WATER QUALITY VARIABILITY IN TRIBUTARIES OF THE CHEAT RIVER, A MINED APPALACHIAN WATERSHED[1]

J. Todd Petty and Jennifer Barker[2]

Abstract. An understanding of the dynamics of metals and other solutes from mine drainage is essential to successful planning and stream remediation in mined Appalachian watersheds. Consequently, we conducted a study designed to quantify the spatial and temporal dynamics of trace metals and other water chemistry variables across a range of mining impairment. Water chemistry was monitored every three weeks in 34 stream segments of the lower Cheat River basin in northeastern West Virginia. Water sampling was conducted regardless of flow levels over a period from May 2002 – October 2003 and produced data on spatial and temporal variation in water temperature, dissolved oxygen, pH, conductivity, alkalinity, acidity, hardness, total dissolved solids, and dissolved concentrations of sulfates, iron, aluminum, manganese, cadmium, chromium, and nickel. Our study produced the following results. 1) Water chemistry was temporally variable in all streams examined; however, variability was generally highest in the moderately impaired streams. 2) Severely impaired waterbodies experienced poorest water quality during periods of extended low flows, whereas moderately impaired streams experienced poorest water quality under a variety of moderate and high flow conditions. 3) Elevated trace metal concentrations (chronic and acute) were common in moderately impaired streams and may provide an explanation for biological degradation in these streams. Our results suggest that water samples must be taken during late winter and late summer seasons in order to properly quantify chemical conditions in moderately impaired streams. Furthermore, full restoration of mining impacted watersheds may not be possible unless remediation approaches target reductions in trace metals and control temporal variability in water quality.

Additional Key Words: acid mine drainage, aquatic chemistry, coal mining, streams, trace metals

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Introduction

There is a critical need for restoration action and more effective watershed management approaches in the Mid-Atlantic Highlands (MAH) region of the eastern U.S. (Jones et al. 1997). The MAH consists of the mountainous portions of Pennsylvania, Maryland, Virginia, and Kentucky, and the entire state of West Virginia. A recent assessment by the USEPA of stream ecological condition in the MAH found that more than 70% of streams are severely or moderately impaired by human related stressors (USEPA 2000a). Impairment to aquatic communities in this region extends from a range of human related activities, including agriculture, forestry, and urban development, but mining related impacts are unquestionably the most severe. For example acid mine drainage (AMD) from abandoned mines has degraded hundreds of miles of streams in West Virginia alone.

Several recent scientific advances and policy directives have improved the likelihood of effectively managing mining impacted watersheds in this region. First, the West Virginia Division of Environmental Protection (WVDEP) has worked in cooperation with the USEPA to conduct watershed assessments and develop Total Maximum Daily Load (TMDL) programs for AMD impacted watersheds throughout the state (WVDEP 1999, USEPA 2000b). The successful implementation of these programs would dramatically improve surface water chemistry and ecological integrity of aquatic ecosystems in the state. Second, the WV state legislature recently passed a stream Anti-Degradation policy, which theoretically will protect remaining high quality aquatic resources in the region. Third, West Virginia, with support from the USEPA, industry representatives, and local watershed organizations is exploring the feasibility of developing watershed specific and statewide water quality trading programs. If successful, the trading program could facilitate implementation of TMDL plans, produce significant improvements in water quality, and reduce the economic burden of meeting clean water goals in the region.

Despite these advances, our understanding of the fundamental physical, chemical, and biological processes in mined Appalachian watersheds remains incomplete. Most importantly, we lack a clear understanding of water quality variability in AMD impacted watersheds and how this variability may ultimately influence stream ecological condition. An understanding of the dynamics of metals and other solutes from mine drainage is essential to the successful management and remediation efforts in mined Appalachian watersheds. Consequently, the specific objectives of our study were to: 1) quantify temporal variability in dissolved metals and other solutes within the lower Cheat River watershed, 2) identify the timing of worst water quality conditions in moderately and severely impacted streams, and 3) quantify spatio-temporal variability in trace metal concentrations and assess the likelihood that trace metals may be causing significant biological degradation in this watershed.

Methods

Study Area and Sampling Design

The Cheat River is part of the upper Ohio River basin and is formed by the confluence of the Shavers Fork and Black Fork in Parsons, WV. From this confluence, the Cheat River flows 135 km north to Point Marion, PA, where it enters the Monongahela River. The Cheat River drains a watershed of approximately 3,700 km^2, and is located almost entirely within north-central West Virginia. The economy in the northern portion of the watershed has been dominated by coal mining over the last century, and as a result, many streams in the lower Cheat River watershed have been degraded by acid mine drainage discharged from abandoned mines (Williams et al. 1999).

Sampling sites in this study were chosen based on their expected level of impairment from acid mine drainage. Thirty-four sites were chosen on 14 tributaries of the lower Cheat River: five sites were chosen as unimpaired reference sites (i.e., stream segments that drain watersheds without any mining activity), four sites were chosen as severely impaired sites (i.e., sites with extremely high acidity levels), and the remaining 25 sites were selected across a range from low to moderately high acidity levels. For brevity we refer to each group of sites as unimpaired, severely impaired, and moderately impaired, respectively.

Field Sampling

We sampled all study sites every three weeks, beginning May 2002 and ending May 2003. Water samples were taken regardless of flow level. Each sampling event generally spanned 2-3 consecutive days. We used area-velocity techniques to calculate stream flow (m^3/s) at each site at the time water sampling occurred. Daily variation in stream flow was also monitored at a single location (Big Sandy Creek) for the entire study period in order to document general flow conditions in the lower Cheat River watershed. Temperature (C), pH, specific conductivity, dissolved oxygen (mg/L), and total dissolved solids (mg/L) were measured on site using a YSI 650 unit with a 600XL sonde. At each site, two water samples were collected. A 500 mL water sample was filtered using a Nalgene polysulfone filter holder and receiver, using mixed cellulose ester membrane disc filters with a 0.45 μm pore size. Filtered samples were immediately treated with 5 mL 1:1 nitric acid to bring the pH below 2. This acidification prevented dissolved metals from dropping out of solution prior to analysis. These filtered water samples were used for analysis of aluminum, iron, manganese, nickel, cadmium, chromium, and hardness (mg/L). An unfiltered 1-liter grab sample was also collected for analysis of alkalinity, acidity, and sulfates. Unfiltered samples were kept on ice after collection, and stored in the laboratory at 4^{o} until analysis could be completed.

Laboratory Analysis

All samples were analyzed at Black Rocks Test Lab in Morgantown, WV, using procedures from the 18^{th} edition of Standard Methods for the Examination of Water and Wastewater (Clesceri et al. 1992). Acidity and alkalinity as $CaCo_3$ were determined using the titration method (methods 2310 and 2320B, respectively). Sulfate was determined using the turbidimetric method (method 426C). Iron, manganese, nickel, cadmium and chromium were analyzed with an AAS (atomic absorption spectrophotometer) using method 3111B. Aluminum was analyzed using an AAS, using method 3111D. Hardness as $CaCo_3$ (SM18-2340B) was measured using an AAS, using calculations from method 3111B.

Our statistical analyses were directed towards describing the degree of water quality variability, the timing of worst chemical conditions, the quantity and types and dynamics of dissolved trace metals and differences in water chemistry dynamics between severely impaired and moderately impaired streams. We used coefficients of variability (CV) of each water quality parameter as a measure of temporal variability in water chemistry in reference and impaired streams.

Results

Streams in the lower Cheat basin experienced significant day-to-day and seasonal variation in stream flow (Fig. 1). Discharge patterns could be separated into three distinct phases. Phase 1 was a relatively wet Spring in April and May 2002. Phase 2 consisted of a prolonged dry period from June – October 2002. This dry period was then followed by an unusually wet Fall 2002 and Winter 2003 (Phase 3) (Fig. 1). These alternating wet and dry periods provided a good opportunity to quantify changes in stream chemistry across a variety of hydrologic conditions.

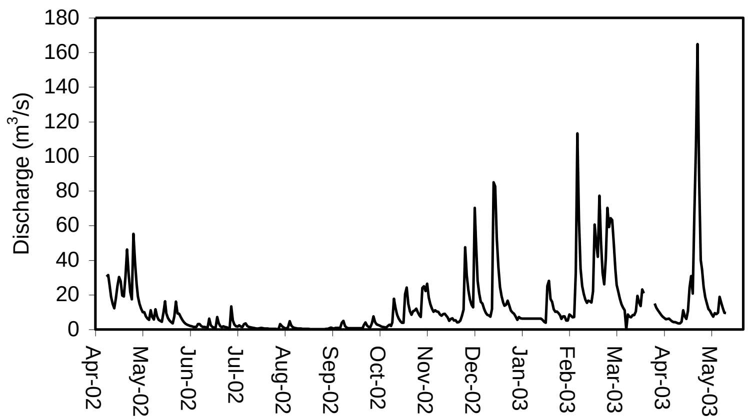


Figure 1. Daily mean discharge during the course of the study. Discharge was gaged continuously on Big Sandy Creek at Rockville, WV (USGS 03070500).

Each stream segment was sampled 17 times over the course of the one year study resulting in a total of 578 samples. Although water chemistry was highly variable, we observed consistent differences in chemical conditions among unimpaired, moderately impaired, and severely impaired stream segments (Table 1). Specifically, unimpaired streams tended to possess the following characteristics relative to moderately and severely impaired segments: higher pH, lower conductivity, higher alkalinity, lower acidity and sulfate concentration, and lower concentrations of dissolved metals (Table 1). Interestingly, differences in dissolved iron and aluminum concentrations between unimpaired and moderately impaired streams were minor (e.g. mean iron concentrations were 0.18 mg/L in unimpaired streams vs. 0.22 mg/L in moderately impaired streams). However, trace metal concentrations (i.e., Mn, Ni, Cd, and Cr) differed between the two stream types by an order of magnitude (Table 1).

Table 1. Summary statistics for water chemistry variables from unimpaired, moderately impaired, and severely impaired stream segments. Mean values were calculated across all sample dates. Avg. CV refers to the average variability of stream segments within each category. The higher the value the more highly variable water chemistry was from sample date to sample date.

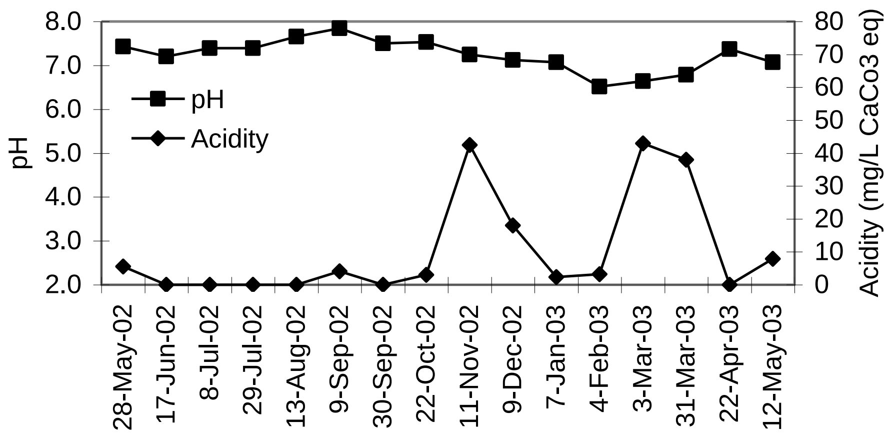
	Unimpaired			Moderately Impaired			Severely Impaired		
	Mean	Range	Avg. CV	Mean	Range	Avg. CV	Mean	Range	Avg. CV
pH	7.2	7.0 - 7.4	7	6.3	4.1 – 7.0	8	3.3	2.7 - 3.9	10
Temperature (^{0}C)	11.5	10.6 - 12.5	7	11.0	10.2 - 14.4	8	9.7	8.1 - 10.4	11
Sp. Conductivity (µS/cm)	103	71 - 154	32	198	35 - 527	53	1222	747 - 1757	38
Total Hardness (mg/L)	29.7	19.1 - 43.9	31	47.8	10.7 - 122.7	50	158.1	100.8 - 261.1	45
Alkalinity (mg/L $CaCO_3$ eq.)	24.7	15.7 - 36.4	40	11.1	0.0 - 25.6	75	0.0	0.0 - 0.0	.
Acidity (mg/L $CaCO_3$ eq.)	6.7	3.5 - 10.5	203	20.5	8.3 - 44.7	105	272.1	130.2 - 460.0	64
Sulfate (mg/L)	16.2	9.1 - 41.5	88	65.9	11.5 - 225.8	68	608.6	363.1 - 908.8	43
Iron (mg/L)	0.18	0.11 - 0.27	104	0.22	0.09 - 0.44	117	24.19	5.27 - 58.47	73
Aluminum (mg/L)	0.15	0.12 - 0.17	66	0.55	0.12 - 2.80	82	17.34	8.51 - 31.77	73
Cadmium (mg/L)	0.0014	0.0012 - 0.0016	74	0.0020	0.0010 - 0.0052	108	0.0029	0.0024 - 0.0038	67
Chromium (mg/L)	0.0009	0.0006 - 0.0012	100	0.0017	0.0006 - 0.0064	117	0.0073	0.0036 - 0.0146	75
Manganese (mg/L)	0.027	0.015 - 0.035	97	0.335	0.045 - 1.645	77	3.752	1.564 - 8.232	58
Nickel (mg/L)	0.009	0.008 - 0.010	87	0.022	0.009 - 0.083	73	0.240	0.147 - 0.390	60

Water Quality Variability

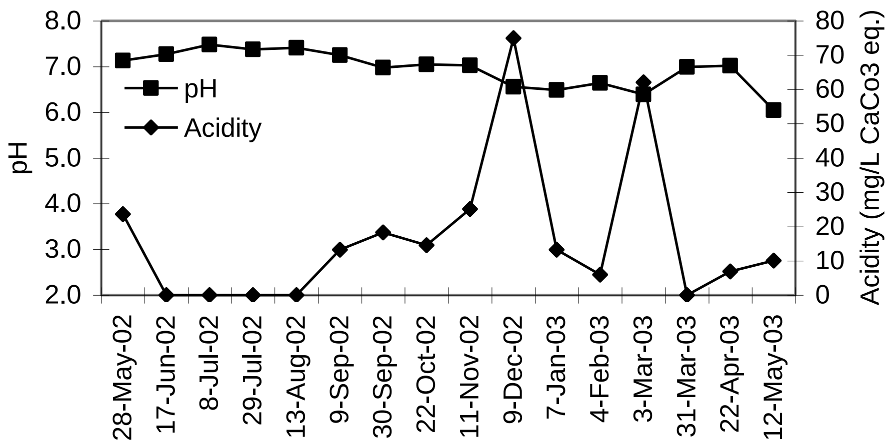
The primary objective of our study was to quantify the degree of temporal variability in water quality in streams of the lower Cheat River watershed. Our analyses indicated that chemical conditions were highly variable in all streams studied, regardless of relative impairment level. Figures 2 – 4 illustrate the typical range of chemical variability in the three stream types examined: unimpaired, moderately impaired and severely impaired. Two important findings emerge from these graphs. First, unimpaired and moderately impaired streams possessed good water quality for most of the year and variability was marked by pulses of poor chemical condition (Fig. 2-4). This was especially true for acidity and dissolved aluminum and iron during periods of increased stream flow (Fig. 2 and 3). In contrast, water chemistry in severely impaired streams tended to remain poor for most of the year and variability was marked by pulses of improved chemical condition, probably as a result of dilution from precipitation events (Fig. 2-4). Second, unimpaired and moderately impaired streams exhibited similar water chemistry dynamics for pH, acidity, aluminum and iron (Fig. 2 and 3). However, unimpaired and moderately impaired streams consistently displayed measurable differences in the dynamics of manganese and trace metals such as nickel (Fig. 4). Specifically, dissolved manganese and trace metal concentrations in unimpaired streams remained low throughout the year. However, chronic levels of manganese persisted throughout the year, and episodic doses of trace metals were common in moderately impaired streams (Fig. 4).

The degree of temporal variability in water chemistry varied as a function of stream type (i.e., unimpaired, moderately impaired, and severely impaired) and depended on the chemical parameter of interest. Generally, we found that temporal variability in condition was highest in the moderately impaired streams and lowest in unimpaired and severely impaired streams (Fig. 5 and 6). This pattern was especially true for trace metals such as cadmium and chromium (Fig. 6). The only exception to this rule was for acidity for which unimpaired streams exhibited the greatest amount of temporal variability (Fig. 5). The low temporal variability in water chemistry observed in unimpaired streams indicates that these streams possess good water quality under most flow conditions. Likewise, low variability in severely impaired streams indicates that these streams typically possess very poor water quality. In contrast, the moderately impaired streams alternate between good and poor water quality, resulting in a high lever of temporal variability in chemical conditions.

A. Roaring Creek 1



B. Muddy Creek 4



C. Martin Creek

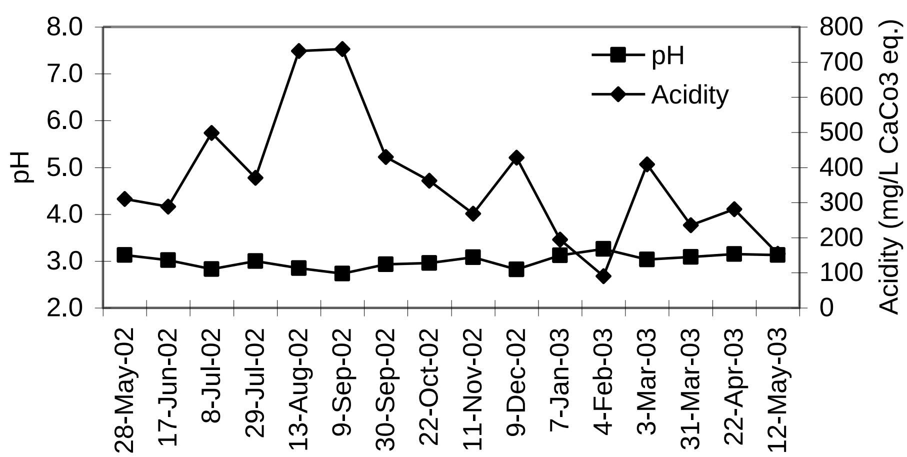
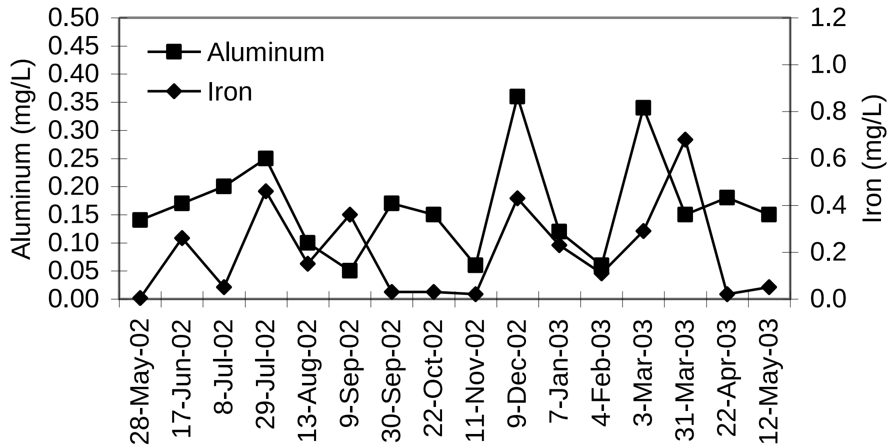


Figure 2. Variability in pH and Acidity within an unimpaired (A), a moderately impaired (B), and a severely impaired (C) stream segment of the lower Cheat River watershed.

A. Roaring Creek 1



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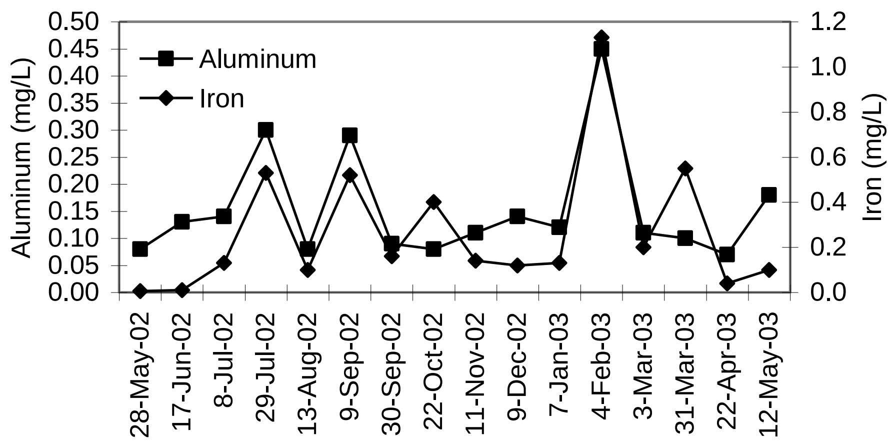

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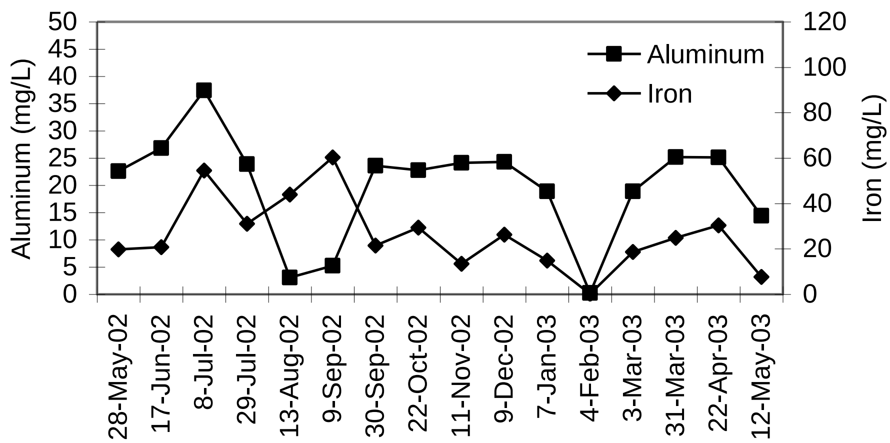
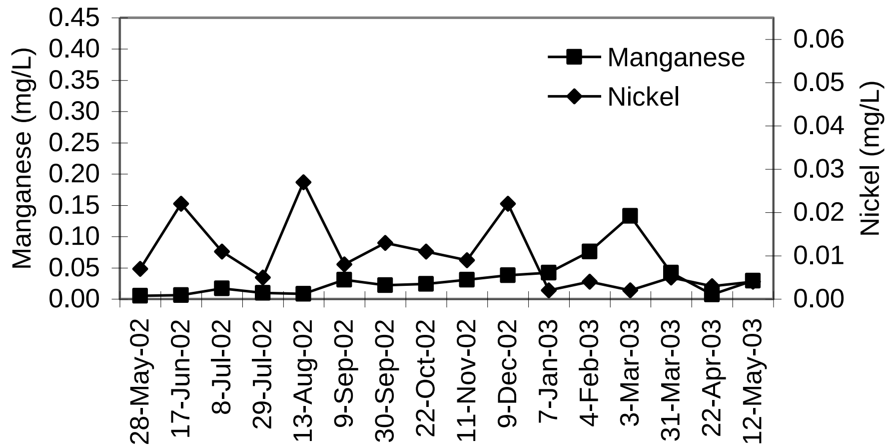
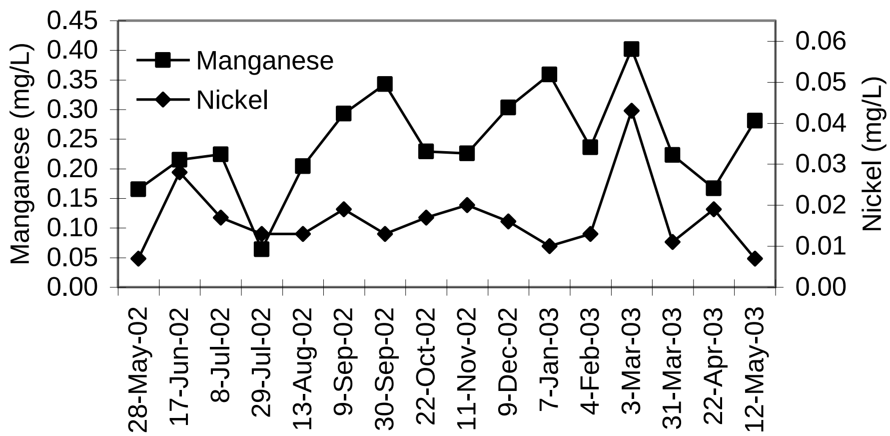


Figure 3. Variability in dissolved Aluminum and Iron concentrations within an unimpaired (A), a moderately impaired (B), and a severely impaired (C) stream segment of the lower Cheat River watershed.

A. Roaring Creek 1



B. Muddy Creek 4



C. Martin Creek

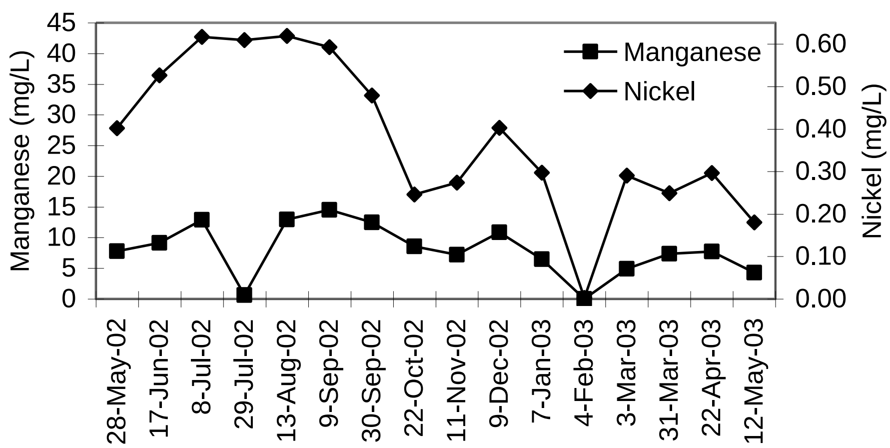


Figure 4. Variability in dissolved Manganese and Nickel concentrations within an unimpaired (A), a moderately impaired (B), and a severely impaired (C) stream segment of the lower Cheat River watershed.

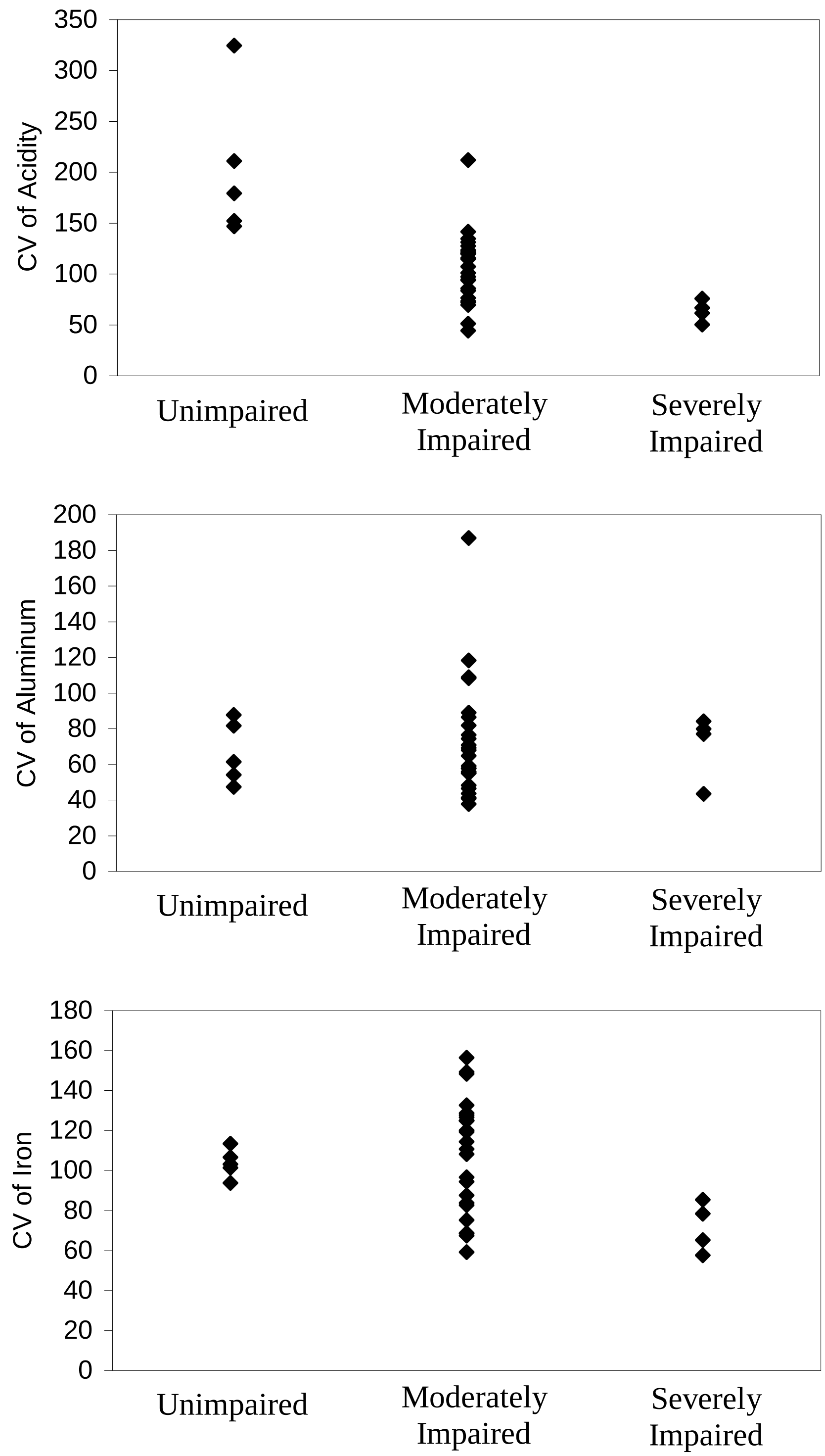


Figure 5. Temporal variability in acidity and dissolved aluminum and iron concentrations within unimpaired, moderately impaired, and severely impaired stream segments of the lower Cheat River watershed. Each symbol represents a relative measure of day-to-day variability in water chemistry at a specific study site.

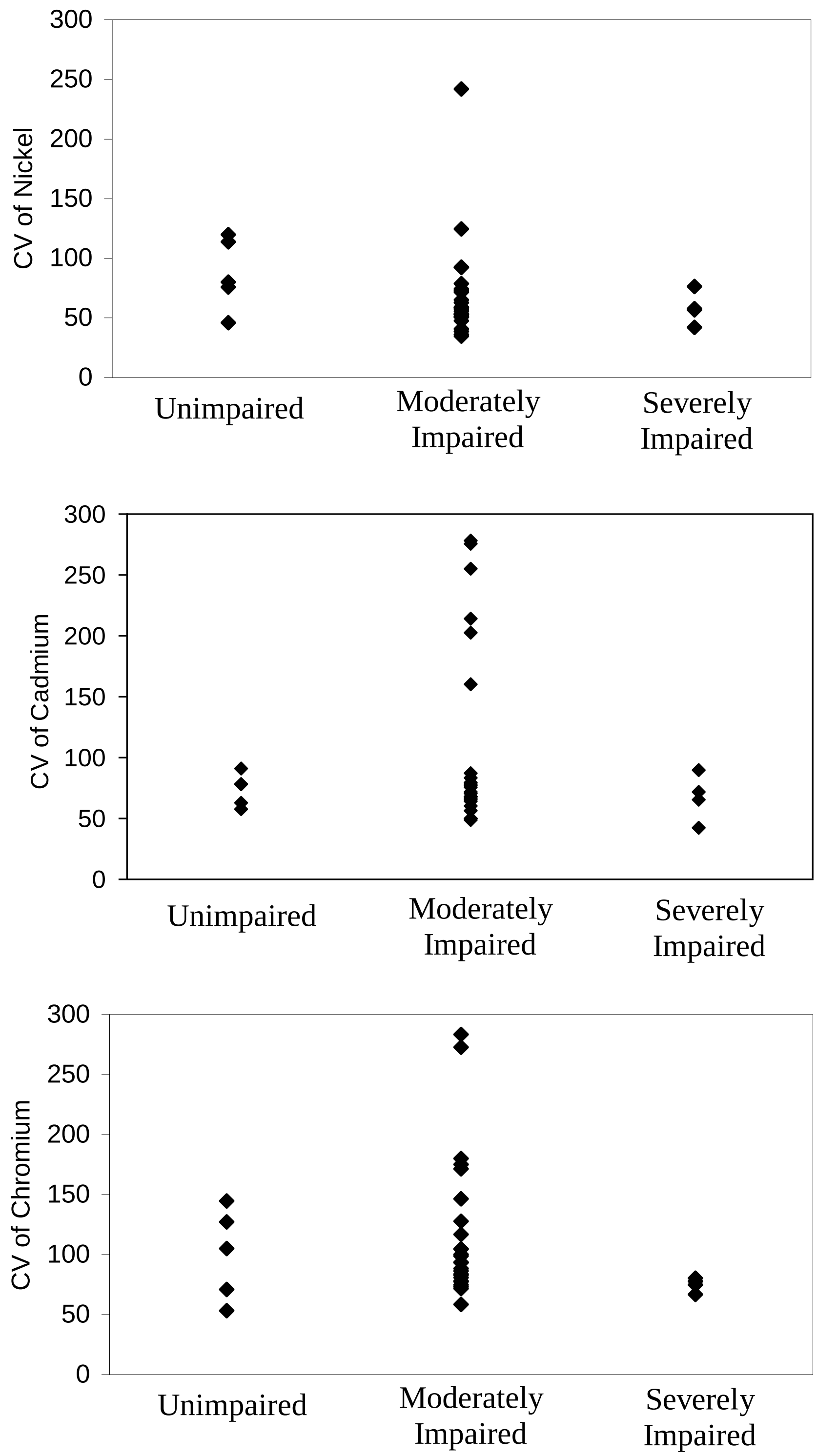


Figure 6. Temporal variability in dissolved trace metal concentrations within unimpaired, moderately impaired, and severely impaired stream segments of the lower Cheat River watershed. Each symbol represents a relative measure of day-to-day variability in water chemistry at a specific study site.

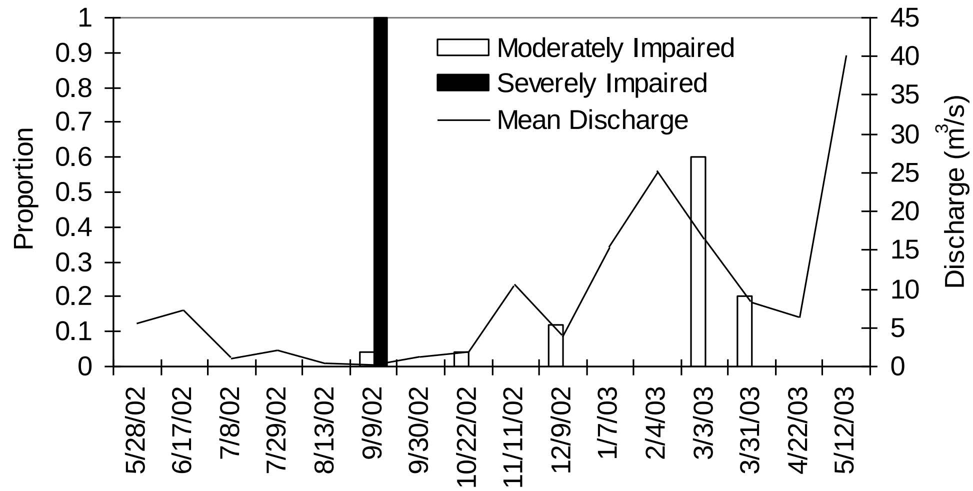
Timing of Worst Water Quality Conditions

Our second objective was to identify times during the year in which water quality was at its worst in moderately and severely impaired streams of the Cheat River watershed. To do this, we identified the sampling date for which a given parameter for a given stream was at its worst condition (e.g., date of minimum pH recorded or date of maximum acidity recorded). We then calculated the proportion of streams for which the parameter was at its worst for each sampling date and constructed frequency histograms for each water quality parameter separately and for all parameters combined. These analyses determined that severely impaired streams were consistently at their worst during prolonged periods of low flow in summer months (Fig. 7 and 8). This pattern was true for all parameters examined. In contrast, we found that conditions in moderately impaired streams typically were at their worst during high flow periods in winter and early spring. This was especially true for parameters such as acidity and iron concentration (Fig. 7). However, there was considerable variation in the timing of worst conditions in moderately impaired streams depending on the parameter examined. For example, maximum nickel concentrations were recorded during dry periods in some streams and during wet periods in others (Fig. 8a). When all parameters were combined, we found that the timing of worst conditions in moderately impaired streams was bimodal: some streams exhibited their worst conditions during dry periods in summer, whereas other streams exhibited poorest conditions during wet periods in winter and early spring (Fig. 8b).

Trace Metal Concentrations

Our third objective was to quantify the spatial and temporal dynamics of trace metal concentrations in streams of the lower Cheat River watershed. We observed significant levels of spatial and temporal variability in dissolved trace metal concentrations. Concentrations of dissolved trace metals were always low in unimpaired streams (Fig. 9). However, trace metal concentrations in moderately and severely impaired streams were extremely variable, with some streams possessing very low concentrations and other streams experiencing significant pulses of dissolved trace metal loads (Fig. 9). Two important results emerged from our analyses of trace metal concentrations. First, many of the highest concentrations of dissolved cadmium and chromium were observed in moderately impaired streams rather than severely impaired streams (Fig. 9). Second, most streams did not possess high concentrations of all trace metals. Instead, some streams possessed high concentrations of cadmium, whereas others possessed high concentrations of chromium (Fig. 9).

A. Acidity



B. Iron Concentration

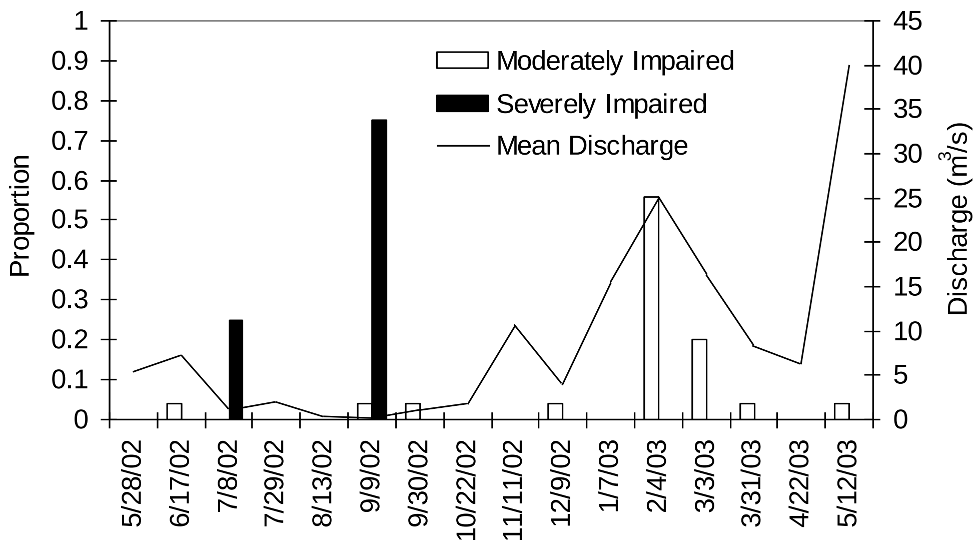
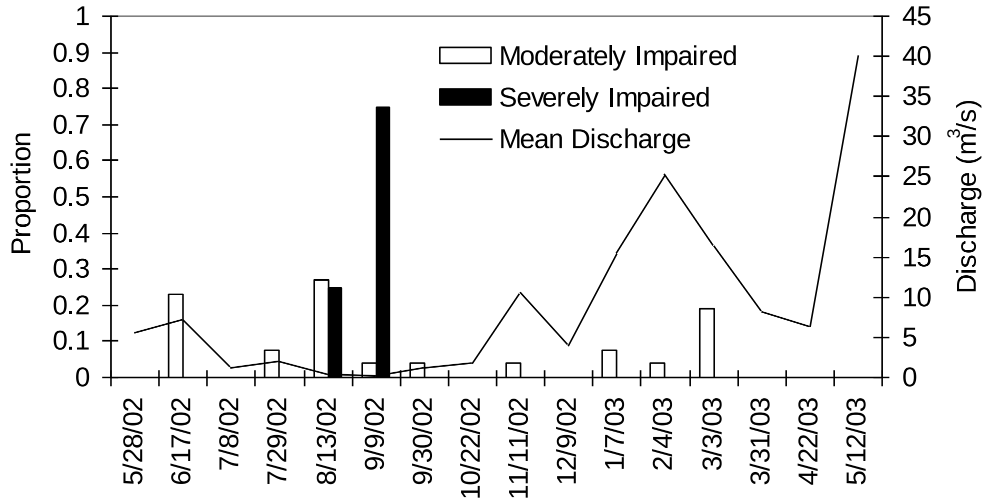


Figure 7. Proportion of streams for which the maximum acidity (A) and iron concentration (B) was recorded on a given date. Data are presented separately for severely impaired and moderately impaired streams. Daily mean discharge recorded on Big Sandy Creek also is presented.

A. Nickel Concentration



B. All Parameters Combined

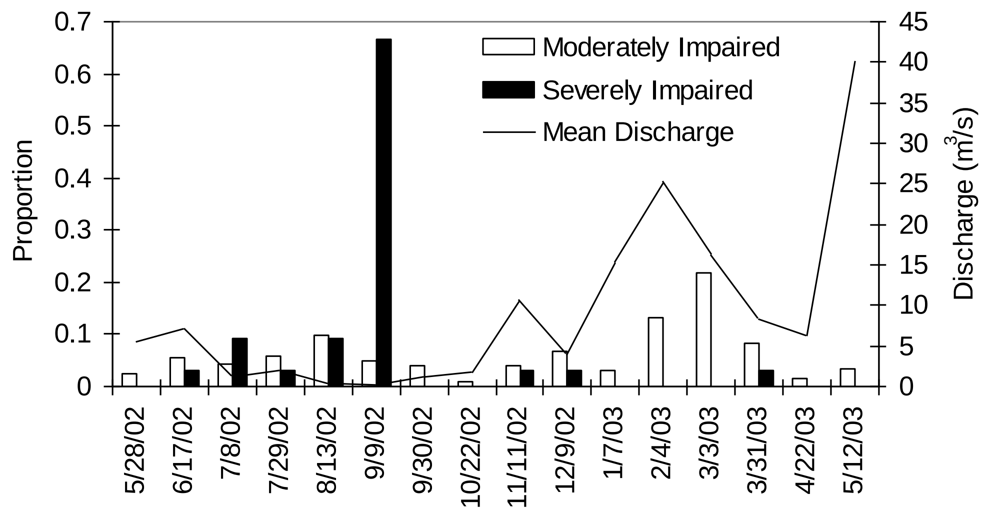


Figure 8. Proportion of streams for which the maximum nickel concentration (A) and minimum or maximum value of all parameters combined (B) was recorded on a given date. Data are presented separately for severely impaired and moderately impaired streams. Daily mean discharge recorded on Big Sandy Creek also is presented.

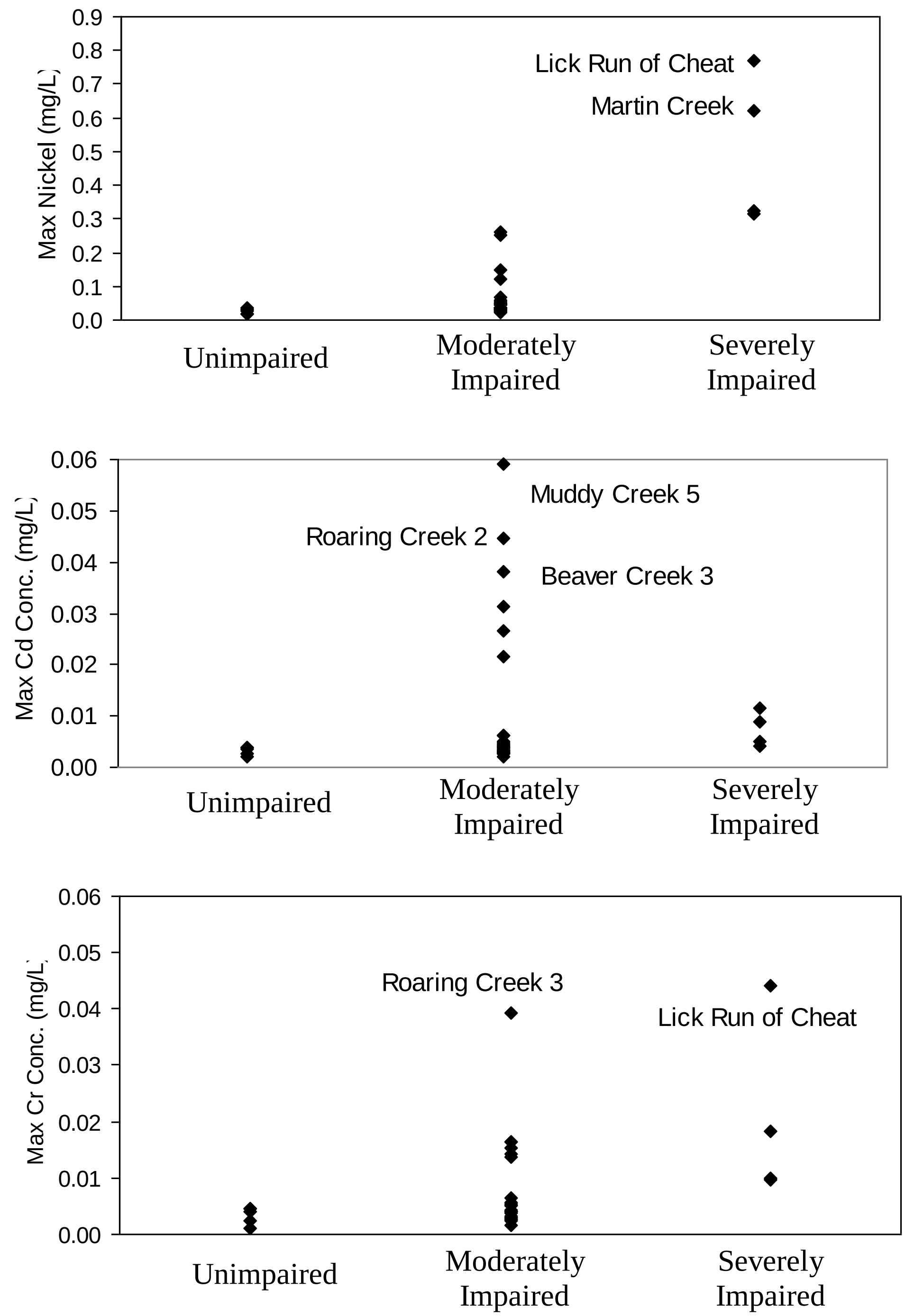


Figure 9. Maximum recorded dissolved concentrations of trace metals from unimpaired, moderately impaired, and severely impaired streams of the lower Cheat River watershed. Names of stream segments with relatively high trace metal concentrations are shown. Note that many of the highest cadmium and chromium concentrations were observed in moderately impaired streams.

Discussion

Water chemistry was extremely variable in streams of the lower Cheat River watershed. Although this was true for all stream types examined, temporal variability in chemical condition was highest in the moderately impaired streams. Several factors influence spatial and temporal variability in water chemistry in streams that receive AMD. This variation results from both hydrologic inputs and instream processes (McKnight and Bencala 1990, Sullivan and Drever 2001). Hydrologic inputs can originate from precipitation, direct overland flow, subsurface flow through shallow soils, drainage from shallow and deep aquifers, as well as direct inputs from flooded deep mines. Instream processes include dilution, acid neutralization, metal release and adsorption from sediments, as well as precipitation and coprecipitation (Nordstrom and Ball 1986, McKnight and Bencala 1990, Jurjovec et al. 2002).

Water quality variability was lowest in the unimpaired streams. The variability that was observed resulted from elevated acidity from precipitation events. However, because these streams were moderately alkaline, pH remained high (i.e., >6.5), and dissolved metals remained at very low concentrations. Consequently, brief doses of elevated acidity are unlikely to have a significant effect on the overall condition of unimpaired streams. Water quality variability also was relatively low in severely impaired streams, but for different reasons. Most of the water in severely impaired streams originates from flooded deep mines. The effluent from these mines has extremely low pH (2-3) and high concentrations of dissolved metals. Because these inputs are relatively constant, instream conditions are almost always poor. Occasionally, however, large precipitation events or snow melt will dilute AMD and severely impaired streams will experience brief periods of relatively good water quality. Moderately impaired streams in the lower Cheat River watershed possessed much more variable water chemistry than either the severely impaired or unimpaired streams. There are several possible reasons for this variability. First, these streams possess a much lower alkalinity than unimpaired streams. Therefore, they are more likely to be impacted by acid precipitation events. Second, pH in these streams was depressed and more likely to move between 4.5 and 6.5. At this level, many metals move between conservative and non-conservative behavior resulting in dramatic variability in dissolved metal concentrations.

The high variability in trace metal concentrations that we observed in moderately impaired streams was particularly interesting. It is also interesting that some of the highest concentrations of dissolved cadmium and chromium were observed in moderately impaired rather than severely impaired streams. A possible explanation for these findings is that moderately impaired streams are receiving large inputs of trace metals from disturbed acidic soils in the surrounding watershed. During wet periods when vegetation is dormant, acidic soil water and water in shallow aquifers may mobilize trace metals and deliver them to the moderately impaired streams. A poorly understood component of trace metal dynamics in the Cheat River watershed is the interaction between trace metals, sediments, and aluminum and iron precipitates. Trace metals are often removed from the water column during mixing by either adsorption to sediment particles such as clay or coprecipitation with aluminum and iron precipitates (Routh and Ikramuddin 1996, Jurjovec et al. 2002). These trace element complexes remain immobilized in the sediment and are only released when the pH decreases. Dissolved trace metal concentrations may be higher in moderately impaired streams than severely impaired streams because there is less iron and aluminum precipitate. Consequently, coprecipitation of trace metals may occur at a lower rate resulting in higher dissolved trace metal concentrations in the moderately impaired streams. Regardless of the mechanisms controlling trace metal dynamics, a more complete understanding of trace metal / sediment / precipitate interactions in the Cheat River watershed is needed.

Our results support numerous studies that have found that severely impaired streams in mined watersheds experience worst conditions during low flow periods (Filipek et al. 1987, Brake et al. 2001, Sulliven and Drever 2001). During these periods, severely impaired streams are dominated by mine water because surrounding soils and shallow aquifers are dry. To our knowledge, our study is one of the first to examine temporal variability in water chemistry across a wide range of moderately impaired streams. In contrast to the severely impaired streams, many of the moderately impaired streams experience their best conditions at low flows and their worst conditions during high flows. This pattern suggests that the dominant sources of impairment to moderately impaired streams come from surface mines and/or disturbed shallow aquifers. During dry periods, soils and shallow aquifers are dry and deeper, alkaline aquifers are the dominant water source to these streams. During wet periods, however, the shallow water sources become saturated and supply water to streams, especially in winter and early spring. It may be at this time that moderately impaired streams are receiving the highest loads of acidity and dissolved metals from the surrounding watershed. It also may be a time when trace metals are being released from the sediments because of lowered pH.

Management Implications

Our results produced two important management implications for mined watersheds. First, our results indicate that water samples taken during dry periods will accurately characterize chemical conditions in severely impaired streams, but not in moderately impaired streams. This is important, because most streams segments in the Cheat Watershed are moderately impaired, rather than severely impaired (WVDEP 1999). Consequently, effective monitoring of these watersheds will require a sampling regime that is most likely to effectively characterize both moderately and severely impaired waterbodies. Our results indicate that water quality monitoring programs must quantify surface water chemistry during both dry and wet periods. Moderately impaired streams exhibit their poorest conditions during moderately wet periods in winter and early spring when terrestrial vegetation is dormant and soils and shallow aquifers are saturated. Second, we believe that effective restoration of mined watersheds will need to consider how to manage water quality variability and trace metal concentrations. Our results suggest that water quality variability and trace metals are probably the most important factors limiting the overall condition of moderately impaired streams. Without proper management of variability and trace metals we may never fully restore AMD impacted ecosystems.

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