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TECHNICAL ARTICLE

Seasonal and Spatial Variation of Metal Loads from Natural Flows in the Upper Tenmile Creek Watershed, Montana

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Abstract Seasonal and spatial variation of metal loads can be significant in mining-impacted mountain watersheds in the western US due to a number of complex physical and biogeochemical factors. Anthropogenic influences, such as seasonal water diversion for municipal supplies, can increase this variability further. This study evaluates the seasonal and spatial variation of metal loads from estimated natural flows in a typical Rocky Mountain watershed impacted by historic hardrock mining and municipal water diversions: the Upper Tenmile Creek Watershed near Helena, Montana. Restoration of natural flows is being considered as part of broader watershed restoration measures, and an understanding of the variation in loads resulting from these flows is needed for restoration planning and design. Estimates of tributary and metal point and nonpoint source natural flows to the creek were used with representative total metals (cadmium, copper, lead, and zinc) concentration data for model input and to evaluate the variation of input loads. These loads were evaluated at key locations in the watershed for two seasons: spring snowmelt high flow in June and summer low flow in August. The Water Quality Analysis Simulation Program was used to model the resulting variation of total and dissolved metal loads with distance along the mainstem for the two seasons. Results show that total metal loads to the creek vary among input locations by up to >9,700-fold in June and up to >740-fold in August for copper. Several tributaries have the greatest loads during both seasons, although adits often exhibit the highest concentrations. For all locations, average input loads are up to 46 times higher in June for copper. Total and dissolved metal loads generally increase with distance along the mainstem and vary by up to >320-fold in August and up to >118-fold in June for zinc. Along the mainstem, average total loads are up to 68 times higher in June for lead. Many watershed and biogeochemical processes contribute to this variation, including variability in estimated natural flows, partitioning of metals between the dissolved and particulate phases, and attenuation in the hyporheic zone. Dissolved phases constitute a large proportion of the total metals and follow patterns very similar to those for total loads along the mainstem, especially for cadmium and zinc. Seasonal load differences are greatest for copper and lead because of greater sorption to solids and particulate loads during high flow associated with increased erosion and transport of solids.

Keywords Metals · Mine waste · Restoration · Montana · Seasonality · Water quality · Watershed modeling

Introduction

Acid mine drainage (AMD) from abandoned hardrock mines in western US mountain watersheds is a major cause of metals contamination of streams (Church et al. 2007; Nimick et al. 2004; USEPA 1997). Metal loads and concentrations are typically highly variable over space and time in these watersheds depending on location, characteristics, and significance of mine waste and metals sources (Caruso and Ward 1998; Church et al. 2007), and underlying

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geology, geochemistry, and weathering of ore deposits (Plumlee 1999; Seal and Foley 2002). Loads also vary in response to seasonal flow variability resulting from storm and spring snowmelt events, summer low flows, water diversions, and sometimes drought conditions (Caruso and Cox 2008; Nimick et al. 2004; Nordstrom 2007). Inter-annual metals variability resulting from year-to-year hydrologic changes and restoration efforts over time can also be significant (Caruso and Cox 2008). Many other watershed and stream biogeochemical processes and metals chemistry, fate and transport processes contribute to variation in metal loads, including surface and subsurface transport pathways (Hazen et al. 2002; Kimball et al. 2002), transformation, speciation and complexation processes dependent on pH and redox conditions/reactions (Langmuir et al. 2004; USEPA 2007), stream hyporheic zone processes and surface water–ground water interactions (Bencala 2000, 2005; Gandy et al. 2007; Runkel et al. 2003; Zaramella et al. 2006), and diel influences (Gammons et al. 2005; Nimick et al. 2003). For example, hyporheic exchange plays a significant role in pollutant transport and transformation in steep, gravel-bedded mountain streams (Bencala 2000, 2005). Processes that affect metals fate and transport in the hyporheic zone include aqueous phase transport in bed sediment pore water, sorption to sediments and metal oxides, precipitation onto metal oxides, hydrological and geomorphological controls, reductive dissolution, microbiological processes, and sediment transport (Gandy et al. 2007; Zaramella et al. 2006).

The Upper Tenmile Creek Watershed in Montana is an example of a western mountain watershed with AMD and metals contamination exhibiting considerable variability of metal loads and concentrations in streams. This 50 km^2 watershed has over 150 abandoned mines with waste rock, tailings, and draining adits, and the stream is the main drinking water supply for the city of Helena (Fig. 1). During summer low flows in some years, water supply diversions and storage in reservoirs almost completely dewater some stream reaches. The entire watershed is a Superfund Site, and the US Environmental Protection Agency (USEPA) has completed a number of investigations and remedial activities (CDM 2001a, 2001b; USEPA and MDEQ 2002). State of Montana water quality standards for total metals are exceeded in many locations (Cleasby and Nimick 2002; Parrett and Hettinger 2000). Metal fate and transport modeling in the watershed has been performed to support site characterization and restoration planning using the Water Quality Analysis Simulation Program (WASP) developed by USEPA (Caruso 2003; Wool et al. 2001). Restoration of natural flows is one important option being considered as part of further remediation and broader watershed restoration for habitat improvement. The effects of potential natural flow restoration on stream total metal concentrations and exceedances of Montana water quality standards (for total metal concentrations) were recently modeled and evaluated (Caruso and Cox 2008).

The objective of this study was to evaluate the seasonal and spatial variation of dissolved and total metal loads from natural flows in the Upper Tenmile Creek Watershed to help understand potential natural flow restoration effects on the sources and variability of metal loads, and to target efforts to reduce loads in the watershed. This information can also be used to provide an understanding of metal load variability and inform management decisions in similar mining-impacted mountain watersheds in the western US.

Methods

Estimates of natural flows and measured total metal concentration/load data were used to evaluate the seasonal and spatial variation of metal loads in tributary and point/nonpoint source inputs to the mainstem of Tenmile Creek. These estimated natural flow and load data were then used as input to the USEPA WASP model to simulate variation of total and dissolved metal loads with distance along the mainstem. Cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) are the constituents of concern in surface water at the site and were evaluated in this study (Caruso 2003; Caruso and Cox 2008).

Stream and Model Input Estimated Natural Flows

Two US Geological Survey (USGS) streamflow gages have been operational in the Upper Tenmile Creek mainstem: near Rimini in the middle of the watershed (06062500, period of record $n = 91$, 1915–2007), and downstream at the watershed outlet near the Tenmile water treatment plant (WTP) (06062750, $n = 6$, 1997–2002). Flows measured at these locations, and other flows measured historically by USEPA and USGS in some tributaries and from point and nonpoint source inputs to the mainstem, are quite variable over time and space in the watershed. This variation is due to inter-annual and seasonal variability of precipitation, snowpack and melt, other watershed processes, and city water diversion and storage timing and quantities. There are six Helena water diversions on the mainstem and several tributaries, and two storage reservoirs (Chessman on upper Beaver Creek and Scott on upper Ruby Creek), that alter the natural flow regime (Fig. 2). The estimated average natural flow diversion ranges from 20% of the average recorded flow in May to 180% of the flow in August, with an annual average diversion of 32% of the recorded flow at the gage near Rimini (Parrett and Hettinger 2000). The average annual hydrograph, based on mean daily flows at

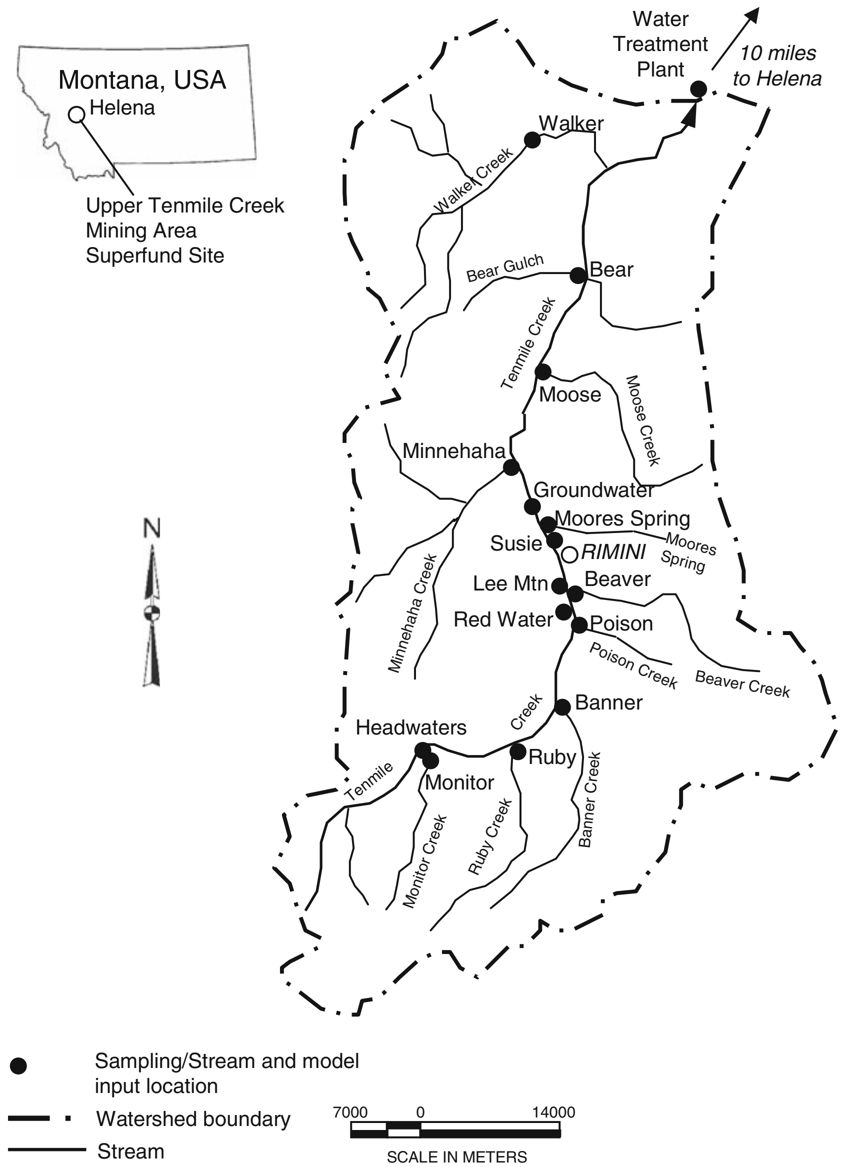


Fig. 1 Map of the Upper Tenmile Creek Watershed with locations of Water Quality Analysis Simulation Program model inputs to the mainstem

the gage near Rimini, averaged over the period of record for each calendar day, is typical of western mountain watersheds (Fig. 3). Flows peak in May and June (maximum of 3.4 m^3/s in late May) due to snowmelt, and flows recede sharply in summer through winter (minimum of 0.03 m^3/s in early February). The typical annual hydrographs downstream at the gage near the WTP and at Rimini in more recent years ($n = 11$, 1996–2007) show a similar pattern. Increasing municipal water demands and diversion, and possibly increasing drought and low flows, over time have reduced the typical annual hydrograph near Rimini (Fig. 3). The mean annual flow over the period of record at the USGS gage near Rimini is 0.48 m^3/s, but over the last 11 years is 0.40 m^3/s (Table 1). The mean annual flow at the WTP is 0.55 m^3/s. Therefore, measured flows increase slightly downstream at the WTP, but the increase is smaller than it would be under natural flow conditions due to water withdrawals upstream of the WTP during parts of the year (Fig. 3).

In previous studies, the WASP model was developed and calibrated using a June 2000 flow and water quality data set from a USEPA synoptic survey (Caruso 2003). A synoptic survey is a discrete field event where flows are measured and water quality samples collected for analysis from upstream to downstream in the watershed on the same day or over a 2-day period under relatively constant flow conditions. The June 2000 data were the most complete data set and intended to represent typical spring snowmelt high-flow conditions. Flow during this sampling event, however, was below normal. June 1997 flow and water quality data collected by the USGS were used for model validation, and flow during this survey was above average

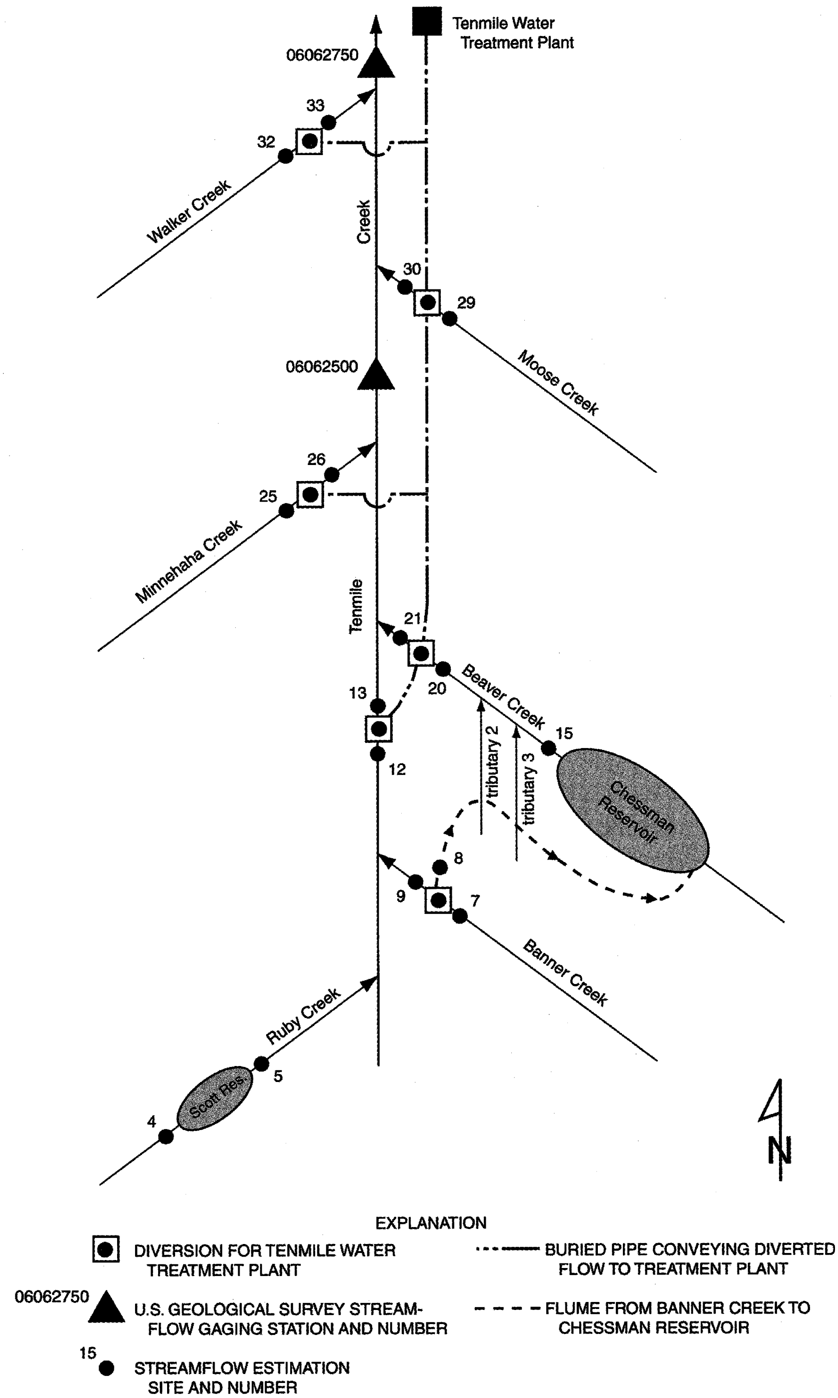


Fig. 2 Water sources, reservoirs, diversions, and conveyances for the Tenmile water treatment plant (taken from Parrett and Hettinger 2000)

(Caruso 2003). These differences illustrate the considerable inter-annual flow variability due to natural processes and water diversion variations from year to year.

Mean monthly flows also show typical variation with the highest values during spring snowmelt runoff (May and June) and the lowest flows in late summer through the winter (Fig. 4). Estimates of monthly natural flows for Upper Tenmile Creek near Rimini and near the WTP, and for major tributaries and point and nonpoint sources to the mainstem, were taken from those in Caruso and Cox (2008). These were derived using several methods, primarily using the mean instantaneous natural flows for August and June estimated by USGS (Parrett and Hettinger 2000) for all available locations (Fig. 1; Table 2) based on operational flow data for the city WTP and diversions, and a regional analysis approach using correlation/regression analysis. Therefore, estimated natural flows, as used in this study, are average flows for a location for a specific time

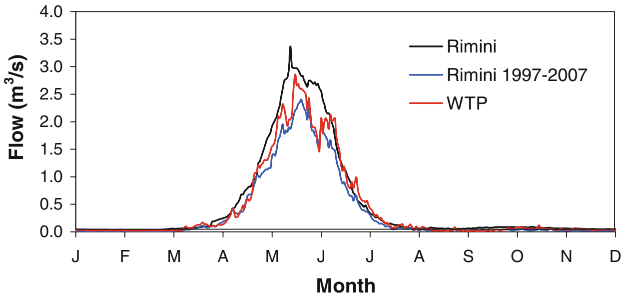


Fig. 3 Average annual hydrographs for Upper Tenmile Creek mean daily discharges at the USGS gage in the middle of the watershed near Rimini for the period of record ($n = 91$, 1915–2007), at the watershed outlet at the City of Helena water treatment plant (*WTP*) ($n = 6$, 1997–2002), and near Rimini for the last 11 years (1996–2007)

Table 1 Upper Tenmile Creek annual discharge statistics (m^3/s)

Statistic	Rimini 1915–2007	Rimini 1996–2007	WTP 1997–2002
Mean	0.48	0.40	0.55
Median	0.45	0.33	0.40
Maximum	1.50	1.28	1.60
Minimum	0.05	0.05	0.05

WTP Water treatment plant

period (1 month) estimated to occur if there were no water supply diversions or storage. Estimated monthly natural flows follow the same pattern of variation among locations as measured flows, but are higher, especially during summer (Fig. 4).

Based on the typical measured and estimated natural monthly flow patterns and past studies, a representative wet month (June), when high flow occurs due to snowmelt runoff, and a representative dry month (August), when runoff is low and municipal water withdrawals are greatest, were used to evaluate and model the seasonal variation of metal loads. Natural flows for the 2 months were estimated for 15 tributary and point and nonpoint source (adits and ground water) locations where total metal concentration data were available (Table 2). The estimated mean monthly natural flows for June and August for these 15 locations were used as model input.

Stream and Model Input Metal Concentrations and Loads

Total metal concentration and load data for the 15 input locations were taken from USEPA and USGS data collected from 1997 to 2004 (Fig. 1), based on the methods presented by Caruso and Cox (2008) (Table 2). These data were also used for model input to simulate resulting metal loads in the mainstem of the creek. The USEPA and US Forest Service have performed some remediation in the watershed since 2001 that has reduced metal concentrations and loads in targeted locations. This remediation included removal of mine waste near Poison and Minnehaha Creeks and onsite treatment of the Lee Mountain Adit discharge using a successive alkalinity producing system (Kepler and McCleary 1994) starting in 2003. The most recent metal concentrations were used for Poison Creek and the Lee Mountain Adit, and the most recent Cu concentrations were used for Minnehaha Creek because analysis of data trends indicated that these remedial activities have reduced concentrations of these metals at these locations (Caruso and Cox 2008).

Two approaches were used to estimate representative total metal concentrations for inputs to the mainstem and the model. The first approach estimated concentration as a function of flow. Linear regression analysis was performed to establish relationships between total metal concentrations and flow (using data collected on the same days) for August and for June for locations with adequate data (sample sizes 4–7: Banner Creek, Minnehaha Creek, Moore's Spring, and Poison Creek). For Banner Creek, there was a significant positive correlation of all metals with flow for both time periods. In June, R^2 values were

Fig. 4 Measured mean monthly flows for Upper Tenmile Creek at the USGS gage near Rimini for the period of record ($n = 91$, 1915–2007), at the City of Helena water treatment plant (*WTP*) ($n = 6$, 1997–2002), and near Rimini for the last 11 years (1996–2007), and estimated natural mean monthly flows for these two locations (from Caruso and Cox 2008)

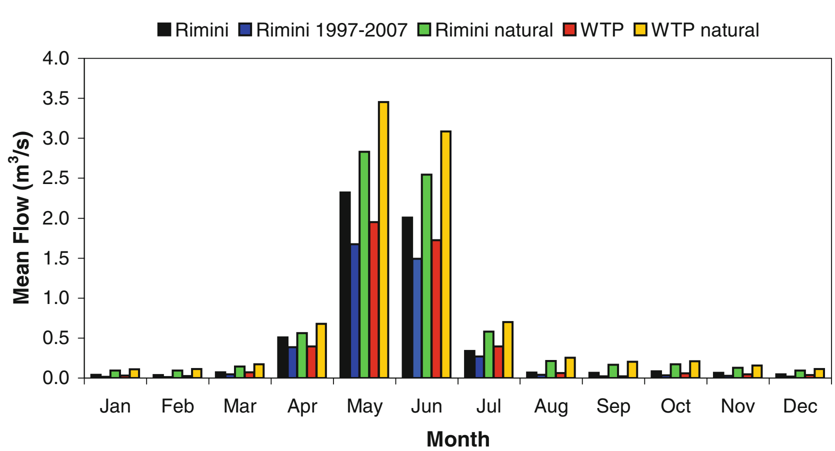


Table 2 June and August tributary, point, and nonpoint source estimated natural flows (m^3/s) and total metals concentrations and loads used for model input

Location	Input type	Model segment	Distance (km) from headwaters	Estimated atural flow	Cd		Cu		Pb		Zn	
					(μg/L)	(g/day)	(μg/L)	(g/day)	(μg/L)	(g/day)	(μg/L)	(g/day)
June												
Headwaters	T	1	0.15	0.28	0.04	0.97	2.18	52.7	0.46	11.1	7.6	183
Monitor Ck	T	2	0.46	0.11	1.1	10.9	6.3	61.8	2.6	25.1	94	922
Ruby Ck	T	8	2.29	0.21	0.05	0.89	21	372	1.5	26.6	5.0	89
Banner Ck	T	12	3.51	0.36	0.25	7.8	6.53	203	4.8	148	36.5	1133
Poison Ck	T	16	4.72	0.017	30	13.0	309	49.4	48.6	12.8	3520	1715
Red Water Adit	PS	18	5.33	0.027	70.4	4.6	34.9	2.3	5.0	0.33	12800	837
Lee Mtn Adit	PS	20	5.94	0.00025	2.5	0.05	3.0	0.1	5.0	0.11	6800	147
Susie Lode Adit	PS	21	6.25	0.0071	193	3.4	39.8	0.7	12.1	0.21	35600	621
Spring Ck	T	21	6.25	0.080	1.0	6.9	9.1	62.5	0.25	1.7	89.0	612
Moores Spring Ck	T	22	6.55	0.0054	4.6	2.1	8.1	3.8	4.02	1.9	614	285
Ground water	NPS	27	8.08	0.025	1.5	3.2	7.0	15.1	0.46	1.0	200	432
Minnehaha Ck	T	28	8.38	0.42	1.6	57.6	9.0	628	1.16	42.5	246	9022
Moose Ck	T	36	10.82	0.068	1.0	5.8	0.74	4.3	0.62	3.6	4.4	25.7
Bear Ck	T	43	12.95	0.027	1.0	2.3	0.68	1.6	1.0	2.3	11.2	26.0
Walker Ck	T	50	15.09	0.39	1.0	33.3	1.6	53.2	0.11	3.7	4.5	149.6
August												
Headwaters	T	1	0.15	0.0085	0.03	0.022	1.3	0.96	0.23	0.17	4.6	3.3
Monitor Ck	T	2	0.46	0.0071	1.7	1.1	6.4	3.9	0.76	0.46	111	67.5
Ruby Ck	T	8	2.29	0.0031	0.05	0.013	3.0	0.81	1.5	0.40	20.0	5.4
Banner Ck	T	12	3.51	0.014	0.12	0.15	2.1	2.5	0.48	0.58	23.1	27.7
Poison Ck	T	16	4.72	0.0023	6.5	1.3	25.9	5.1	5.6	1.1	1050	205
Red Water Adit	PS	18	5.33	0.00076	56.5	3.7	20.8	1.4	2.0	0.13	12000	784
Lee Mtn Adit	PS	20	5.94	0.0001	2.5	0.022	3.0	0.03	5.0	0.04	6800	58.7
Susie Lode Adit	PS	21	6.25	0.00025	216	4.7	58.5	1.3	10.0	0.22	31700	684
Spring Ck	T	21	6.25	0.0085	1	0.73	9.1	6.7	0.25	0.18	89	65.3
Moores Spring Ck	T	22	6.55	0.0048	4.7	2.0	6.2	2.6	0.80	0.33	644	268
Ground water	NPS	27	8.08	0.025	1.5	3.2	7.0	15.1	0.46	1.0	200	432
Minnehaha Ck	T	28	8.38	0.034	1.6	4.7	6.6	19.4	0.50	1.5	270	792
Moose Ck	T	36	10.82	0.019	1.0	1.6	0.74	1.2	0.62	1.0	4.4	7.2
Bear Ck	T	43	12.95	0.0034	1.0	0.29	0.68	0.20	1.0	0.29	11.2	3.3
Walker Ck	T	50	15.09	0.029	1.0	2.5	1.6	4.0	0.11	0.28	4.5	11.3

T Tributary, *PS* point source, *NPS* nonpoint source

>0.96 for all metals with P values <0.01. In August, R^2 values were >0.96 with P values <0.01 for metals except Pb ($R^2 = 0.62$, P value <0.1). For Minnehaha Creek, there was only a significant positive correlation of the Cu concentration with flow for June ($R^2 > 0.96$, P value <0.01). The regression equations developed for these locations, metals, and months were used to estimate input concentrations as a function of the estimated natural flow. There were no significant correlations between concentrations and flows in Moore's Spring or Poison Creek.

The second approach for estimating input concentrations was used for all locations with limited data sets (sample size <4) where regression could not be performed, or for locations and metals that did not have significant correlations with flow. For these locations and metals, the median concentrations for August and June were used. Only a single concentration value for August and single value for June were available and used for several sites. The median metals concentration based on all other measured data for a particular location was used when no data were available for August or June. Metal concentrations from the June 2000 synoptic survey were used for both August and June for Spring, Moose, and Walker Creeks, Bear Gulch, and the nonpoint source ground water input at segment 27 because they were the only data available (Table 2).

Because more recent streambed sediment metals concentration data were not available, the June 2000 synoptic survey bed sediment metal concentrations were used as initial input for the model (Caruso 2003).

WASP Model

The Upper Tenmile Creek Watershed WASP model, Version 6 (Caruso 2003; Wool et al. 2001) was used to evaluate the seasonal and spatial variation of total and dissolved metal loads from estimated natural flows in the mainstem. The estimated monthly natural flows, and total metal concentrations and loads for inputs to the mainstem discussed above, were used as model input. The model can simulate steady state or dynamic solute advection and dispersion in streams and other water bodies in up to three dimensions. WASP uses a simple lumped partition coefficient (K_d) to model metals dissolved and particulate fractions associated with sediment and precipitates. The model also simulates particulate settling/re-suspension and bed sediment diffusive exchanges. The K_d values and solute vertical dispersion and diffusion coefficients for exchanges between benthic porewater and the overlying water column are important kinetic and transport calibration parameters in the model (Caruso 2004).

The Upper Tenmile Creek Watershed WASP model simulates one-dimensional steady-state conditions. It has 58 mainstem water column segments, 6 underlying benthic segments, and 15 tributary, adit, and ground water nonpoint source inputs (Caruso 2003). The original calibrated model includes the six water diversions for the city of Helena. The model was modified in this study by removing these diversions and changing the mainstem hydraulics in the model to account for flow changes (Caruso and Cox 2008). As discussed above, adjustments were also made to the tributary, point and nonpoint source inputs for the calibrated model using the monthly natural flow estimates and best estimates of metal concentrations.

Model output included flow and dissolved and total metal concentrations with distance along the mainstem (for the 58 mainstem segments). Cumulative dissolved and total loads were computed based on the modeled flows and concentrations, and graphed with distance along the mainstem.

Results and Discussion

Flows

Monthly estimated natural flows for the tributary and point and nonpoint source inputs to the Upper Tenmile Creek mainstem for June (spring snowmelt high flow) and August (summer low flow) used for the WASP model input vary among locations by up to 2,100-fold in June and up to 340-fold in August, and between the two seasons by up to 66-fold (Fig. 5; Table 3). The highest estimated natural flows in June are in Minnehaha, Banner, and Walker Creeks and the headwaters (Table 2) (0.28–0.42 m^3/s). The highest flows in August occur in Minnehaha and Walker Creeks and from the nonpoint source ground water discharge (0.025–0.034 m^3/s). In June, the three adits have low flows (0.00025–0.027 m^3/s), and Moore's Spring and Poison Creek also have unusually low flows (0.0054–0.017 m^3/s). In August, the adits have the lowest flows (0.0001–0.00076 m^3/s). The adits also have the smallest flow variation among locations and between seasons. Modeled natural flows increase with distance along the mainstem, ranging from 0.28 to 1.98 m^3/s (7-fold) in June, and from to 0.01 to 0.13 m^3/s (15-fold) in August (Table 3).

Metal Loads

Results show that total metal loads to the creek vary among input locations by up to >9,700-fold in June and up to >740-fold in August for Cu (Table 3). The smallest variation occurs for Zn in June (350-fold) and for Pb in August (33-fold). Several tributaries have the greatest loads during both seasons, although adits often exhibit the highest concentrations (Table 2). At all locations, average input loads exhibit the greatest seasonal variation for Cu (46-fold) and the smallest variation for Zn (12-fold). Total and dissolved metal loads generally increase with distance along the mainstem and vary by up to >320-fold in August and up to >118-fold in June for Zn (Table 3). Cd has the smallest variation (13-fold in June and 26-fold in August). On average, along the mainstem, Pb exhibits the greatest seasonal variation (68-fold), and Cd and Zn have the smallest variation (15-fold).

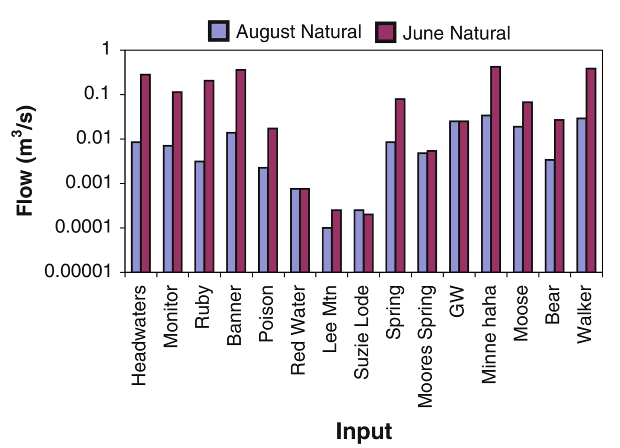


Fig. 5 August and June estimated natural flow inputs to mainstem of Upper Tenmile Creek

Table 3 Variation of estimated natural flows (m^3/s) and metal loads (g/day) for all measured inputs to Upper Tenmile Creek, and for the mainstem, for June and August; factor = maximum/minimum

	Flow		Cd		Cu		Pb		Zn	
	June	August	June	August	June	August	June	August	June	August
Inputs										
Total load										
Minimum	0.0002	0.0001	0.05	0.01	0.06	0.03	0.11	0.04	25.7	3.3
Maximum	0.42	0.034	57.6	4.7	628	19.4	148	1.5	9022	792
Factor	2103	339	1067	348	9707	747	1366	33.0	350	240
Mainstem										
Total load										
Minimum	0.28	0.01	11.7	0.45	52.81	1.1	11.2	0.18	0.18	0.01
Maximum	2.0	0.13	149	11.9	1216	42.7	277	5.5	21.8	2.2
Factor	7.1	15.3	12.8	26.3	23.0	38.9	24.8	30.2	118	322
Dissolved load										
Minimum			9.7	0.38	33.0	0.69	8.0	0.13	0.18	0.01
Maximum			129	10.4	926	34.2	212	4.7	21.5	2.2
Factor			13.2	27.5	28.1	49.9	26.6	35.8	119	324

Cadmium

Total Cd loads from estimated natural high flows in June for the tributary and point and nonpoint source inputs to the mainstem are lowest from the Lee Mountain Adit, headwaters, and Ruby Creek (0.05–0.97 g/day, Fig. 6a). These smaller loads are expected because these streams have the lowest total Cd concentrations (0.04–0.05 μg/L), and some remedial actions were implemented at Lee Mountain in recent years, reducing concentrations (to 2.5 μg/L) in conjunction with its very low flow (0.00025 m^3/s). June loads are highest from Minnehaha, Walker, and Poison Creeks (13–57.6 g/day), resulting from high Cd concentrations (up to 30 μg/L for Poison Creek) and the highest flows (up to 0.42 m^3/s for Minnehaha Creek) compared to other inputs. Total Cd loads from estimated natural flows in August for inputs are lowest for Ruby Creek, the headwaters, and Lee Mountain (0.013–0.022 g/day), and greatest for Susie Lode, Red Water Adit, and Minnehaha Creek (3.7–4.7 g/day, Fig. 6a). The same spatial pattern occurs for the lowest total Cd input loads during both June and August. The greatest loads in August, however, are from Susie Lode and Red Water Adit in addition to Minnehaha Creek. Although the flows from these adits are very low (0.00025–0.00076 m^3/s), the total Cd concentrations are the highest measured in the watershed (57–216 μg/L). The total Cd load seasonal differences are greatest for the headwaters and Ruby and Banner Creeks, but are fairly consistent for the adits.

Simulation of the total Cd load with distance along the mainstem for June estimated natural flows shows a constant load above 10 g/day from Monitor Creek to Banner Creek, a gradual increase from Banner Creek to the ground water input, and then a sharp increase to approximately 100 g/day at Minnehaha Creek (Fig. 7a). There is a fairly constant load along the rest of the mainstem with a slight increase to over 100 g/day at Walker Creek. The increasing total Cd load reflects the inputs between Ruby and Minnehaha Creeks, including the three adits near Rimini. The leveling off of the load to the mouth reflects the lack of additional major Cd inputs, and possibly a loss of some load that balances any additional small inputs. The simulated dissolved Cd load in the mainstem in June follows this pattern very closely, and is only slightly less than the total load. Simulation of August estimated natural flows shows that the total Cd load along the mainstem is generally an order of magnitude less than the June load (Fig. 7a). The total Cd load decreases from 1 g/day at Monitor Creek to 0.8 g/day in the vicinity of Banner Creek, and then increases sharply to approximately 8 g/day at the Lee Mountain Adit. The total Cd load then fluctuates, but increases to greater than 10 g/day at Minnehaha Creek. The load remains relatively constant at approximately 10 g/day through the remainder of the mainstem. Again, the simulated dissolved Cd load in August is only slightly less than the total load, and follows the same pattern. The dissolved load makes up a very large percentage of the total Cd load throughout the mainstem and during both seasons (on average 86%, Fig. 7a). The small loss of Cd is more apparent during the August low-flow simulation than in June.

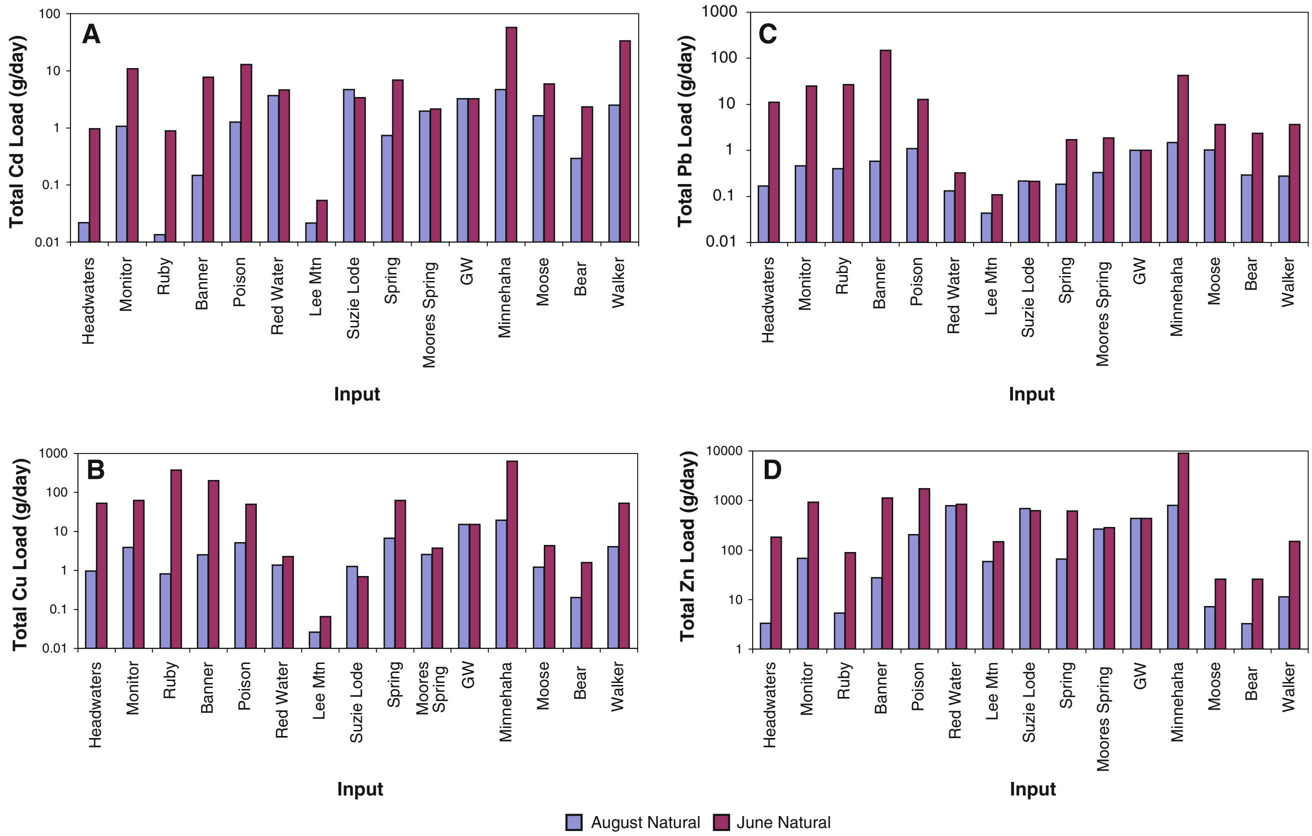


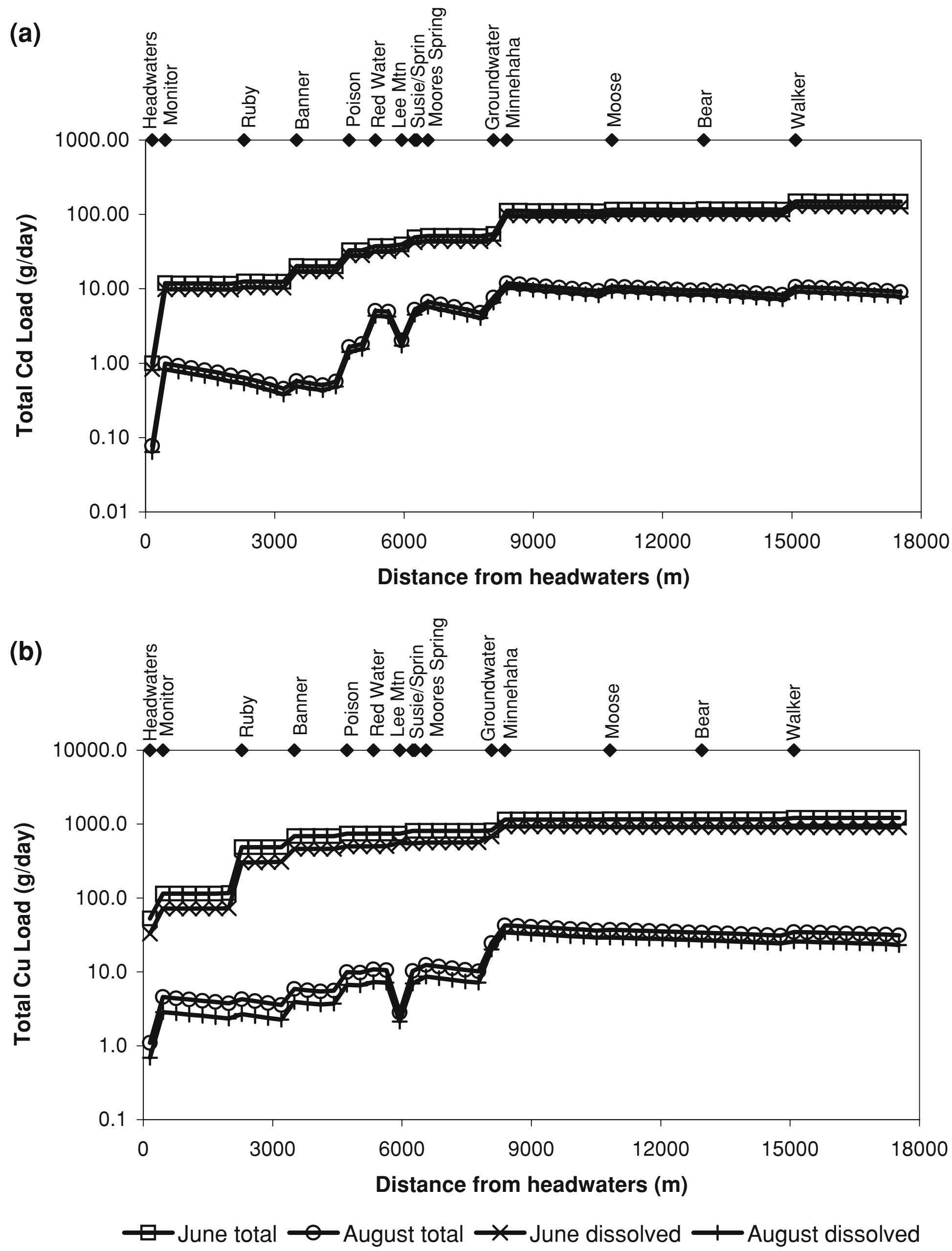
Fig. 6 Upper Tenmile Creek mainstem input total metal loads for (**a**) Cd, (**b**) Cu, (**c**) Pb, and (**d**) Zn

Copper

June total Cu loads from estimated natural flows for mainstem inputs are lowest from the Lee Mountain Adit, Susie Lode, and Bear Creek (0.1–1.6 g/day), and greatest from Minnehaha, Ruby, and Banner Creeks (203–628 g/day, Fig. 6b). The small loads result from the very low flows from all three sources (0.00025–0.027 m^3/s) and the low concentrations in Bear Creek (0.68 µg/L) compared to other inputs. The highest loads are due to much higher flows (0.21–0.42 m^3/s) and relatively high concentrations (6.5–21 µg/L) in the streams. August total Cu loads are lowest for Lee Mountain, and Bear and Ruby Creeks (0.03–0.81 g/day), and greatest for Minnehaha Creek, the ground water input at segment 27, and Spring Creek (6.7–19.4 g/day, Fig. 6b). The same spatial pattern generally occurs in June and August for the smallest input loads, except that Ruby Creek has a smaller input than Susie Lode because of the lower concentration in the creek during August. In August, the greatest total Cu loads result from the relatively high tributary flows (0.025–0.034 m^3/s), and from Spring Creek due to its high concentration (9.1 µg/L). The seasonal load differences are greatest for the headwaters and Ruby and Banner Creeks.

Total Cu load simulation in the mainstem for June shows values slightly above 100 g/day from Monitor Creek to Ruby Creek, and a sharp increase to approximately 800 g/day at Ruby Creek (Fig. 7b). The load then increases gradually to almost 1,000 g/day to the ground water input, and then increases again to over 1,000 g/day at Minnehaha Creek downstream to the mouth. These increases reflect inputs from the three adits in this reach. Like Cd, the relatively constant load to the mouth shows no additional significant Cu inputs, and may indicate a small loss of Cu load, which balances any unmonitored additional small inputs. The dissolved Cu load follows a very similar pattern to the total load. The difference between total and dissolved Cu loads is greater than the difference for Cd loads. The total Cu load simulation for August shows a similar pattern to June, but the August load is more than an order of magnitude less than the June load (in some locations, almost two orders of magnitude less, Fig. 7b). The load decreases slightly from approximately 6 g/day at Monitor Creek, and then increases while fluctuating to approximately 10 g/day at the ground water input. The total Cu load increases sharply to approximately 70 g/day at Minnehaha Creek, and then decreases slightly to the mouth. The simulated dissolved Cu load follows a very similar pattern, with the difference between total and dissolved

Fig. 7 Variation of total and dissolved metal loads over distance in the Upper Tenmile Creek mainstem in June and August for (**a**) Cd, (**b**) Cu, (**c**) Pb, and (**d**) Zn

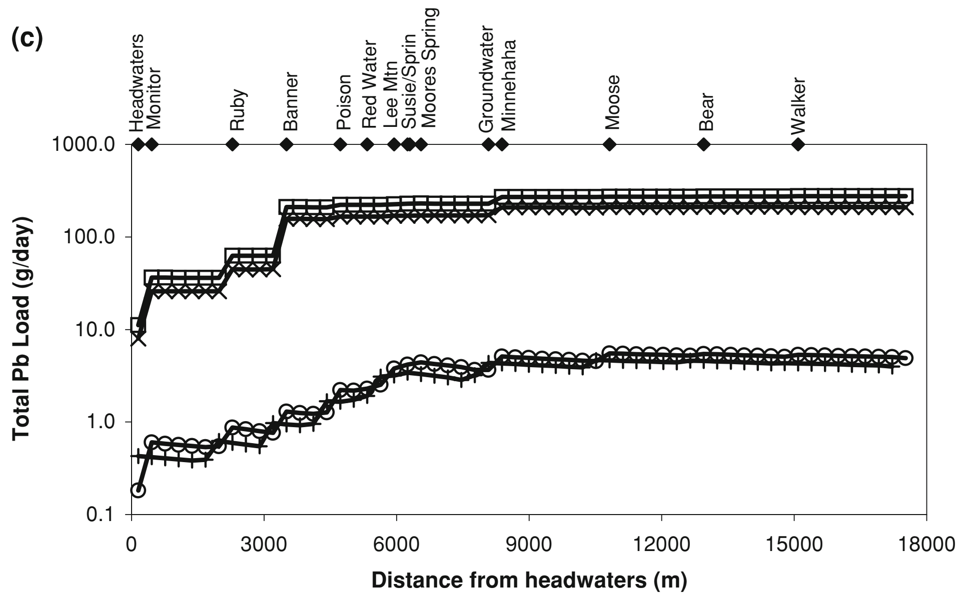


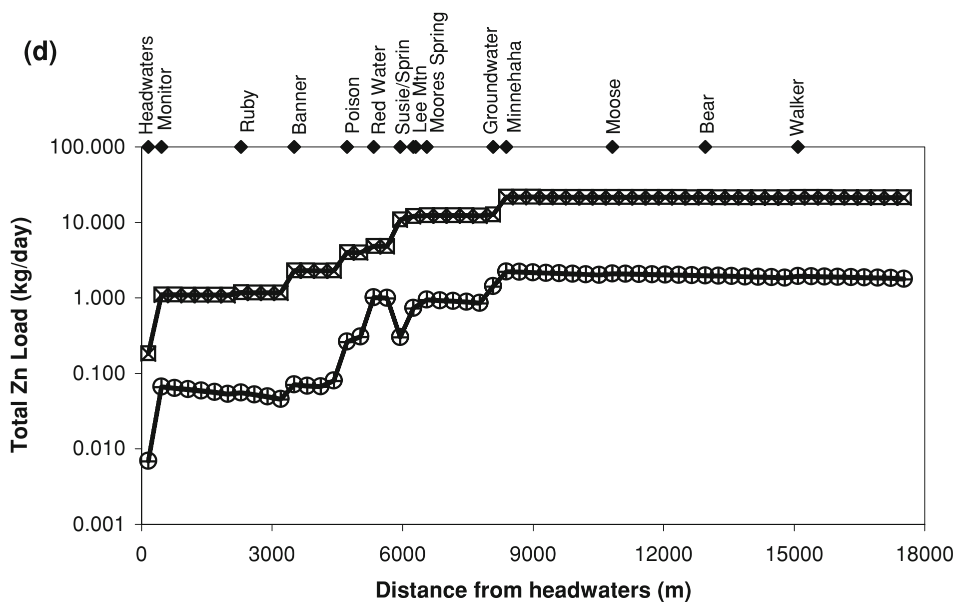
loads greater than for Cd. Dissolved Cu constitutes a smaller percentage of the total load (on average, 73%, Fig. 7b) between seasons and over distance in the mainstem compared to Cd because Cu is more highly sorbed to particulates.

Lead

Total Pb loads from estimated natural flows for mainstem inputs in June are smallest from the three adits (Lee Mountain, Susie Lode, and Red Water, 0.1–0.33 g/day), and highest from Banner, Minnehaha, Ruby, and Monitor Creeks (25.1–148 g/day, Fig. 6c). The small loads from the adits result from their relatively low flows (0.00025–0.027 m^3/s) compared to the tributary streams. The greatest loads are due to the combination of much higher flows (0.11–0.42 m^3/s) and elevated concentrations (1.5–4.8 μg/L) in the streams. Total input Pb loads in August are smallest for the three adits, headwaters, and Spring Creek (0.04–0.22 g/day), and greatest for Minnehaha, Poison, and Moose Creeks, and the ground water input (1–1.5 g/day, Fig. 6c). The same spatial pattern of the smallest loads from the three adits occurs in June and August due to their low flows. Loads from the headwaters and Spring Creek are also very small due to their low flows and low concentrations during August. The greatest loads result from

Fig. 7 continued





the relatively high flows (0.019–0.034 m^3/s) in these streams, and the high concentration (5.6 μg/L) in Poison Creek. Input total Pb loads in June are considerably greater than in August, with the greatest seasonal differences in streams in the upper watershed.

Simulation of the total Pb load in the mainstem for June shows step increases from approximately 10 g/day in the headwaters to approximately 200 g/day at Banner Creek, resulting from the tributary inputs (Fig. 7c). The load is then relatively constant, only increasing slightly to the mouth, indicating no significant Pb inputs. The simulated dissolved Pb load follows this pattern closely, and is only slightly lower than the total load. August low-flow simulation shows that the total Pb load increases gradually from <1 g/day in the headwaters to approximately 5 g/day in the vicinity of Lee Mountain and Susie Lode (Fig. 7c). The load then fluctuates and decreases somewhat to the mouth. Again, the dissolved Pb load in August is slightly less than the total load, and follows the same pattern. The total Pb load along the mainstem in August is almost two orders of magnitude less than the June load. This difference between June and August loads is greatest for Pb relative to the other metals. Similar to Cu, the dissolved Pb makes up a smaller percentage of the total load (on average 78%, Fig. 7c) throughout the creek and between seasons.

Zinc

June total Zn input loads from estimated natural flows are smallest from Moose and Bear Creeks (25.7–26 g/day), and greatest from Minnehaha, Poison, and Banner Creeks (1,133–9,022 g/day, Fig. 6d). The small loads are expected because these streams have some of the lowest total Zn concentrations (4.4–4.5 μg/L) and lowest flows in the watershed (0.027–0.068 m^3/s). Although flows from some of the adits are lower, adit concentrations are much higher. The high loads from Minnehaha and Banner Creeks result from relatively high total Zn concentrations (36.5–246 μg/L) combined with the greatest flows (0.36–0.42 m^3/day), and high loads in Poison Creek are due to the highest stream concentration (3,520 μg/L) compared to other inputs. August total Zn input loads are smallest for Bear and Ruby Creeks and the headwaters (3.3–5.4 g/day), and highest for the Red Water and Susie Lode adits and Minnehaha Creek (684–792 g/day, Fig. 6d). The spatial pattern for the smaller load changes in August compared to June are primarily due to the low flows in these streams in August (0.0031–0.0085 m^3/s). The greatest loads result from the extremely high total zinc concentrations for the two adits (12,000–31,700 μg/L) and the highest flow in the watershed from Minnehaha Creek (0.034 m^3/s). Total Zn tributary input loads in June are approximately an order of magnitude higher than in August, while adit loads are much more constant between the two seasons.

Total Zn load simulation in the mainstem for June shows values increasing from approximately 0.2 g/day in the headwaters to 1 g/day at Monitor Creek (Fig. 7d). The load stays relatively constant at approximately 1 g/day to Banner Creek, and then increases in a step-wise fashion to approximately 20 g/day at Minnehaha Creek in response to inputs between Ruby and Minnehaha Creeks, including the three adits. The load remains relatively constant to the mouth, reflecting the lack of additional major Zn inputs, and possibly loss of some load that balances any additional small inputs. Results for dissolved Zn show a similar pattern to the total Zn load. The total Zn load simulation for August shows a similar pattern to June, but loads are approximately an order of magnitude less than in June (Fig. 7d). There is also a much sharper increase at Lee Mountain, showing the greater influence of the adits during seasonal low flows. In August, a sharp, temporary drop at Spring Creek is apparent due to the greater relative loss of Zn through in-stream processes. The total Zn load also decreases slightly from Minnehaha Creek to the mouth. For both June and August, the dissolved load is almost exactly the same as the total load, so almost all the Zn is in the dissolved phase (on average, 98%, Fig. 7d). Small losses are more apparent during the August low-flow simulation.

Processes Affecting Metal Load Variation

Numerous watershed and stream biogeochemical processes contribute to the variation in metal loads evaluated in this study. These include surface and subsurface transport pathways (Hazen et al. 2002; Kimball et al. 2002); transformation, speciation and complexation processes dependent on pH and redox conditions/reactions (Langmuir et al. 2004; USEPA 2007); stream hyporheic zone processes and surface water–ground water interactions (Bencala 2000, 2005; Gandy et al. 2007; Runkel et al. 2003; Zaramella et al. 2006); and diel influences (Gammons et al. 2005; Nimick et al. 2003). Mine waste and AMD/metals source locations, characteristics, and magnitudes are primary factors influencing the variation of watershed input loads to the mainstem, particularly the spatial variation (Caruso and Ward 1998; Church et al. 2007; Nimick et al. 2004). The greatest total metal loads are from locations with the highest concentrations or greatest discharges in combination with some elevated metal concentrations. The three adits draining underground mine workings, and the streams draining sub-basins with the greatest number of tailings and waste rock piles, such as Poison and Minnehaha Creeks, exhibit the highest concentrations. Locations with the highest flows include Minnehaha and Walker Creeks; Minnehaha Creek has the greatest resultant loads.

The underlying geology and locations and characteristics of mineral deposit types also influence the spatial variation of metal loads in the watershed (Church et al. 2007; Nimick et al. 2004; Plumlee 1999; Plumlee et al. 1999). Ore mineralogy, geochemistry, host rock lithology, and weathering of pyrite exposed to oxygen and water contribute to natural geochemical and metal load variations (Hammarstrom and Smith 2002; Seal and Foley 2002). Geoenvironmental mineral-deposit models (GEMs) are compilations of relevant data based on the different mineral-deposit types according to similarities in geologic characteristics, which in turn result in similar environmental impacts (Plumlee 1999; Plumlee et al. 1999). GEMs have been developed to help to define critical geologic variables, identify primary potential environmental impacts, and assist screening-level prediction of metals sources and transport in mined watersheds (du Bray 1995; Seal and Foley 2002; Seal and Hammarstrom 2003).

Seasonal flow variability resulting from storm and spring snowmelt events and summer low flows is a major influence on spatial and temporal variation of loads (Caruso and Cox 2008; Church et al. 2007; Kimball et al. 2007; Nimick et al. 2004). Seasonal flow changes, watershed and metal source characteristics, and geology also influence surface and subsurface transport pathways, which in turn affect the spatial and seasonal variation of loads (Kimball et al. 2002; Hazen et al. 2002). The amount and residence time of water in contact with geologic materials, ore, and mine waste exposed to oxygen influence concentrations and loads in subsurface and surface water. Surface runoff in contact with exposed mine waste erodes sediment, tailings, and waste rock with sorbed metals contributing particulate metal loads, which are greater during high flow from spring snowmelt and precipitation events (Caruso 2003). High flows during spring snowmelt and precipitation can also leach and flush dissolved metals from mine waste and natural sources, increasing these loads compared to baseflows (Kimball et al. 2007; Nordstrom 2007). Total metal loads in tributaries to Upper Tenmile Creek are greatest in June due to the higher flows, even though concentrations may decrease somewhat from dilution during this time. Restoration of natural flows tends to increase these loads, especially in spring (Caruso and Cox 2008). Loads from the adits and nonpoint source ground water inputs are generally more constant over seasons because they are not influenced by precipitation and snowmelt runoff as much as surface sources. In a historically heavily coal-mined catchment in northeast England, Mayes et al. (2008) found that approximately 50% of in-stream loading of mine water pollution to a river under low-flows conditions came from diffuse sources dominated by discharge of contaminated ground water in the lower reaches of the stream. This increased to 98% during high flows, primarily due to resuspended Fe-rich sediments that are both naturally occurring and derived from historic mining.

The variation of dissolved and total metal loads with distance along the mainstem generally follows the same pattern for all metals, with distinct increases near Rimini from adit and contaminated stream input loads. Loads tend to level off, and, in some cases, decrease somewhat to the mouth. Decreases in metal loads are more apparent during August low-flow conditions. Spatial and temporal variation and decreases in the mainstem in both June and August can result from a number of transformation, complexation, and attenuation processes (Langmuir et al. 2004; USEPA 2007; Wilkin 2008). Hyporheic exchange and surface water–ground water interactions play a significant role in pollutant transport and transformation in steep, gravel-bedded mountain streams (Bencala 2000, 2005; Runkel et al. 2003). Hyporheic zone processes, in particular, can attenuate metals in mining-impacted streams (Environment Agency 2006; Gandy et al. 2007; Zaramella et al. 2006). Processes that affect metals fate and transport in the hyporheic zone include aqueous phase transport in bed sediment pore water, sorption to sediments and other solids, precipitation onto metal oxides, and hydrological and geomorphological controls, including dilution and mixing, complexation, reductive dissolution, microbiological processes, and sediment transport (Gandy et al. 2007; Zaramella et al. 2006).

Precipitation/dissolution reactions and corresponding pH and redox effects can drive the variation of metals loads, especially in highly acidic waters where concentrations reach saturation (Medine et al. 2002; USEPA 2007). Because metal concentrations are not high enough to reach saturation in Upper Tenmile Creek, loss via precipitation is unlikely and most partitioning is probably due to adsorption and other physical processes. However, co-precipitation with oxy-hydroxides, including hydrous ferrous oxide and hydrous aluminum oxide, can also occur in some streams (Butler 2005; Medine et al. 2002).

Adsorption/desorption reactions drive the distribution of metals between the solid and dissolved phases and influence metal load variation. Sorption of dissolved metals can occur onto bed and suspended sediment and other solids including metal oxides, colloids, particulate and dissolved organic carbon, and biological membranes and films (Caruso and Cox 2008; Farag et al. 2007; USEPA 2007). Temperature, pH, and sediment/solids concentrations can all affect partitioning and estimation of partition coefficients (Allison and Allison 2005; USEPA 1989, 1996).

Previous studies suggest that bed sediments are not a significant source of metals during the June and August simulation periods (Caruso and Cox 2008). In the Upper Tenmile Creek WASP model, the calibrated K_d value for Cd (1×10^5 L/kg) represents moderate partitioning to the particulate form (Allison and Allison 2005). The calibrated K_d values for Cu (3×10^5 L/kg) and Pb (2×10^5 L/kg) in the model represent relatively strong partitioning (Allison and Allison 2005). For Cd, Cu, and Pb, there is a concentration gradient from the benthic sediment to the overlying water column, but sorption to the bed and particulate settling appear to dominate dissolved phase diffusion in the simulations (Caruso and Cox 2008). Although the benthic sediments do not appear to be a major metals source or sink in Tenmile Creek, sorption to the sediments or other solids can result in a net loss of these metals from the water column to the bed. The greater sorption of Cu and Pb results in a greater proportion of these metal loads in the particulate phase, and greater seasonal variation from higher loads during spring snowmelt and precipitation high-flow events, compared to Cd or Zn. Zn is more conservative than the other metals and not as highly sorbed (calibrated $K_d = 1 \times 10^4$ L/kg) or susceptible to transport in the particulate form during higher flows. In a previous study, modeled results for a flow restoration scenario were higher than conservative mixing estimates, indicating that some additional Zn is released to the water column from contaminated bed sediment under these higher flow conditions (Caruso and Cox 2008). This may be somewhat reflected in the increase or constant Zn load along the mainstem in this study.

In addition to seasonal and inter-annual variation of metals loads, diel variation of metal concentrations and loads can be significant in near-neutral pH mountain streams in the Rocky Mountains and has been studied extensively in recent years. This variation results from several complex processes, such as adsorption/desorption and co-precipitation reactions dependent on temperature (Gammons et al. 2005; Nimick et al. 2003, 2005) and light- and photosynthetically mediated removal from the water column and uptake in biofilms (Morris et al. 2005, 2006). Diurnal variation of pH due to the diurnal cycle of algae photosynthesis (Gammons et al. 2007) and photochemical reductive dissolution of ferric iron precipitates (Collienne 1983) could play a role in decreasing metal loads along the creek.

In summary, a range of watershed and stream biogeochemical processes contribute to the seasonal and spatial variation in metal loads to, and in, Upper Tenmile Creek. It is believed that the most likely, primary causes of the variation in this watershed are mine waste and AMD/metals source locations, characteristics, and magnitudes; seasonal snowmelt, precipitation, and flow patterns; and metals transformation, speciation and complexation processes, including those due to hyporheic zone processes and surface water–ground water interactions.

Modeling Issues

A common issue for studies attempting to fully characterize pollutant load variation in watersheds and streams are data gaps for seasonal and inter-annual variability of flows and concentrations, and for specific locations of nonpoint source loads and stream losses. Although this watershed is a Superfund site with a significant amount of data collected during several synoptic studies, only two representative seasons were evaluated where adequate spatial flow and chemistry data were available and used as model input. It is often difficult in these mining-impacted mountainous watersheds to adequately measure flows and concentrations over appropriate spatial and temporal scales to fully understand seasonal and spatial metal loads variation (Caruso and Ward 1998; Church et al. 2007; Nimick et al. 2004). Kimball et al. (2002, 2004) and other USGS studies have used tracer injection in combination with synoptic sampling during low flows for detailed evaluation of metal loads and sources and spatial variation along streams. Metals fate and transport modeling can be used in conjunction with synoptic sampling to better evaluate these processes and resulting variation in concentrations and loads, and as a management tool for more informed restoration planning (Caruso et al. 2008).

The WASP lumped partition coefficient approach is an attempt to average most of the important physical and biochemical processes for each metal, although it can vary over space. However, K_d does not explicitly incorporate each contributing factor. For example, it does not explicitly account for pH variability or co-precipitation. In addition to the porewater dispersion and diffusion coefficients, K_d is still an important calibration parameter. K_d values can be estimated based on representative bed sediment chemical sampling, analysis, and laboratory adsorption/desorption tests. Recent literature values can also be used as default values (Allison and Allison 2005). Laboratory tests on the mainstem sediments were performed at key locations, and calibrated K_d values for the model were within the ranges estimated by these tests and in the literature (Caruso 2004). The evaluation performed for this study could be improved with additional and more recent bed sediment concentration data.

Although limitations in the data and the WASP model exist, numerical models are useful for evaluating the variation of metal loads from estimated natural flows. A new module for WASP, the Metals Exposure, Transformation and Assessment (META4) code, explicitly incorporates pH, redox, and precipitation reactions and could be used to potentially improve modeling results (Medine et al. 2002; Medine 2003). Other recently developed watershed models that could be used for future studies include the Two-Dimensional Runoff, Erosion, and Export (TREX) program for watershed metals transport (Velleux 2005; Velleux et al. 2006) and the USGS One-Dimensional Transport with Equilibrium Chemistry (OTEQ) code for metals fate and transport in streams (Runkel et al. 1999; Runkel and Kimball 2002).

Conclusions

There is considerable seasonal and spatial variation of total metals loads from estimated natural flows for tributary and point and nonpoint source inputs to the mainstem of Upper Tenmile Creek. Total and dissolved metals loads also exhibit significant variation between seasons and with distance along the mainstem. This variation is due to the spatial distribution of mine waste sources in the watershed, variation of flows and metal concentrations over space and time, and complex physical and biogeochemical processes affecting the distribution of metals between the dissolved and particulate phases and attenuation in the mainstem. These processes can include adsorption/desorption to different types of solids, precipitation/co-precipitation and redox reactions, surface water/ground water interactions and hyporheic zone processes, and diel influences. The dissolved phase generally constitutes a large proportion of the total metals and follows patterns very similar to those for total loads along the mainstem. Seasonal load differences are greatest for Cu and Pb because their particulate loads during high flow are associated with increased erosion and transport of solids. It is difficult to fully characterize seasonal and spatial variation of metal loads due to these complex processes and some data gaps over time and space. The use of deterministic fate and transport models, such as WASP, can aid in understanding these processes, evaluating variability, and targeting, planning, and designing remediation of sources.

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