CHARACTERIZATION AND LEACH TEST ASSESSMENT AT THE TIP TOP MINE, A MARGINALLY IMPACTED SITE[1]

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Abstract: The Tip Top Mine in Gamble Gulch, Colorado is a high mountain site where the stream above the mine is pristine and below the influx of acid rock drainage, the aquatic ecosystem appears to be impacted. An aquatic toxicity assessment study was carried out to determine the impact of contaminants on the stream and to test the leaching methods and simple toxicity tests that have been developed at the Colorado School of Mines. All tests show that the stream water above the adit inflow is pristine. However, the stream below shows concentrations of Al, Cu and Zn that are slightly above acute aquatic toxicity limits. Leaching tests on stream sediment samples taken below the adit entrance show concentrations of contaminants that are on the borderline of being toxic. Physical and chemical assessments of the mine waste piles on the site show that they are not impairing the immediate vicinity or the stream. It appears that the cause of any aquatic toxicity is the adit water entering the gulch or the heavy oxyhydroxide precipitates lining the streambed below the mine site.

Additional Key Words: metal contamination, mine wastes, contaminated soils and sediments, toxicity testing

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Introduction

Recently, a simple method for the assessment of mine waste piles has been developed (Wildeman, et al., 2002; Hageman and Briggs, 2000). The method has been used on marginally impacted sites (Bazin, et al. 2003) to determine how well decisions on whether or not to remediate can be made. Also, regions with many mine waste piles have been assessed to determine prioritization of site cleanup (Hageman, 2004; Heflin et al., 2004). Also, scientists from the US Geological Survey (USGS) and the Colorado School of Mines (CSM) have separately sampled a mine site to determine how well sampling, preparation, and analytical methods will compare (Hageman et al., 2005). In addition, for mining impacted sites where in-vitro toxicity tests are necessary, simple enzyme bioassay tests are being studied to see how well they correlate with the traditional tests that use *Ceriodaphnia dubia.* To test how well all these assessment tools work, it was decided to find a mine site that is at the headwaters of stream basin and that appears to cause aquatic damage to the watershed, and then test out all of the assessment tools to see if they give the same indications of toxicity as those found at the mine site. The site found for this study was the Tip Top Mine in the Perigo site at the headwaters of Gamble Gulch in Colorado. In July of 2004, waters, stream sediments, and the waste rock piles at the Tip Top mine were sampled and leachate tests were conducted on the sediments and waste pile samples. This paper gives the results of the sampling and analysis at the site.

The Tip Top Mine is an abandoned metal mining site in Gamble Gulch, a perennial stream that is part of the Boulder Creek watershed. Fig. 1 is a plan view of the site showing the sampling locations. The water which continuously flows from the adit is the first spot on the gulch to cause contaminant problems in the stream. Fig. 2 and 3 show the conditions of Gamble Gulch above and below the point where the adit water enters. Below this metal mine, there are other point and non-point abandoned metal mining operations that cause contamination in the stream. In addition to the adit water, there are two waste rock piles on the site from which contaminated water could possibly flow into the gulch.

Over the last decade, efforts have been made to reduce the amount of water seeping into the mine and this has met with some success. The pH of the water has been raised from 3.3 to 3.7 and dissolved iron has dropped from 42 to 3.8 mg/L. Nevertheless, as seen in Table 1, the water coming from the adit is slightly higher in Al, Cd, Cu, Fe, Mn, and Zn than the aquatic limits for cold waters in Colorado. In the stream below the mine, Al, Cu, and Zn are still slightly above the aquatic limits.

Based on the one July 2004 visit, the mine site fits the criteria of being the first definite place on Gamble Gulch, as shown in Figures 2 and 3, where the water turns toxic to aquatic organisms. The initial phase of the study sought to answer these questions:

- Is the adit water definitely affecting the aquatic health of the stream?
- Are contaminants leached from the sediments above and below the stream possibly contributing to the toxicity?
- Could water draining from the waste rock piles on the site contribute to the aquatic toxicity found in the stream?

This paper gives the results from this sampling event and answers the above questions.

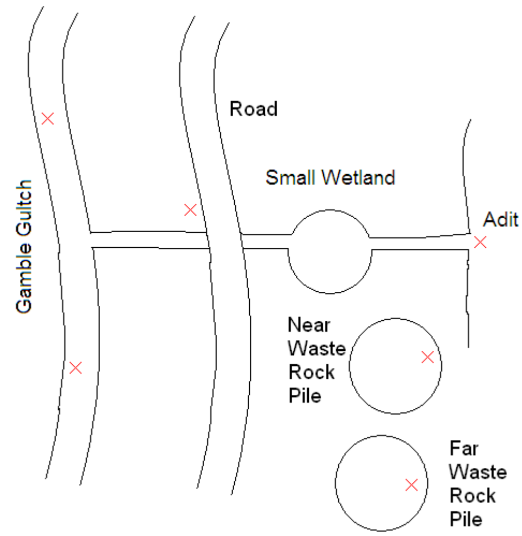

Figure 1. A plan view of the Tip Top mine site. The distances are not to scale.

Figure 2. Gamble Gulch above the inflow from Tip Top adit. Note that the streambed is filled with organic litter and small cobbles that are free of precipitates.

Figure 3. Gamble Gulch below the inflow from the Tip Top adit. Note that the streambed is completely covered with aluminum and iron oxyhydroxide precipitates.

Table 1. Concentrations of contaminants in mg/L in the waters at the Tip Top site.

Toxic & Aquatic Levels (Conc. In mg/L)
Tip Top and Gamble Gulch Waters

Element	Det. Limits	Stream Stds. Aquatic	Stream Stds. Toxic	STREAM ABOVE	ADIT WATER	ROAD WATER	STREAM BELOW
Ag	0.0014	0.00015	5	B.D.L	B.D.L	B.D.L	B.D.L
Al	0.0173	0.1		B.D.L	5.4	4.9	0.77
As	0.0610	0.05	5	B.D.L	B.D.L	B.D.L	B.D.L
Be	0.0001	0.6		B.D.L	0.002	0.002	0.000
Cd	0.0015	0.005	1	B.D.L	0.011	0.011	0.003
Cr	0.0039	0.125	10	B.D.L	B.D.L	B.D.L	B.D.L
Cu	0.0015	0.01		0.004	0.199	0.185	0.046
Fe	0.0044	1		0.156	3.8	1.4	0.24
Mn	0.0005	1		0.001	2.7	2.6	0.72
Ni	0.0035	0.2		B.D.L	0.055	0.059	0.016
Pb	0.0137	0.05	5	B.D.L	B.D.L	B.D.L	B.D.L
Se	0.0504	0.05	1	B.D.L	B.D.L	B.D.L	B.D.L
Zn	0.0013	0.1		0.048	1.65	1.66	0.48

Sampling and Analytical Methods

Sampling Methods

During the July 2004 visit, composite samples of the stream sediments above and below the point of adit inflow were taken. The method for taking a composite sample was developed by Smith et al. (2000) that calls for dividing the site into 30 sections of roughly equal area and then taking a sample from each section. In the actual securing of a composite sample, these roughly 30 equal sections are modified by what portions of the stream bed and waste pile are accessible. The study by Hageman et al. (2005) provides evidence that the elemental concentrations from leachates tests on duplicate composite samples will be within a factor of four. Water samples were taken from the gulch approximately 200 meters above and below the adit inflow. In addition the water flowing from the mine was sampled at the adit and at a point before the water flows through a culvert under a road about 100 meters from the adit and 200 meters from the gulch. For the water samples, pH, Eh, and ionic conductivity were measured in the field. If applicable, alkalinity was measured in the field using a Hach kit.

Analytical Methods

The composite waste pile samples were split and portions were used to perform leaching tests that are integral to the Assessment Decision Tree that has been devised for mine water piles (Wildeman et al., 2002). The three leachate tests are described below.

Colorado Division of Minerals and Geology (CDMG) Test This test was developed by Herron et al. (2000) of the Colorado Division of Minerals and Geology. It uses a volume basis to determine the potential for metal release from soils when exposed to natural waters. The procedure is as follows: 150 ml of whole sediment sample are placed into an 800 ml plastic beaker and 300 ml of deionized water is added. The sample is stirred vigorously for 15 seconds and then the beaker is covered with Para film. The contents are allowed to settle for 90 minutes. After this time, approximately 10 ml of leachate is filtered with a 0.45 μm syringe filter, acidified with nitric acid, and analyzed using ICP-AES. Also after 90 minutes, the pH, Eh, ionic conductivity, and alkalinity are measured on the leachate.

United States Geological Survey (USGS) Field Leach Test This test was developed by the United States Geological Survey and also determines the potential for metal release from soils when exposed to natural waters (Hageman and Briggs, 2000). However, this test uses a mass basis. 50 g of <10 mesh sediment sample are massed into a 1 L Nalgene® bottle. Approximately 1 L deionized water is added slowly so that no dust would be lost. The bottle is capped and vigorously hand shaken for 5 minutes. The contents are then allowed to settle for 10 minutes. The leachate is then filtered with a 0.45 μm syringe filter, acidified with nitric acid, and analyzed using ICP-AES. The pH of the sample is also measured after 10 minutes.

Toxicity Characteristic Leaching Procedure (TCLP) This test is a modified version of Method 1311 developed by the Environmental Protection Agency (EPA). The test as originally conceived by the EPA was to test metals mobility in landfills. Here, the test determines the mobility of metal in the presence of mildly acidic waters. It also closely approximates the carbonate mobility step that is performed in sequential leaching studies (Tessier et al., 1979). An extraction fluid is prepared by adding 5.7 ml of concentrated glacial acetic acid to 500 ml of water. 64.3 ml of 1 N NaOH is added to the solution and then the solution was brought to a volume of 1 L using deionized water. The pH of this solution should be 4.93 $\pm$ 0.05. A volume of 40 ml of this extraction fluid is added to 2.00 g of < 80 mesh sediment sample in a 125 ml Nalgene® bottle. The bottle is then agitated end over end using a rotary tumbler for 24 hours. The leachate is then filtered with a 0.45 µm syringe filter, acidified with nitric acid, and analyzed using ICP-AES.

Although the CDMG and USGS test both use deionized water, there are some notable differences. The CDMG test uses a volume basis and the USGS test a mass basis. The USGS test uses a 20:1 mass ratio of water to solid, which is the ratio used for the regulatory EPA extraction tests (USEPA, 2001). The volume ratio for the CDMG test is 2:1 of water to solid, which would normally be less than a 2:1 mass ratio. Also, in the USGS test, the water is in contact with the solid for a total of 10 minutes, while the water is in contact with the solid for 90 minutes in the CDMG test. All these procedure differences cause the CDMG test to leach more ions from the solid than the USGS test. For the modified TCLP test, there is a question of whether the acetate extraction solution should be at a pH of 3 or 5. Because this is a not a strict regulatory procedure it was decided to use a pH of 5 because the results would possibly produce a difference from the other two tests. Also, most sequential extractions procedures use an acetate solution buffered to a pH of 5 as one of the steps (Tessier et al., 1979).

Elemental Analyses At CSM, the water samples and the leachate solutions are analyzed for elemental concentrations using ICP-AES. Approximately 10 ml of filtered sample, acidified with nitric acid, is required. The samples are then analyzed on a Perkin Elmer Optima 3000 ICP-AES for the following 31 elements: Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, Sb, Se, Si, Sn, Sr, Ti, V, and Zn. All concentration results are given in mg/L. During the ICP-AES analysis, an internal standard of Sc is used to correct for adjustments in sample uptake and plasma conditions. Also, concentration check standards are analyzed in the beginning and after every 20 samples to monitor the stability of all analytical conditions. Results on collocated water samples show the relative standard deviation of a concentration value is about 5 % as long as the concentration is 10 times the limit of detection. Thus, even though the Excel tables often show many significant figures, the results are good to 2 or maybe 3 significant figures.

Results

Figures 4-7 use Element Concentration Pattern Graphs (ECPG) to compare the concentrations of elements in the leachates and various waters. The ECPG uses the analytical power of the ICP-AES so that 13 elements make up the graph and this establishment of a pattern helps to corroborate the concentrations of important contaminants. For the ECPG, the concentrations are plotted on a logarithmic scale so that relative differences in concentrations among samples can be better determined even if the values are relatively low. Then, the order of elements is standardized so that correlations can be better established. The x-axis order of elements is as follows:

1. Na, K, and S: These are readily soluble elements and should correlate best among the samples. Note this assumes that the sulfur species in the water is primarily sulfate.

2. Ca, Mg, and Sr: Carbonate minerals could control the concentrations of these elements if these were present in the sediment/water system.
3. Pb, Cu, Zn and Ni: Either sulfide minerals or carbonate minerals could control the concentrations of these elements if these were present in the sediment/water system.
4. Fe, Mn, and Al: Oxide minerals could control the concentrations of these elements if these sedimentary minerals were present in the sediment/water system.

The concentrations of the elements in the stream waters, the adit water, and the water from the adit at the road 100 meters from the adit at the Tip Top site are given in Table 1 and Fig. 4 is the ECPG of these waters. All values are in mg/L. Fig. 5, 6, and 7, are ECPG's of solutions from leachate tests conducted on three of the composite samples taken from the site:

- Sediment from Gamble Gulch above the inflow of the Tip Tip mine water (Fig. 5).
- Sediment from Gamble Gulch below the inflow of the Tip Top mine water (Fig. 6).
- Composite sample of the surface of the waste rock pile that is furthest from the Tip Top Adit (Fig. 7).

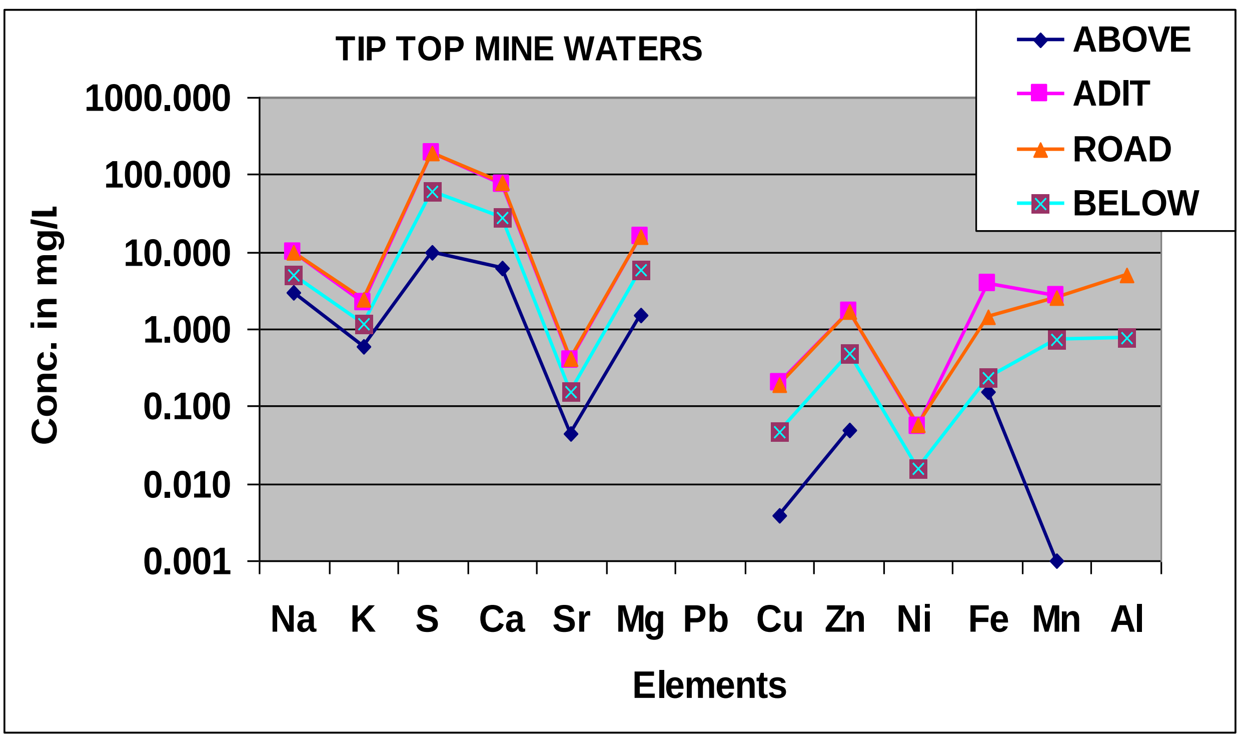

Figure 4. Element Concentration Pattern Graph for the stream waters, the adit water, and the water from the adit at the road 100 meters from the adit at the Tip Top site.

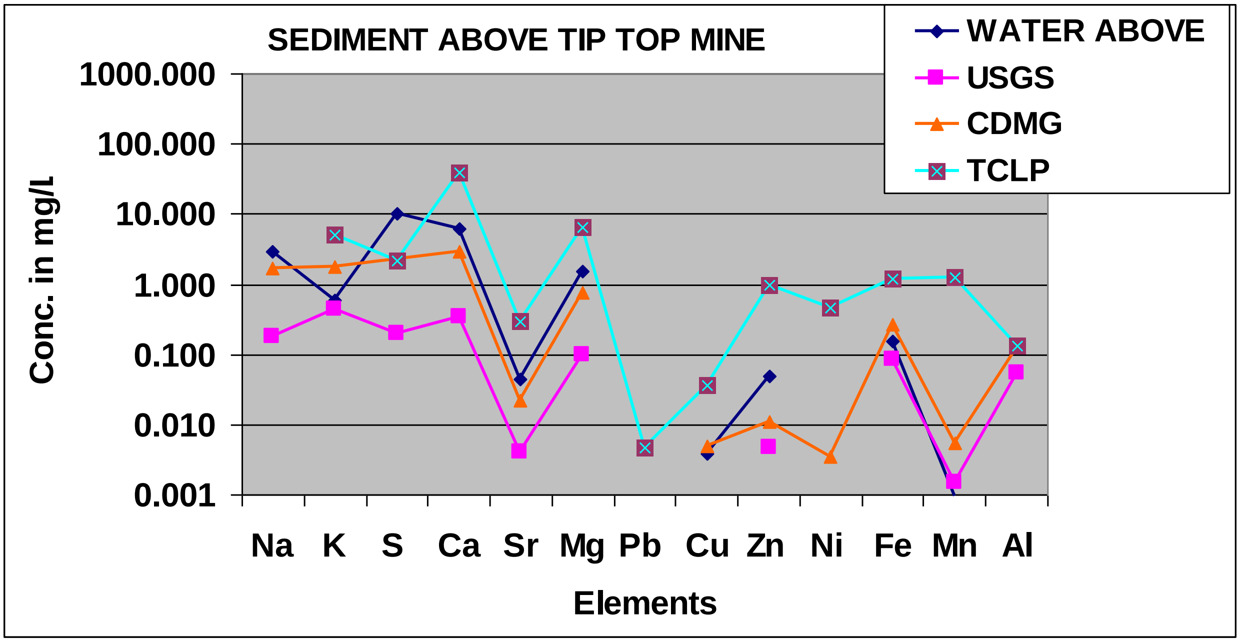

Figure 5. Element Concentration Pattern Graph for the solutions from the three leachate tests for the sediment in Gamble Gulch above the inflow of the Tip Top adit water.

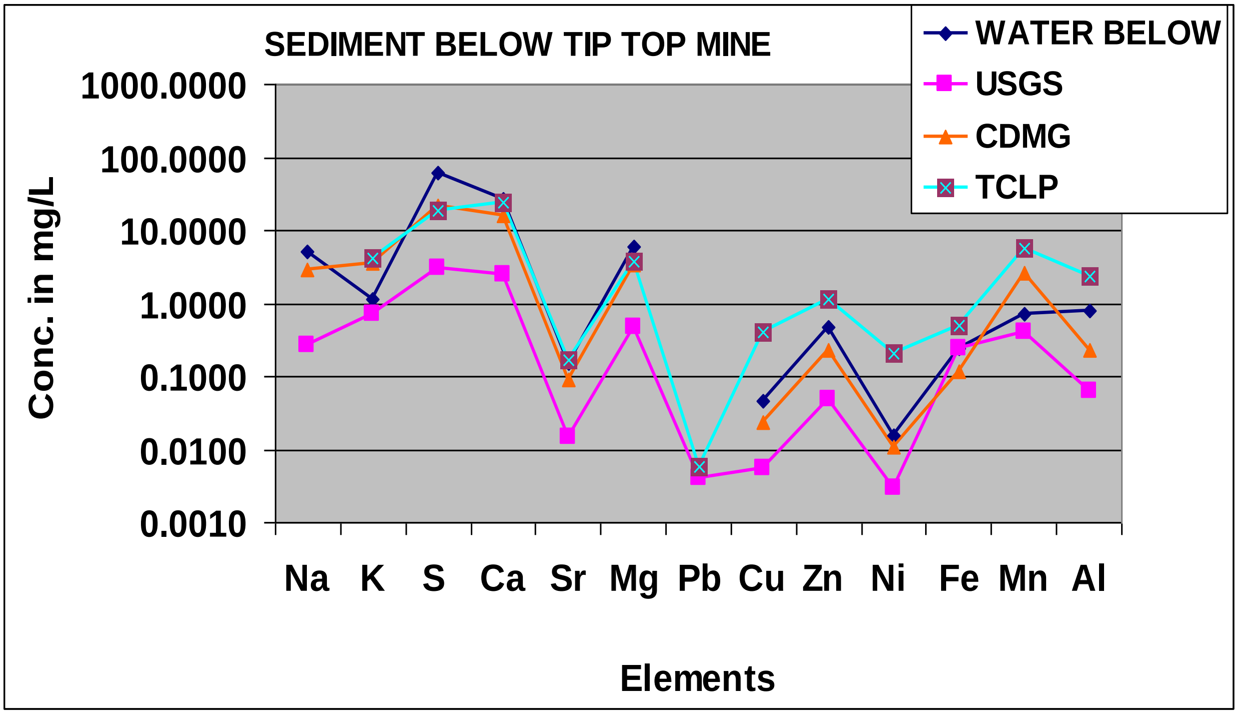

Figure 6. Element Concentration Pattern Graph for the solutions from the three leachate tests for the sediment in Gamble Gulch below the inflow of the Tip Top adit water.

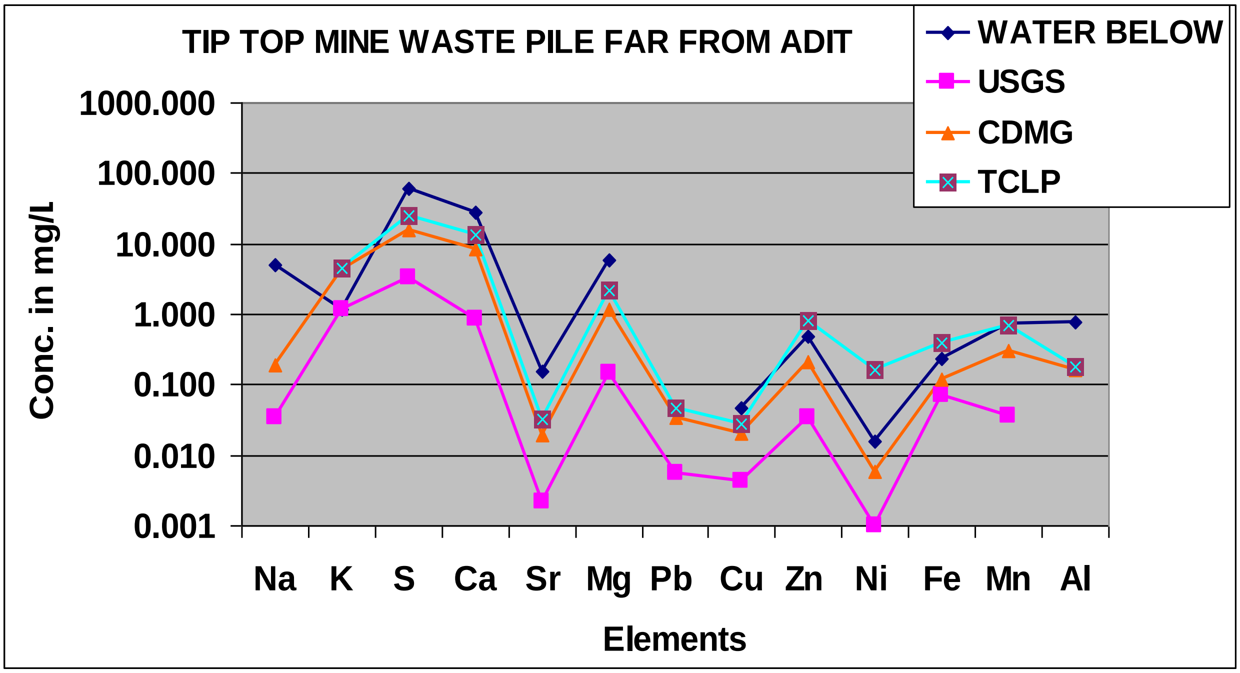

Figure 7. Element Concentration Pattern Graph for the solutions from the three leachate tests for the far waste rock pile at the Tip Top site.

Discussion

Comparison of the Waters at the Tip Top Site

In comparing the water samples it is clear that heavy metal contamination is occurring. In order to compare the samples copper and zinc concentrations will be examined. The copper and zinc concentrations are below a toxic level, 0.004 mg/L and 0.048 mg/L respectively, in the water above the adit. Below the adit the water becomes marginally toxic based on total metal concentration with copper at 0.046 mg/L and zinc at 0.48 mg/L. This change in toxicity indicates that somewhere below the adit metal contamination is occurring. The adit has concentrations of copper and zinc that are well above the toxic level, 0.199 mg/L and 1.65 mg/L respectively. There is a point in the stream where the clear water from above the adit and the deep orange water from the adit merge and flow downstream. There is a small water source that runs along the road and has high levels of copper and zinc as well. The 0.185 mg/L of copper and the 1.66 mg/L of zinc indicate that this runoff may be coming from the adit and thus providing another point of contamination downstream. The sampling visit was in mid-July, and by this time, spring runoff was over and the stream was at base flow conditions. In an analysis of nearby North Clear Creek, Harvey et al. (2003) found that dissolved metals concentrations are significantly lowered during high flow conditions. Assuming the concentrations of the metals in the adit water remain constant, the concentrations of dissolved Al, Cu, and Zn, which were above aquatic toxicity levels in July 2004, could be reduced to below those toxicity levels during high flows.

Results of the Leachate Tests on the Sediments

Three different processes for leachate tests were conducted to determine the range of concentrations that could be expected when water interacts with sediments and waste rock samples. As expected, (see Fig. 5 and 6) the USGS test extracted fewer metals than the CDMG test. Note in Fig. 5 that the metals extracted by the CDMG and USGS tests from sediment taken from above the adit inflow have concentrations that are generally above the concentrations in the gulch water. On the other hand, gulch water from below the adit inflow has metal concentrations that are at or above the metal concentrations extracted by the USGS and CDMG tests. It appears that aquatic toxicity due to metals is primarily because of the adit water and not from metals leached from the sediments.

Note from Fig. 5 and 6 that both above and below the adit inflow that the modified TCLP test releases concentrations of heavy metals that are significantly above what is in the water or is leached from the sediments by the other tests. The large release of metals by the TCLP was also noted in a project that studied sediments and soils from a mine site in Brazil (Wildeman et al., 2004). It is assumed that complexation by the acetate and the reduced pH in the TCLP solution causes this release of metals. Because the sediment above the adit inflow also shows this metals release, it can be assumed that some of these metals are due to the mineralization signature that occurs in all of the sediments and soils in the area.

Results of the Leachate Tests on the Waste Rock Piles

The leachate results for the waste rock pile farthest from the adit are shown in Fig. 7. The results for the near waste rock pile are comparable, but, in general showed low enough leachate concentrations that there is no aquatic toxicity. For the waste rock pile farthest from the adit, the CDMG leachate test extracted 0.021 mg/L of copper and 0.21 mg/L of zinc. These concentrations are marginally toxic, but below the concentrations of copper and zinc that are in the stream below adit inflow. Figure 7, a view from the top of the far waste rock, shows that plants are growing on the slopes of the piles and that there is no vegetative kill zone below the pile. Both of these conditions are signs that the pile is not impacting the environment to any great extent (Wildeman et al., 2003). These results lead to the conclusion that Gamble Gulch is not being affected by metals leaching from the waste rocks piles.

Future Studies

An important next step in our development of simple toxicity assessment procedures is to take the solutions from the leachate tests and use them in simple in-vitro toxicity tests that use an enzyme to monitor a biological response to the heavy metals present in the leachate. Currently, it appears that MetPLATE enzyme tests using the bacteria, *Escherichia coli* are the most sensitive to contaminant metals. The TCLP procedure requires the addition of acetic acid, which would lower the pH of the aqueous sample. This drop in pH could kill the test organisms, in this case the bacteria used in the enzyme tests. The USGS test almost always yields lower concentrations of metals and so using this solution could generate a false negative where the in-vitro test would show no toxicity when there is toxicity present. Therefore, the CDMG leachate test will be used in the enzyme testing because it almost always generates the higher concentrations of metals and results from this and previous studies have shown that in situations of marginal toxicity the metal concentrations from the CDMG test are closer to the actual mine water that is found on the site (Wildeman et al., 2003; Bazin et al., 2003; Wildeman et al., 2004).

Figure 7, A view from the top of the far waste rock pile, Note that vegetation is growing on the pile and that there is no kill zone below the pile.

Conclusions

Gamble Gulch, the stream running beside the TipTop Mine site, is marginally contaminated by heavy metals primarily coming from the adit water that flows into stream. There are slightly elevated levels of zinc and copper in the leachate from the sediment collected below the adit, but not enough to account for the levels in the stream. It is also unlikely that the water draining from the waste rock piles is contributing to the aquatic toxicity of the stream. In order to confirm these predictions MetPLATE enzyme tests using the bacteria, *Escherichia coli* will be run on the leachate from above and below the adit, the leachates from the two waste rock piles, and water from above, below, and the adit. For these tests, the CDMG leachate will be used because that solution leaches that largest metal concentrations that are usually closest to the concentrations in waters found on the site.

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