard input includes values input to the model that are not estimated using the model or used for calibration.

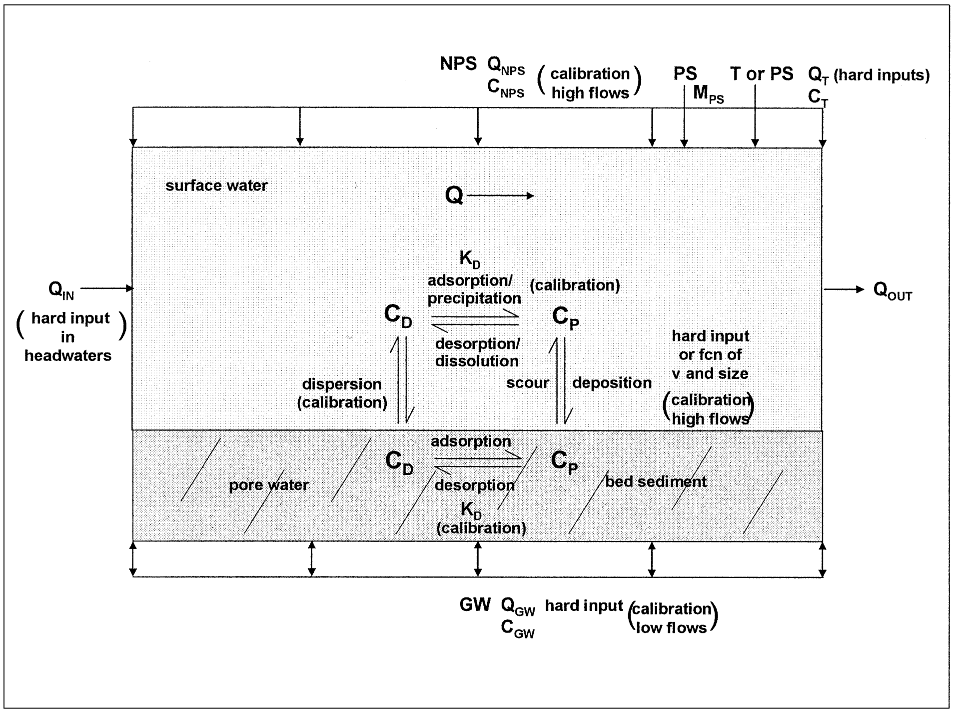


Figure 2. Schematic Diagram of Major Metals Fate and Transport Processes in WASP.

Flows are calculated for each segment based on user specified headwater and tributary inflows. Stream hydraulics can be calculated with a separate dynamic flow package and then linked to WASP5, or calculated within the model using user defined power equations. Sediment loadings are estimated outside of the model, and sediment is transported through the system based on flows and user specified vertical transport rates (net settling/scour). Solute loadings are specified using either tributary flows and concentrations or simply point source mass loads. Solutes are transported via advection and diffusion/dispersion in up to three dimensions. Diffusion/dispersion is simulated with user specified exchange coefficients and mixing lengths.

Metals are distributed between the dissolved and particulate (includes both sorbed and precipitated metals) phases according to a lumped partition coefficient (K_d). The pH range in the Tenmile Creek main stem varies between 5 and 8.9 based on June 2000 data. This lumped partition coefficient approach can provide reasonable results for this pH range in comparison to some other streams where acid mine drainage can cause pH values to vary even more widely or fall below 4. In these cases a separate geochemical equilibrium model, such as MINTEQ, may be necessary in addition to an advective transport model because important metals precipitation/ dissolution reactions are pH dependent. The WASP K_d values can be user input as spatially variable or constant values, or can be calculated internally based on suspended solids concentrations and/or organic carbon fractions. Sorption/desorption of metals between the water column and underlying sediment bed can be achieved using a dispersion/ diffusion exchange and partitioning within the bed layer. Achieving the proper exchange requires manipulation of K_d values, dispersion/diffusion coefficients, and bed concentrations. Transport of particulate metals is based on sediment transport.

METHODS

A synoptic water quality and flow survey was performed by USEPA throughout the watershed in June 2000 under base flow conditions (downstream flow of approximately 0.1 cubic meters per second) (Table 1). Large spikes in metals concentrations generally begin immediately downstream of the Suzie Load and/or Lee Mountain Mine area, approximately 5,000 m downstream from the headwaters (Table 1). A survey was also performed in June 1997 by the USGS under higher flow conditions (flow of approximately 3 cms). Concentrations of most metals were generally lower

TABLE 1. Upper Tenmile Creek Main Stem Flows and Metals Concentrations From 1997 USGS Sampling Event (for validation) and 2000 USEPA Sampling Event (for calibration).

Station	Distance Downstream (m)	Date	Flow (cms)	As (µg/L) Total	As (µg/L) Dissolved	Cd (µg/L) Total	Cd (µg/L) Dissolved	Cu (µg/L) Total	Cu (µg/L) Dissolved	Pb (µg/L) Total	Pb (µg/L) Dissolved	Zn (µg/L) Total	Zn (µg/L) Dissolved
USGS Data													
2	152.5	Jun 3, '97	0.906	1.5	NA	0.2	NA	23	NA	1.5	NA	50	NA
3	1,982.5	Jun 3, '97	1.189	1.5	NA	0.2	NA	19	NA	1.5	NA	50	NA
12	5,337.5	Jun 3, '97	2.690	1.5	NA	0.6	NA	19	NA	1.5	NA	120	NA
23	6,557.5	Jun 3, '97	2.577	6	NA	1.2	NA	11	NA	0	NA	160	NA
28	10,522.5	Jun 3, '97	2.719	9	NA	1.1	NA	17	NA	1.5	NA	170	NA
34	17,232.5	Jun 3, '97	3.059	10	NA	1	NA	10	NA	10	NA	135	NA
USEPA Data													
ST001	152.5	Jun 22, '00	0.064	2.1	1.4	0.058	0.5	1.6	1	0.97	0.15	8.5	5.6
ST004	1,982.5	Jun 22, '00	0.089	1.3	1.1	0.06	0.054	1.8	3.6	0.49	0.76	11.1	12.8
ST006	3,202.5	Jun 22, '00	0.185	2.5	2.3	0.087	0.066	2.2	1.6	0.73	0.32	12.5	9.7
ST008	4,727.5	Jun 22, '00	0.201	5.4	4.7	0.05	0.05	2.5	2.2	0.5	0.5	11.2	10.1
ST009	5,337.5	Jun 22, '00	0.224	3.7	3	0.63	0.52	5.4	5.7	2.3	1	110	97.1
ST011	5,947.5	Jun 21, '00	0.010	13	9.5	2.2	2.2	7	6.3	12.2	6.4	344	338
ST013	6,252.5	Jun 21, '00	0.007	14.2	8	4.4	4.2	12.4	9	12.5	4.2	665	635
ST015	6,557.5	Jun 21, '00	0.020	41.8	23.9	4.1	3.7	10.1	7	6.8	3.5	940	872
ST016	8,082.5	Jun 21, '00	0.045	27.2	22.3	1.9	1.7	6.6	5.3	2.4	1.3	387	352
ST017	10,210.5	Jun 21, '00	0.077	24.4	20.6	1.6	1.4	5.3	4.3	1.7	0.89	337	302
ST019	10,522.5	Jun 21, '00	0.099	24	21.6	1.5	1.4	4.9	4.2	1.6	0.69	322	311
ST021	12,962.5	Jun 20, '00	0.091	25.8	23.2	0.96	0.88	4.6	4	0.81	0.32	169	159
ST023	14,792.5	Jun 20, '00	0.108	24.9	22	0.9	0.83	4.3	4	0.66	5.5	148	210

NA – Not analyzed.

during this event, although patterns with distance were similar to those observed during the 2000 sampling event (Table 1).

The WASP5 model for the main stem of Tenmile Creek was developed for steady state, low flow conditions with constant loadings to compute equilibrium concentrations and loadings of key metals (As, Cd, Cu, Pb, and Zn). Calibration and modeling was performed for these conditions because the sampling showed that stream metals concentrations are generally greater than during high flows. The June 2000 data set was also the more comprehensive of the two data sets. The model extends from the headwaters approximately 17 km to where the creek enters a major valley (Figure 3). In Figure 3, values above the line (1 through 55) are stream segment numbers used in the model. Values below the line (59 through 64) are stream bed segment numbers. Arrows pointing into the line are flow or mass inputs from headwaters, tributaries, or nonpoint or point source pollution sources. Flows are shown in cubic meters per second (cms). Loads are metal mass inputs without flows. Arrows pointing out of the line are city diversions. Numbers in parentheses are input numbers for each source (maximum of 10 in WASP). All of the Moose and Walker Creek input flows are diverted out of the stream by city diversions. The water column layer was divided into 58 uniform segments (length of approximately 300 m each). The benthic layer was divided into six segments, each with a uniform benthic concentration with lengths varying from approximately 1,200 to 5,500 m, depending on how many water column reaches the benthic segment interacts with. The benthic segments were chosen and delineated based on bed sediment sampling locations and resulting metals concentrations, and homogeneity of the physical characteristics of the bed with distance along the stream.

Flows were simulated using constant headwater and tributary flows, and the city water supply diversions were included. An apparent ground water discharge to the stream was observed near the Lee Mountain Mine during the June 2000 sampling event and also incorporated into the model. Channel hydraulic parameters were based on average depth, width, and velocity measurements at two stations

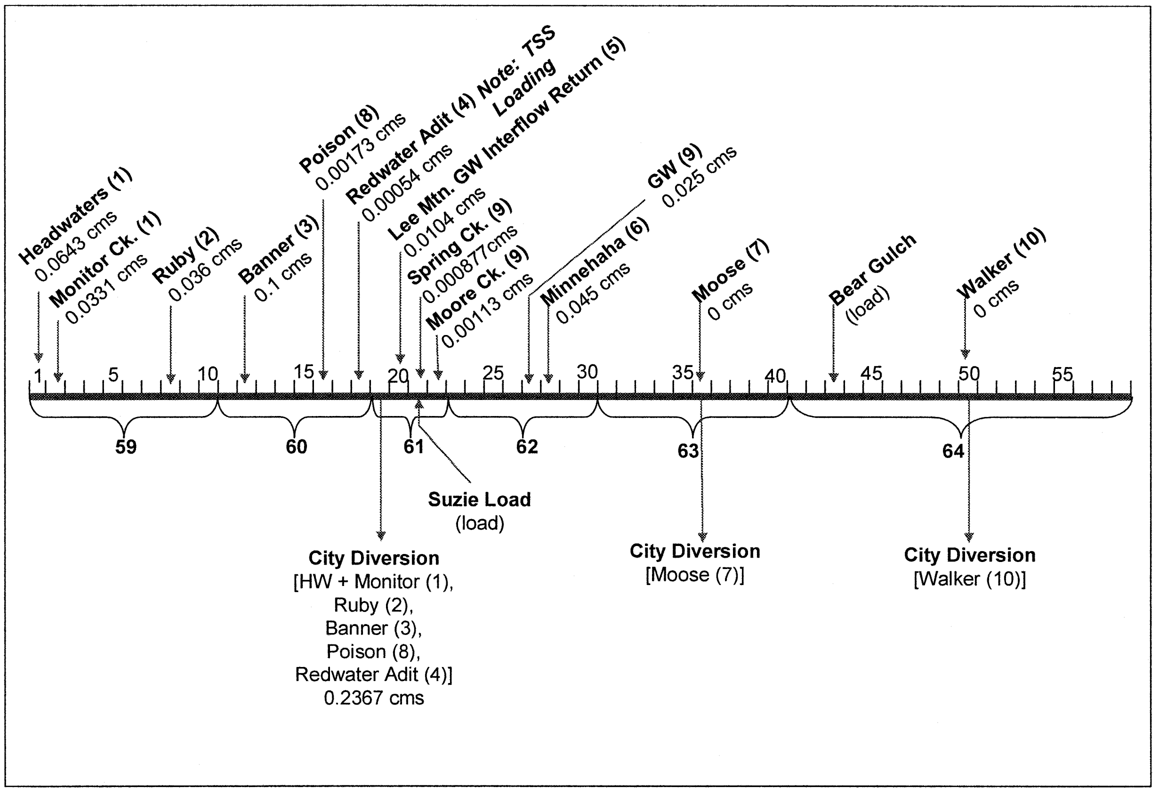


Figure 3. Schematic Diagram for Upper Tenmile Creek Main Stem WASP Model With Segmentation and Flow Inputs/Outputs.

where flow and channel measurements were made during June 2000. Sediment settling/scour rates were assumed to be zero because they may generally be considered insignificant under low flow, steady state conditions. Therefore, settling and scour were set equal to zero for calibration, validation, and simulation of remedial alternatives. However, under high flow, dynamic conditions such as storm or snowmelt events, these processes are more important and values must be estimated outside of the model.

Metals loadings were input based on a series of point source tributary flows, concentrations and loadings (Figure 3). Initial bed sediment metals concentrations were based on June 2000 measured values (Table 2). A low dispersion coefficient (1 m^2/s) was initially used for longitudinal dispersion. Vertical dispersion/diffusion was used to simulate the exchange of dissolved metals between the water and underlying benthic layer (initial value of 1 x 10^5 m^2/s). Initial K_d values were taken from in the WASP5 User's Manual (Ambrose *et al.,* 1993). According to the manual and other references (USEPA 1989; 1996), these values are a function of solids concentrations, so that the higher the solids concentration, the higher the K_d. A relationship presented in USEPA (1996) was used with solids concentrations of 4 mg/L for the water column and ranging from 500 to 1,000 g/L for the benthic layer. To help calibrate the model, laboratory adsorption/desorption batch tests were also performed to estimate K_d values for equilibrium metals partitioning between bed sediment and pore water for different solids/water ratios at key locations in the creek (CDM, 2001b).

TABLE 2. Upper Tenmile Creek Main Stem Benthic Sediment Concentrations (mg/kg) Based on June 2000 Sampling Data and Initial Values Used in WASP5 Model.

Segment No.	As	Cd	Cu	Pb	Zn
59	1	0.45	3.8	16	40
60	68	1.2	11	90	132
61	2,770	40	47	97	4,047
62	123	3	18	90	325
63	132	3	33	75	299
64	87	3	21	49	355

The June 2000 low flow synoptic survey data were used to calibrate the model (downstream flows of approximately 0.1 cms). Calibration parameters included the K_d values, vertical dispersion/diffusion coefficients, and unaccounted inflows and associated concentrations. Flows were calibrated first, which indicated an unaccounted inflow to the system upstream of Minnehaha Creek. This is probably from ground water discharge or a small tributary, and was subsequently included in the model. Calibration of water quality was achieved by manipulating K_d values within ranges estimated from the batch tests and presented in the WASP5 User's Manual (Ambrose *et al.,* 1993), dispersion/diffusion coefficients within published ranges, and metals concentrations in unaccounted ground water inflow (see results section for calibrated parameter values and comparison of observed and calibrated model metals concentrations).

The model was validated using June 1997 USGS data from the synoptic survey during higher flows (downstream flows were approximately 3 cms). This data set included fewer sampling locations than the 2000 calibration data set and dissolved metals concentrations were not analyzed. As for the calibration phase, bed sediment settling and scour were not explicitly modeled as part of validation (these values were set equal to 0). This could potentially have the effect of under-predicting total metals concentrations in the water column as part of validation for higher flow conditions (see results section for comparison of observed and validated model metals concentrations).

Eight remedial alternatives were modeled using the steady state, low flow (June 2000 flows) conditions, including treatment of adit discharges, bypass of different flow amounts through the city's diversion to Tenmile Creek, and combinations of these alternatives. The alternative that is discussed here assumes all other metals sources are remediated, including point source adit discharges and mine waste near the water courses to evaluate the effects of contaminated bed sediment on water column metals concentrations. For this scenario, the model was run with all loadings to the creek equal to zero and using measured bed sediment metals concentrations (Table 2) and mean K_d values for each analyte from the batch test results. This alternative represents only present, worst case conditions because the sediment metals concentrations will decrease over time.

In a separate analysis outside of the model, equilibrium benthic pore water concentrations for each analyte estimated from the desorption batch tests at four key locations were also used to evaluate the effects of contaminated bed sediments on water quality. Equilibrium low flow conditions were assumed, where the mass in the pore water resulting from desorption from the bed sediment was distributed throughout both the pore water and overlying water column. Additional assumptions included a bed sediment porosity of 0.4, density of 1.8 kg/L, depth of 0.3 m (1 ft), and water depth of 0.3 m (1 ft) under low flow conditions based on physical characteristics measured in the laboratory and in the field during the June 2000 low flow sampling event.

RESULTS AND DISCUSSION

Sampling results showed that exceedances of Montana State water quality standards are widespread throughout the stream during base flow. Adits and point sources contribute significant metals loadings to the stream, particularly near Lee Mountain and the Suzie Load, approximately 5,000 meters downstream from the headwaters (Table 1). Aquatic life chronic, and acute criteria for most metals vary along the length of the creek based on the hardness measured during June 2000.

Calibrated flows generally matched observed flows well (Figure 4). Some values of the calibrated model parameters (K_d values and dispersion/diffusion coefficients) varied with stream segment modeled (Table 3). All values, however, were within ranges presented by Ambrose *et al.* (1993). Calibrated model K_d values were also generally in agreement with estimated values based on the laboratory adsorption/desorption batch tests (within an order of magnitude) (Table 3). In general, a relatively good calibration was achieved for all metals: predicted total and dissolved metal concentrations were within 10 percent, and in almost all cases were within 25 percent, of measured values. A very close match between modeled and observed values was achieved for As, Cd, and Zn, but results for Cu and Pb were not as close (Figure 5). Correlation coefficients between modeled and observed concentrations along the main stem ranged from 0.72 for dissolved Cu (all others were greater than or equal to 0.87) to 0.99 for total Cd (Table 4, Figure 6 for Cd). Standard errors ranged from 12 percent (total Cd) to 51 percent (dissolved Pb) of observed mean concentrations (Table 4). Although the standard errors for dissolved and total Zn were relatively high (36 and 41 percent, respectively), much of this is due to relatively large errors in the modeled peak values at one monitoring station 6,200 m downstream from the headwaters. At this location, the modeled peak dissolved and total Zn concentrations are displaced only 200 m upstream from the actual peaks.

Validation results indicated that flows were generally modeled well in the main stem (Figure 7A). Flows were somewhat underpredicted (by approximately 10 percent) about 5,000 m downstream of the headwaters, indicating additional water sources in this area

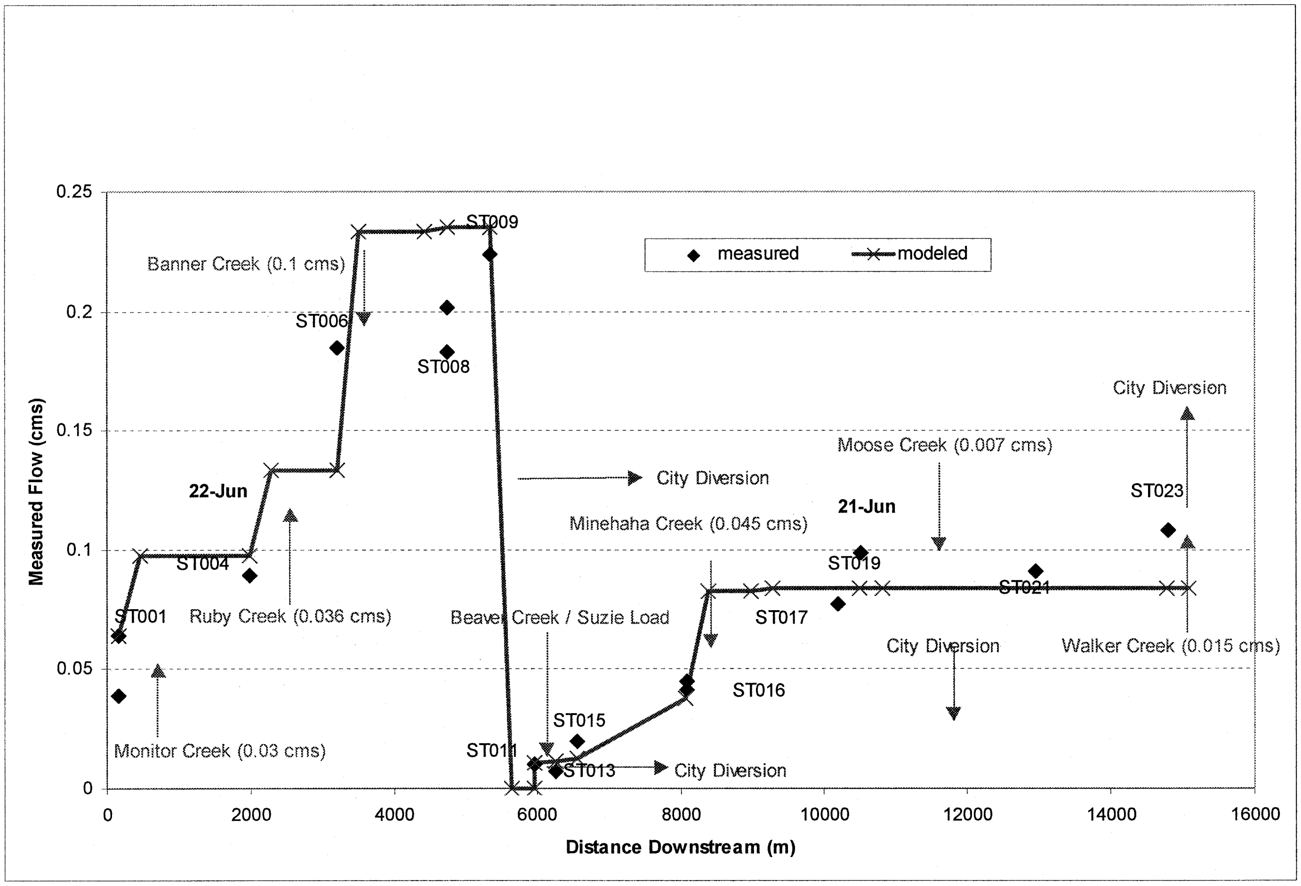
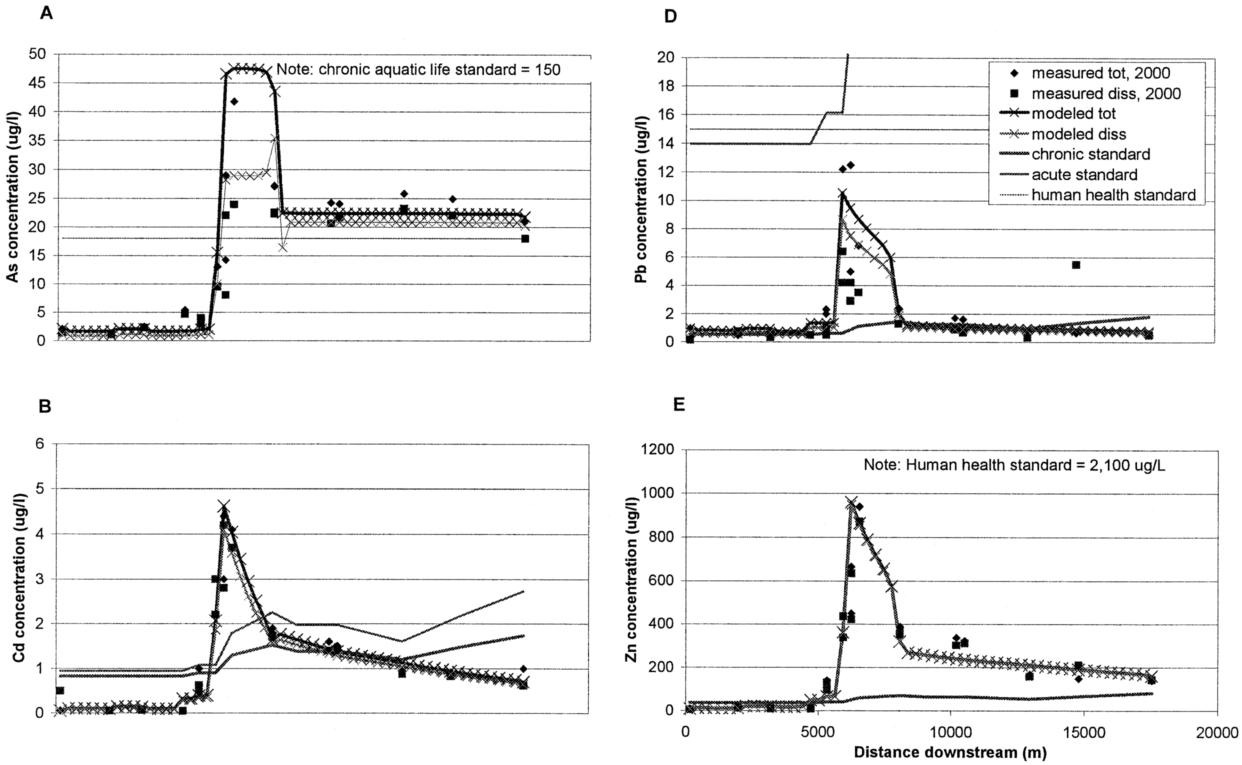


Figure 4. Comparison of Measured (June 2000) and Modeled Flows (cms) Versus Distance in Upper Tenmile Creek Main Stem With Major Inflows and Outflows.

TABLE 3. Calibrated Parameter Values for Upper Tenmile Creek WASP5 Model Based on June 2000 Data, and Estimated K_d Values from Laboratory Adsorption/desorption Batch Tests

Constituent	Model: Pore Water Diffusion Coefficient (m^2/s)	Model: K_d (L/kg)	Batch Test: K_d (L/kg)
As	1×10^{-8} - 9×10^{-5}	1×10^{5} - 5×10^{5}	5.1×10^{4} - 1.3×10^{6}
Cd	2×10^{-6} - 1×10^{-5}	1×10^{5}	1.5×10^{4} - 2.3×10^{5}
Cu	1×10^{-7} - 1.5×10^{-6}	3×10^{5}	3.4×10^{4} - 3.8×10^{5}
Pb	1×10^{-6}	2×10^{5}	8×10^{4} - 1.0×10^{6}
Zn	1×10^{-6} - 1.5×10^{-6}	1×10^{4}	1×10^{4} - 3×10^{5}

that are not accounted for in the model. Flows were also overpredicted slightly (by 8 percent) 17,000 m downstream, indicating some losses in this area. Validation results for metals concentrations were generally reasonable, but the peak total concentrations in the Rimini area of Tenmile Creek were significantly under-predicted for Zn and overpredicted for Cu (Figure 7). This may be the result of variability or uncertainty in some model inputs, such as tributary flow or point source loading data. Additional loadings of contaminants from nonpoint sources associated with sediment loadings and transport could also play an important role under higher flow conditions, but were not explicitly modeled as part of this steady state, low flow study. Locations where measured concentrations were higher than predicted may indicate additional nonpoint sources of pollution generated by higher flows that are not accounted for by the calibrated base



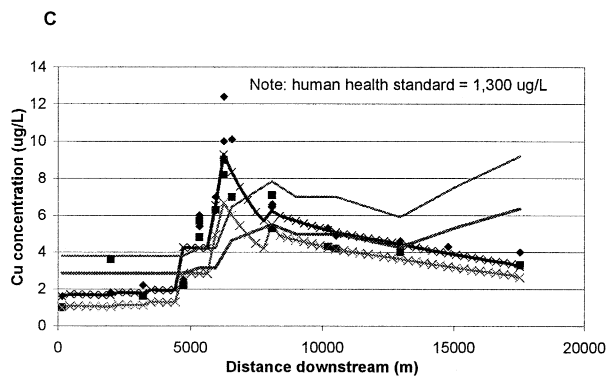


Figure 5. Comparison of Measured (June 2000) and Modeled (A) As, (B) Cd, (C) Cu, (D) Pb, and (E) Zn Total and Dissolved Concentrations Versus Distance in Upper Tenmile Creek Main Stem Based on Calibrated Model, With Applicable State of Montana Water Quality Standards.

TABLE 4. Model Efficiencies for Upper Tenmile Creek Metals Concentrations (μg/L).

	As		Cd		Cu		Pb		Zn	
	Dissolved	**Total**	**Dissolved**	**Total**	**Dissolved**	**Total**	**Dissolved**	**Total**	**Dissolved**	**Total**
R^2 - Correlation Coefficient	0.90	0.87	0.98	0.99	0.72	0.90	0.94	0.93	0.91	0.90
Standard Error	4.04	6.38	0.19	0.17	0.98	0.70	0.76	0.98	92.79	99.86
Observed Mean	13.97	17.56	1.27	1.41	4.36	5.02	1.51	3.13	257.31	245.29
Standard Error Percent of Mean	29	36	15	12	22	14	51	31	36	41

flow model. A sensitivity analysis to further evaluate these potential sources will be performed as part of future studies. However, the application of the model for prediction under low flow conditions when instream metals concentrations are generally highest is useful for planning a range of point source/adit discharge remediation measures. Unaccounted nonpoint source pollutant and sediment loadings identified on a preliminary basis as part of this validation can be evaluated in more detail as part of future modeling of the watershed.

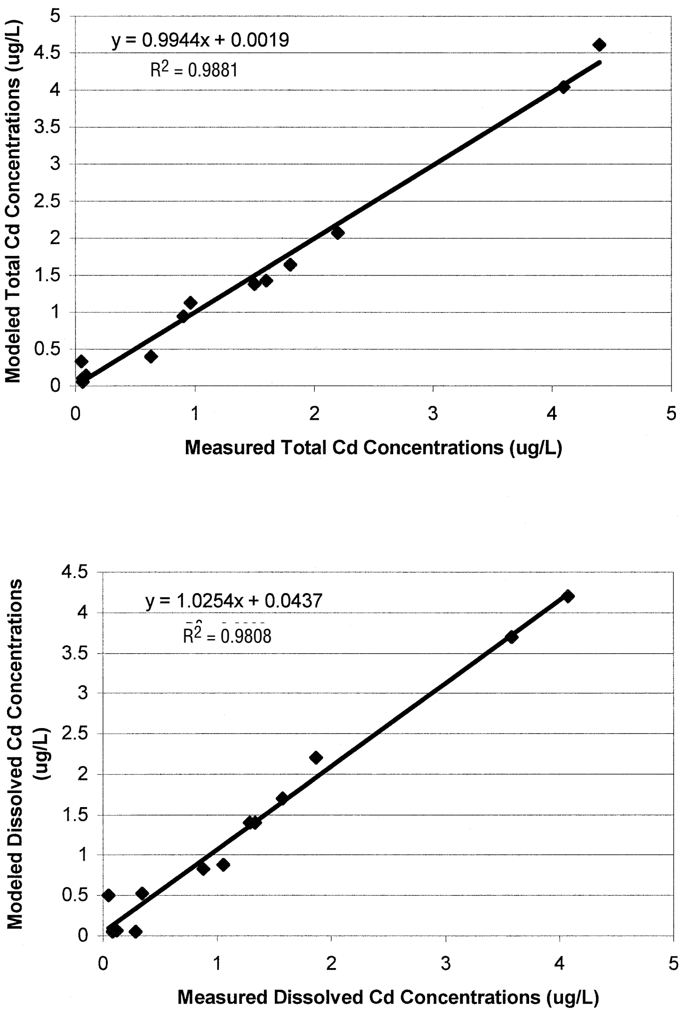


Figure 6. Measured Versus Modeled Concentrations for (A) Total Cd and (B) Dissolved Cd in Upper Tenmile Creek Main Stem Based on Calibrated Model.

Sampling and modeling results indicate that shallow ground water and bed sediment contribute metals in some key locations, where metals concentrations increase in the stream without corresponding tributary or point source inputs. Losses from the water column occur in some areas, primarily due to adsorption and precipitation onto bed sediments. Some uncertainty exists in the metal partition coefficients associated with sediment, significance of precipitation reactions, and in the specific locations of unidentified sources and losses of metals.

Modeling results generally indicated that the present contaminated sediments contribute a relatively small amount of total metal loadings to the water column under low flow conditions (Figure 8 for Cd). The exception appeared to be As, which has the potential to desorb from bed sediment and cause stream dissolved concentrations (up to 80 mg/L) to exceed the human health standard of 18 mg/L, as well as to exceed existing concentrations (up to about 25 mg/L). The cause of this anomaly is not clear. Total and dissolved Cd and Pb concentrations (up to approximately 1.5 and 3 mg/L, respectively) could also exceeded chronic criteria in the vicinity of the Suzie Load, and Zn approached the chronic and acute criteria. Copper from sediment remained below all criteria.

Equilibrium metals concentrations in the water column estimated outside of the model based on the desorption batch test results indicated that exceedances of chronic standards (using average hardness in the creek) and the As human health standard could occur at several locations evaluated (Table 5). These results were based only on low flow conditions and were in general agreement with the modeling results (but in most cases were somewhat higher). These values could occur in near stagnant water under extreme low flow conditions. The somewhat lower values for the model are probably due to the fact that the model simulates advective flow that reduces water column concentrations, whereas the equilibrium method using the batch test results does not take into account flowing water, resulting in higher concentration estimates. These results based on modeling and analysis of the sediment loads generally represent existing, worst case conditions because the sediment metals concentrations will decrease over time.

Although results of modeling all of the remedial alternatives are not presented here, the model generally showed that remediation of point sources can help improve water quality significantly for most metals. Concentrations of all modeled metals in Tenmile Creek near Rimini decreased by approximately 60 to 90 percent with treatment of the primary point sources/adit discharges, including at the Suzie Load and Lee Mountain, and/or increasing instream base flows. However, remediation of mine waste near watercourses and streambed sediment may also be required for some metals. Alteration of the water supply scheme and increasing base flow in the main stem will probably be required to meet all water quality criteria, particularly for Zn.

CONCLUSIONS

In general, good calibration based on June 2000 low flow data and validation based on June 1997 data for higher flow conditions was achieved for the Upper Tenmile Creek WASP5 model. Use of the model helped to identify and evaluate important metals fate and transport processes within the creek and watershed, unaccounted flows and metals loadings, and uncertainties in transport processes and in the model

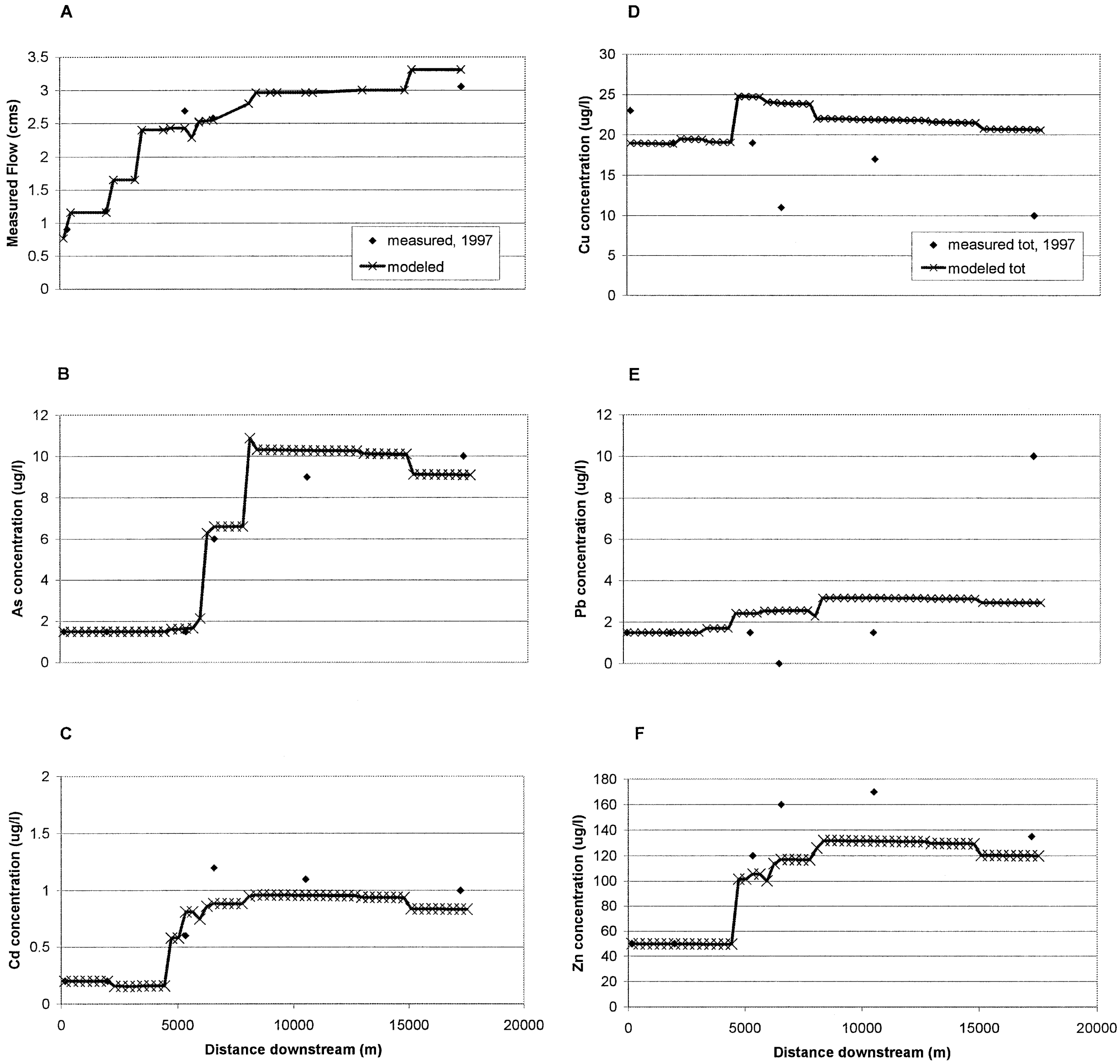


Figure 7. Comparison of Measured (June 1997) and Modeled (A) Flow (cms), (B) As, (C) Cd, (D) Cu, (E) Pb, and (F) Zn Total Concentrations Versus Distance in Upper Tenmile Creek Main Stem Based on Validation.

itself. The potential effectiveness of source remediation with contaminated stream bed sediment remaining in place was also evaluated. Modeling results showed that metals interactions with stream bed sediment and water are important processes that must be considered for effective remedial measures. However, the contribution of metals loadings from bed sediment to stream water under low-flow conditions are generally not as great as from other sources, such as point source adit discharges and mine waste near the water courses. Results also indicated that alteration of the city of Helena water supply scheme and increasing base flow will probably be required to meet all state water quality standards for metals, especially for Zn. These findings are being used for planning, design, and implementation of remediation measures in the watershed.

The model can be revised in the future to improve its accuracy for further decision making, and to evaluate sediment and associated metals loadings under high-flow conditions during snowmelt and storm runoff. Although in-stream concentrations are generally higher during the low-flow conditions modeled as part of this study, metals loadings are greatest during these higher flows. Revisions to the model could

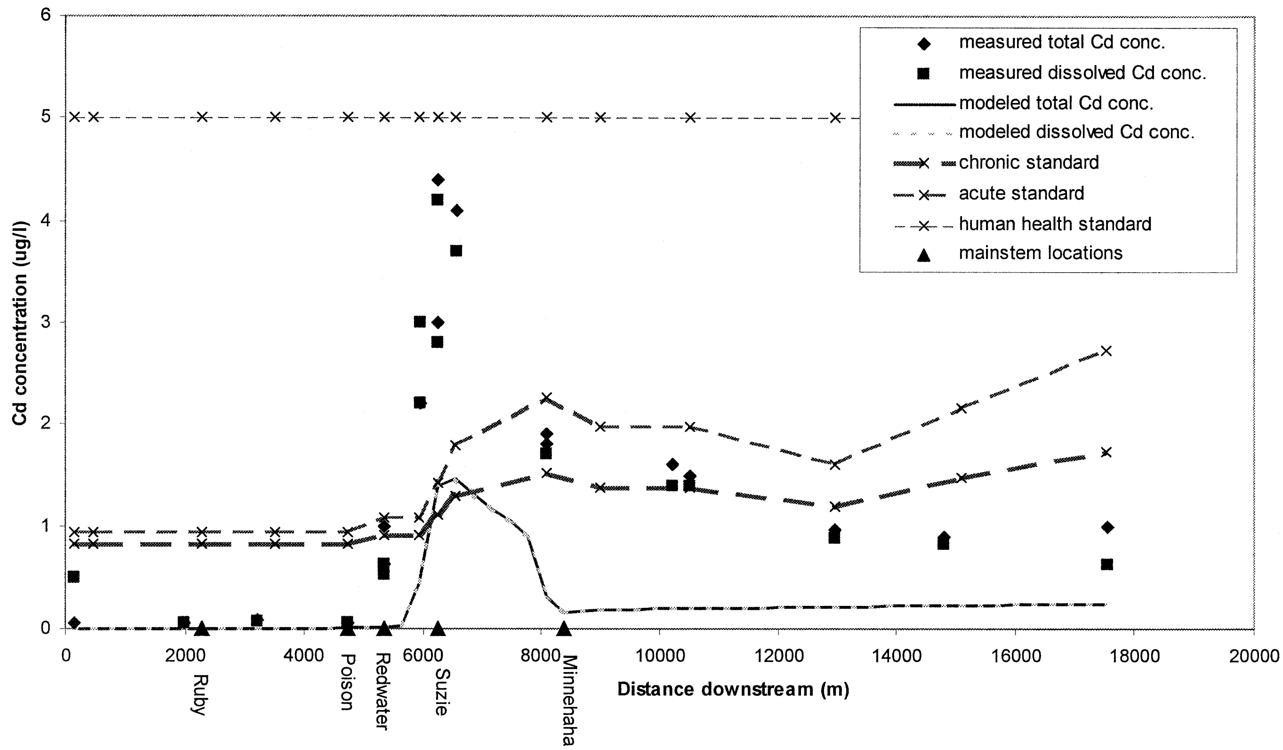


Figure 8. Comparison of Measured (June 2000) and Modeled Cd Concentrations Versus Distance in Upper Tenmile Creek Main Stem Based Only on Bed Sediment Contamination, With Applicable State of Montana Standards. This scenario assumes that all other contaminant sources, including point source adit discharges and mine waste near the water courses, are remediated.

TABLE 5. Initial Benthic Pore Water Concentrations and Equilibrium Metal Concentrations in Upper Tenmile Creek Water From Bed Sediment Metals Based on Desorption Batch Tests, and State of Montana Standards (μg/L).

Analyte	**As**	**Cd**	**Cu**	**Pb**	**Zn**	**As**	**Cd**	**Cu**	**Pb**	**Zn**
Standard	18	1.14	4.03	0.94	52.17	18	1.14	4.03	0.94	52.17
Location	**Pore Water Concentration**					**Stream Water Concentration**				
Segment 61	600	7	35	140	700	**86**	1	**5**	**20**	**101**
Segment 62	120	5	30	50	800	17	0.7	4	**7**	**115**
Tenmile below Suzie Adit	200	2	11	55	100	**29**	0.3	2	**8**	14
Poison Creek Near Red Mountain	205	14	90	160	1,450	**30**	**2**	**13**	**23**	**209**

Notes: Pore water concentrations from batch tests (desorption tests).
Based on sediment depth of 0.3 m (1 ft), density of 1.8 kg/L, porosity of 0.4, and water depth of 0.3 m (1 ft).
Values in bold exceed standards for stream.
All standards are aquatic life chronic criteria based on average hardness in Tenmile Creek, except As, which is human health standard.

include the new WASP module META4 (J.L. Martin and A.J. Medine, unpublished manuscript) which, in addition to adsorption/desorption, explicitly models precipitation/dissolution reactions important in metals fate and transport at mining sites, particularly with variable and extreme pH conditions.

This study has demonstrated the application and usefulness of the USEPA WASP5 model for simulating metals transport and sediment/water interactions in a mining impacted mountain stream. This model and methodology can be applied to other watersheds where metals and other contaminants with complex fate and transport processes are problems to aid in evaluating sources, transport, sediment interactions, and alternative remediation measures.

LITERATURE CITED

Ambrose, R.B., T.A. Wool, and J.L. Martin, 1993. WASP 5, The Water Quality Analysis Simulation Program Version 5.00. AscI Corporation, Athens, Georgia.

Banwart, S.A. and M.E. Malmstrom, 2001. Hydrochemical Modelling for Preliminary Assessment of Minewater Pollution. Journal of Geochemical Exploration 74:73-97.

Bouchard, D.C, R.B. Ambrose, T.O. Barnwell, and D.W. Disney, 1995. Environmental Modeling Software at the U.S. Environmental Protection Agency's Center for Exposure Assessment Modeling. *In:* Computer Supported Risk Management, G.E.G. Beroggi & W.A. Wallace (Editors). U.S. Government, Printed in the Netherlands, pp. 321-360.

Caruso, B.S. and R.C. Ward, 1998. Assessment of Nonpoint Source Pollution From Inactive Mines Using a Watershed-Based Approach. Environmental Management 22(2):225-243.

CDM, 2001a. Draft Remedial Investigation Report, Upper Tenmile Creek Mining Area Superfund Site, Lewis and Clark County, Montana, Helena, Montana. U.S. Environmental Protection Agency, Region 8, Denver, Colorado.

CDM, 2001b. Surface Water and Sediment Investigation Batch Tests of Stream Sediment and Waste Material Adsorption/Desorption Characteristics. Denver, Colorado. Prepared for USEPA. U.S. Environmental Protection Agency, Region 8, Denver, Colorado.

Combest, K.B., 1991. Trace Metals in Sediment: Spatial Trends and Sorption Processes. Water Resources Research 27(1):19-28.

Jenne, E.A. and J.M. Zachara, 1987. Factors Influencing the Sorption of Metals. *In:* Fate and Effects of Sediment-Bound Chemicals in Aquatic Systems, K.L. Dickson, A.W. Maki, and W.A. Brunge (Editors). Society of Environmental Toxicology and Chemistry, Pergamon Press, Elmsford, New York, pp. 83-98.

Malmqvist, B. and P. Hoffsten, 1999. Influence of Drainage From Old Mine Deposits on Benthic Macroinvertebrates in Central Swedish Streams. Water Research 33(10):2415-2423.

Nimick, D.A. and J.N. Moore, 1991. Prediction of Water-Soluble Metal Concentrations in Fluvially Deposited Tailings Sediments, Upper Clark Fork Valley, Montana, USA. Applied Geochemistry 6(6):635-646.

Pitt, J.L., R.Y. Surampalli, N.H. Crisp and L.C. Ferrington, 1998. Predicting Aqueous Metal Species in a Stream Impacted by Mining Activity. Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management 2(4):166-171.

Runkel, R.L. and B.A. Kimball, 2002. Evaluating Remedial Alternatives for an Acid Mine Drainage Stream: Application of a Reactive Transport Model. Environmental Science and Technology 36(5):1093-1101.

Runkel, R.L., B. A. Kimball, D.M. McKnight, and K.E. Bencala, 1999. Reactive Solute Transport in Streams: A Surface Complexation Approach for Trace Metal Sorption. Water Resources Research 35(12):3829-3840.

Sanden, P., 1991. Estimation and Simulation of Metals Mass Transport in an Old Mining Area. Water, Air, and Soil Pollution 57-58:387-397.

Simons, R.K., D.B. Simons and G.E. Canali, 1995. Analysis of Tailings and Mine Waste Sediment Transport in Rivers. *In:* Tailings and Mine Waste '95. A.A. Balkema, The Netherlands, pp. 91-103.

Tonkin, J.W., L.S. Balistrieri, and J.W. Murray, 2002. Modeling Metal Removal Onto Natural Particles Formed During Mixing of Acid Rock Drainage With Ambient Surface Water. Environmental Science and Technology 36(3):484-492.

USEPA (U.S. Environmental Protection Agency), 1989. Briefing Report to the EPA Science Advisory Board on the Equilibrium Partitioning Approach to Generating Sediment Quality Criteria. EPA 440/5-89-002.

USEPA, (U.S. Environmental Protection Agency), 1996. The Metals Translator: Guidance for Calculating a Total Recoverable Permit Limit From a Dissolved Criterion. EPA 823-B-96-007.

USEPA (U.S. Environmental Protection Agency), 1997. EPA's National Hardrock Mining Framework. USEPA Office of Water. Washington, D.C.

Whitehead, P. and H. Jeffrey, 1995. Heavy Metals From Acid Mine Drainage – Impacts and Modeling Strategies. *In:* Man's Influence on Freshwater Ecosystems and Water Use (Proceedings). IAHS Publ. No. 230, pp. 55-66.

Williams, T.M. and B. Smith, 2000. Hydrochemical Characterization of Acute Acid Mine Drainage at Iron Duke Mine, Mazowe, Zimbabwe. Environmental Geology 39(3):272-278.