

Eagle River Water Quality: Limits to Trout Recovery

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Abstract – In 1986 the EPA placed the Eagle River of Central Colorado on the National Priorities list. With the help of the current owner of the Eagle Mine, Viacom, and the Colorado Department of Public Health, a mitigation process was begun. In 2000 a five year review of the process was conducted and it concluded that the “public health risks have been eliminated.”¹ Still, some fish species had not yet returned, and levels of metals in the river were still elevated so that on-going monitoring was called for. On March 28, 2003, before the spring snowmelt had begun, we collected fish, water, and sediment samples from 6 miles (10 km) above to 20 miles (30 km) below the Eagle Mine in Eagle County near Minturn. These were analyzed for their heavy metal content using ICP-OES. Sediments were fractionated using a modification of Tessier, et al’s procedure.² Both the stream and sediment metal concentrations, as expected, peaked in the mining district with a trend toward lower levels downstream. Significant fractions of heavy metals were sequestered in the moderately labile carbonate, hydroxide, and organic fractions, indicating full mineralization has not yet been achieved. Although most aqueous metals were low enough to allow some fish to return to the river around Minturn, zinc, manganese, and copper were still at levels that are lethal to rainbow trout for at least 10 miles (15 km) below the mine. Concentrations in the stream and sediment were comparable to values reported for 1995-1998 by the USGS^{3,4} after the concentrations were corrected for the difference in stream flow rates. Although concentrations of the elements measured in the flesh of brown trout caught at various sites are low enough to be of little concern for human consumption, it is apparent that the fish are concentrating metals from the water and levels of copper reached 1900 ppm (dry weight) in brown trout liver at the most contaminated site near Cross Creek. This level suggests that only trout with the ability to sequester heavy metals in the liver with metallothionein can survive in the river at this stage. Because Cd, Zn, and Mn levels in the river around Minturn are dictated by labile exchange with carbonate sediments, it will take at least three more half-lives ($t_{1/2} = 4$ to 7 years, or a total of 10 to 20 years) before the zinc and manganese levels will have consistently dropped far enough for the successful hatching of brown trout each year. More sensitive species such as rainbow and cutthroat trout should take even longer; especially as copper levels are dropping more slowly ($t_{1/2} = 10$ years).

¹ <http://www.epa.gov/region8/superfund/sites/co/eaglmine.html>, (The following file is the full report.

Note: This is a very large, 10 MB file!) <ftp://ftp.epa.gov/r8/FiveYearRev/EagleMine5yrScan.pdf>

² A. Tessier, P. G. C. Cambell, and M. Bisson, “A Sequential Extraction Procedure for the Speciation of Particulate Trace Metals” *Analytical Chemistry* 51(7) 844-851, 1979.

³ <http://water.usgs.gov/>

⁴ J. R. Deacon and V. C. Stephens, “Water-Resources Investigations Report 98-4124,” U. S. Geological Survey, Denver, Colorado 1998. (<http://water.usgs.gov/pubs/wri/wri98-4124/pdf/WRIR98-4124.pdf>)

Introduction

The Eagle and other mines of the Battle Mountain mining district, Eagle County, Colorado, are located just a few miles upstream of the residents of Minturn along the Eagle River. This district produced primarily gold (Au), silver (Ag), and lead (Pb) from the Leadville Dolomite in which the first mines were dug in 1879.¹ But by the turn of the century these were exhausted and the district switched to mining zinc (Zn), lead (Pb) and copper (Cu) from sulfide ores. Production from these mines continued until their closure in 1978. Large quantities of smelter slag and mining waste were dumped and some 70 miles of tunnels were dug over the century of operation. These roaster and tailings piles and the open mines expose relatively high concentrations of iron (Fe), manganese (Mn), Ag, Pb, and Zn as well as the highly toxic elements arsenic (As) and cadmium (Cd) to oxidation and mobilization. In 1986, the EPA put the site on the National Priorities List and with help from Colorado and Viacom (the owner of the Mine) mitigation efforts were begun. Because zinc sulfide is especially subject to air oxidation, thus creating acids that further leach toxic metals, flooding of the mines to limit the air was implemented as part of the remediation. As a result Zn levels (used as an indicator of the other metals) have been dropping by a factor of two every 3 to 5 years at monitoring stations at seeps. Further cleanup included plugging mines, consolidating and capping tailings, diverting water, construction of a treatment plant, and development of a biologically based water quality standard.²

In 2001 the Colorado Division of Wildlife completed a biological study of the Eagle mine site suggesting that the threat from heavy metal pollution from the mine had been nearly eliminated.³ The proof used was the steadily increasing population of brown and brook trout in the area. Their study focused on water samples and the quantity of several inhabiting organisms for their evaluation. The lower Eagle River holds a steady population of rainbow trout (*Oncorhynchus mykiss*), which tend to be more sensitive to toxins and pH changes in the water. Brown trout (*Salmo trutta*) tend to have higher tolerances to pH changes in their environment and could possibly be less affected by high levels of metals in the waters. The researchers did not include a metals analysis of either the sediments or the fish from the upper Eagle River as a part of their biological study, and thus we undertook this limited analysis in order to provide additional, third party data.

Sample Collection

A total of 12 water, 6 soil and 3 fish samples were collected from the streams in the vicinity of the Eagle mine. Eleven water samples were collected from the Eagle River above and below the mine, and one from Gore Creek. (See sites numbered 1 to 12 in Fig. 1.) The 500 mL water samples were collected in clean PETE bottles without preservative, placed in a cooler, and the time of sampling recorded so that flow rates in Fig. 2 could be determined from the nearest USGS stream-flow data site, which averaged 38 cubic ft/sec that day but had 41 cfs at the time of collection (Appendix 1). These were subsequently filtered (0.45 micron filter) and analyzed upon returning to the lab.

Six sediment samples were collected mid-stream using a small steel bucket (lettered A through F in Fig. 1). The sediments were placed in PE (Ziploc) bags and refrigerated until analysis.

Live brown trout (*Salmo Trutta*) were caught with rod and reel downstream of the mine and ranged in size from 9.5 to 13.2 inches. The fish caught at each location were kept on ice until analysis. Fish I (13.2 inches: 515 g⁴) was caught 2.5 miles below Eagle mine; fish II (9.5 inches: 183 g) is from 8.5 miles downstream; and fish III (11.5 inches: 334 g) was obtained 19.2 miles below the mine after the confluence of Gore Creek with the Eagle River. The liver, spleen and (separately) muscle tissue were targeted for testing since the organs are most likely to absorb environmental toxins while the flesh is of interest to those who might eat fish caught in these rivers.⁵

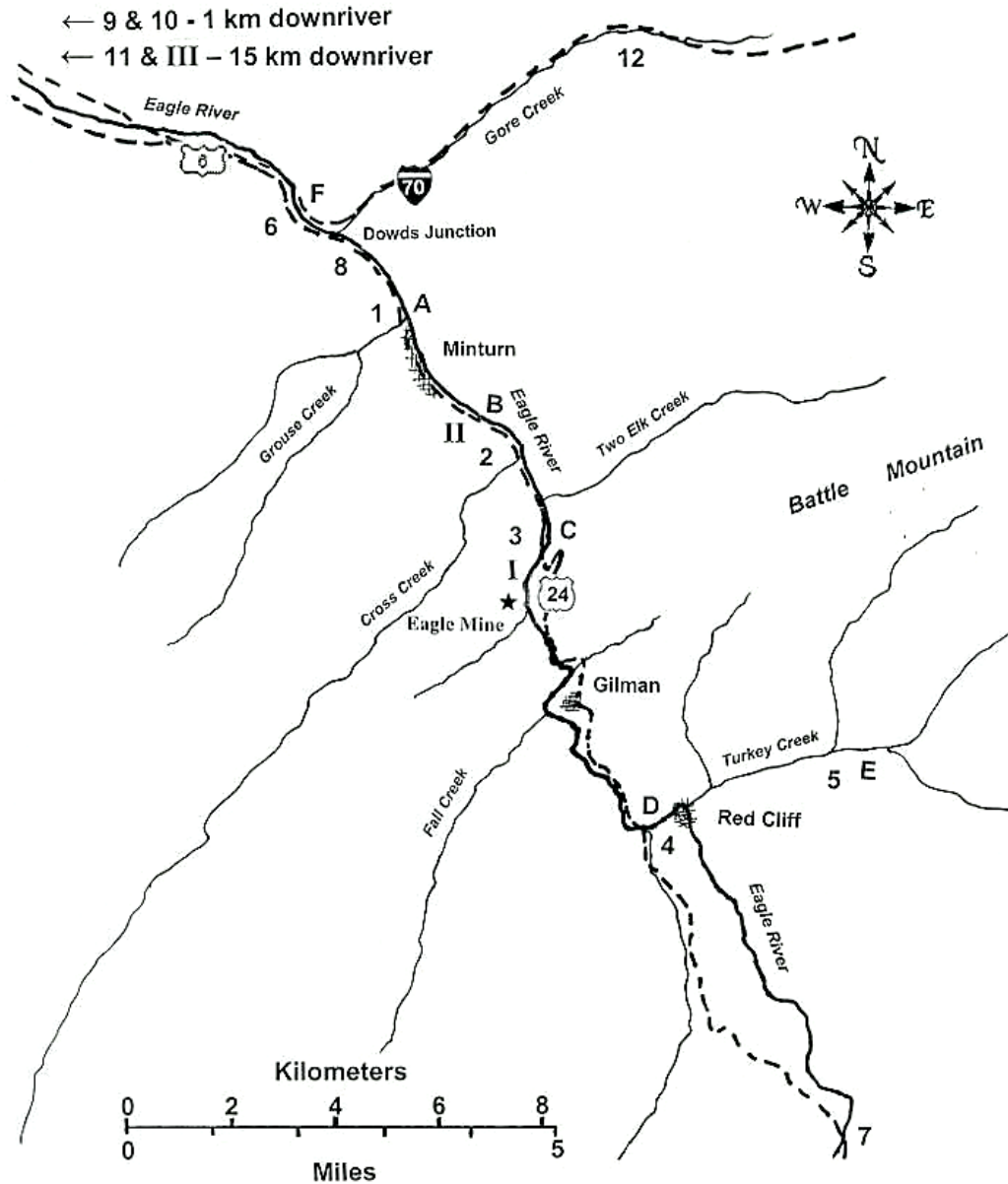


Fig. 1 – Sampled sites from the Eagle River and surroundings for water (1 to 12), sediment (A to F), and brown trout (I to III)

Sample Preparation and Analysis

After filtering with 0.45 micron polycarbonate filters, the concentration of aluminum (Al), cadmium (Cd), copper (Cu), iron (Fe), lead (Pb), nickel (Ni), manganese (Mn) and zinc (Zn) were measured using a Thermo-Jarrell Ash Atomscan-16 sequential ICP-OES using the instrument settings listed in Table 1. The pH for each water sample was also measured at the lab using an Orion pH meter.

Table 1. Power levels were default settings by the manufacturer.

Element	Wavelength (nm)	Background offset (nm)
Ba	455.403	±0.05
Al	309.271	±0.05
Cu	324.754	±0.05
Mn	257.610	±0.05
Ni	231.604	±0.05
Pb	220.353	-0.05, none
Fe	259.940	±0.05
Cd	214.403	±0.05
Zn	213.856	±0.05

The six soil samples from sites A to F were manually palpitated and then picked over to remove particles larger than 2 mm. One-gram portions were subsequently analyzed using a modified fractionation procedure.⁶ The five reactions extracted from the sediments were: (1) ion exchangeable “clay bound” fraction (extracted with 20 mL of 0.1M MgCl₂ per gram of soil for 10 min.); (2) carbonate bound fraction (20 mL of 1M sodium acetate buffered at a pH of 4.5 for 1 hr at 85° C); (3) iron-manganese hydroxide bound fraction (a 0.1M ascorbic acid and 25% acetic acid mix for 1 hr at 85° C); (4) organic bound fraction (5% H₂O₂ and 0.2M HNO₃ for 1 hr at 85° C); and (5) mineral fraction, leached with 10% concentrated 3:1 HCl:HNO₃ for 1 hr at 85° C). The extraction solutions were filtered through 1-micron glass filters (Whatman 934-AH) and analyzed by ICP-OES using the same instrumental parameters as before.

Fish tissue samples (6 to 10 g each) or whole liver and spleen samples (1 to 5 g) were excised using a stainless steel scalpel, weighed to get a fresh weight, and then placed in a muffle furnace in ceramic crucibles. The temperature was ramped to 350°C for 2 hours and then to 575°C where it was held for 12 hours. The ash was wet with a few drops of 18 M-ohm water and then dissolved with 2 mL of trace metal grade 16M HNO₃. The solutions were filtered through 1-micron glass filters and diluted to 20 g for ICP-OES analysis. This procedure may lose some of the more volatile elements (e.g., As and Pb), but it minimizes the contamination from additional reagents.

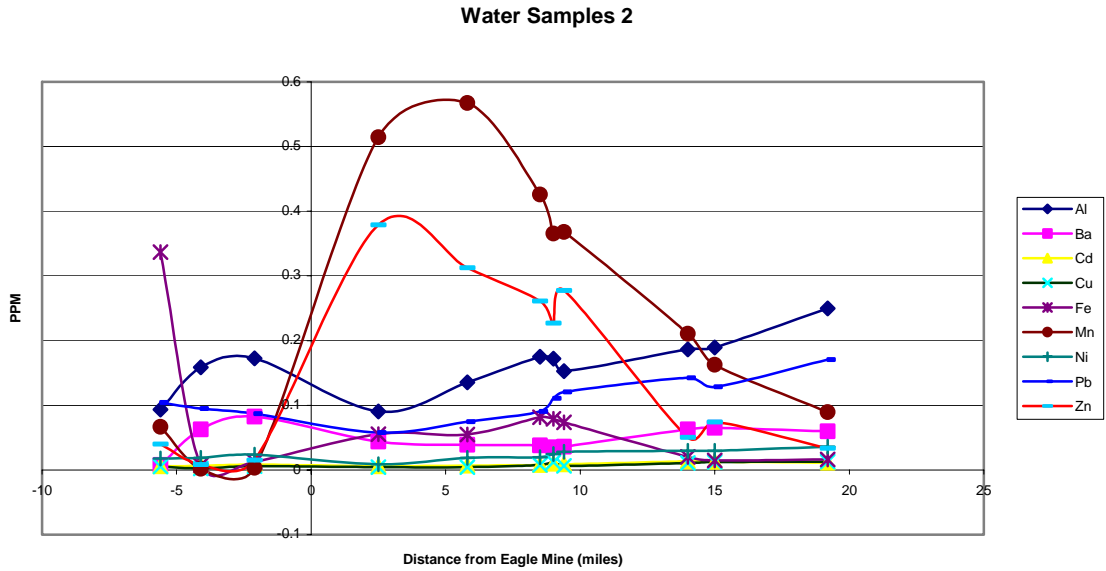


Fig. 2 – Variation of river water metal concentrations around Eagle Mine

Results and Discussion

The data for the water samples show a profile of metals still being released in significant quantities in the aquatic environment below the Eagle mine. In Fig. 2 most of the metal levels in the water samples peak just below the mine and then follow a gradual downward trend in concentration as the distance increases from the mine. (Appendix 2.) A few of the less concentrated constituents (Al, Ni, and Pb) show a pattern that seems to be the inverse of the main trend. We are uncertain of the reason for this inverse relationship at this time, but posit that the high levels of bicarbonate ion being released from the mines may affect the solubility of these specific metals so they are less soluble. The levels of some metals (Zn and Mn) are significantly higher than the reported, long-term toxicity levels for brown trout of 0.30 ppm for zinc and 0.027 ppm for Mn.⁷ Other concentrations of metals found in the water, although high, are not much above the tolerance ranges for brown trout under the stream flow rates present during the low flow period when these samples were collected. As there have been below average amounts of precipitation for the last few years, we suspect these levels are somewhat higher in this year (2003) than is the norm. Still, the overall levels and trends fit well with previous values reported in the literature when stream flow rates, sample location, and time since remediation began are taken into account.⁸

The sediment samples display a similar trend in the metal concentrations. Generally, the elements bonded to the ion exchangeable fraction (the first extraction) are the most mobile, representing elements that are in a free ionic state, adhering lightly to the surface of clay particles. As the metals become bound to one of the next three fractions (carbonate, iron-manganese hydroxide, or organic matter), they become less mobile, but are still moderately labile. These, over a period of months to years become bound into less unreactive minerals that are less toxic to aquatic life.

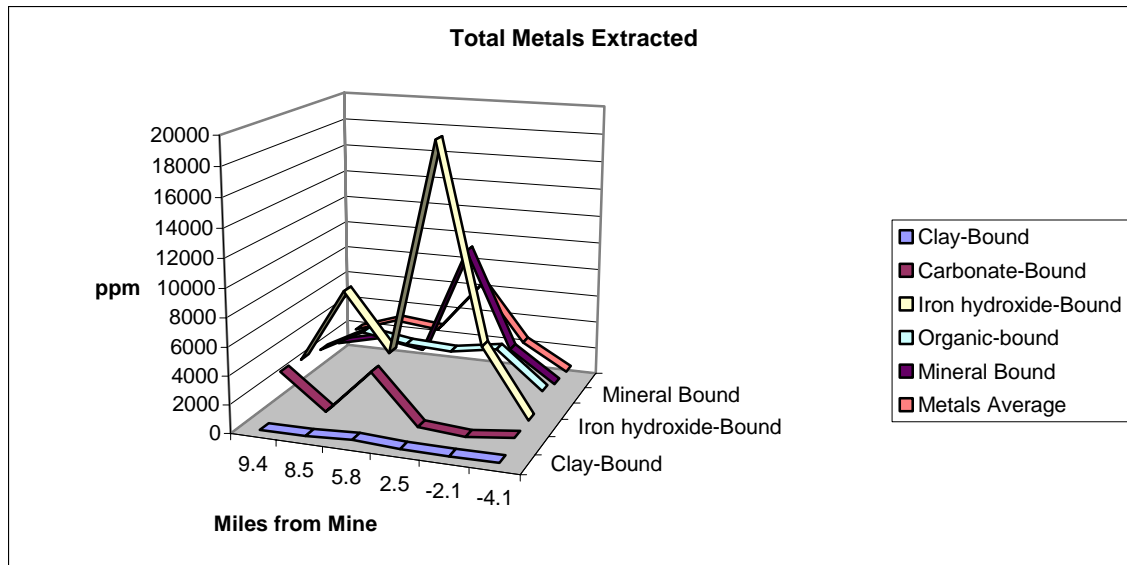


Fig. 3 – Combined metal fractionation profiles for sediment samples collected at 9.4, 8.5, 5.8, and 2.5 miles below and 2.1 and 4.5 miles above the Eagle mine effluent.

Such redistribution is observable in Figure 3 where the largest total of the metals in the sediment is found just below the Eagle Mine effluent in the form of iron hydroxide bound matter. Downstream, the major bound fraction varies between the iron hydroxides and the carbonates. A large fraction of the metal load still is in moderately labile, readily remobilized fractions, especially if the pH decreases. The contribution of the Leadville Dolomite parent ore body and the iron and manganese hydroxides from the oxidized and hydrated sulfide ores are apparent in the dominance of these fractions in this aquatic system, especially around Minturn. Copper, which preferentially moves to organic matter before becoming fully mineralized, is highest in this fraction except at the initial release point nearest the mine. (Appendix 3.) The total metal load in the sediments measured by this fractionation procedure fits well with previous literature values for both the trend in zinc values downstream⁹ and the total metal concentrations.¹⁰

The data from the fish is separated into liver plus spleen (the organs that tend to concentrate heavy metals) and muscle tissue (the portion consumed by humans). A general trend towards lower concentrations is observable in Fig. 4 as the distance from the mine increases. These levels interface smoothly with the literature values reported for fish collected starting at Dowd's Junction and proceeding down-river to the Colorado River.¹¹ The muscle tissue from each fish contained easily measured levels (all < 20 ppm) of iron, aluminum, zinc and manganese, but none seem likely to present a significant health risk for the typical quantities eaten by people.¹² The fish liver plus spleen, on the other hand, showed unusually high levels of copper, higher than any reported anywhere else in Colorado.¹³ These high levels imply the fish are under significant metal stress such that they must manufacture additional metalloproteins such as metallothionein to sequester the additional metals entering their body. The liver acts as a repository for these organo-metallic compounds, and copper is especially strongly bound in this form. As noted for the stream sediments, copper is enriched in the organic detritus in the river. Probably the trout are concentrating the copper from the water directly, but they may also be getting it from prey they consume that are contaminated,

leading to a bioconcentration effect. These levels, as well as the zinc concentrations, should be monitored, as both will play a role in determining when the fish hatcheries on the Eagle River will be restored to their historic prominence.

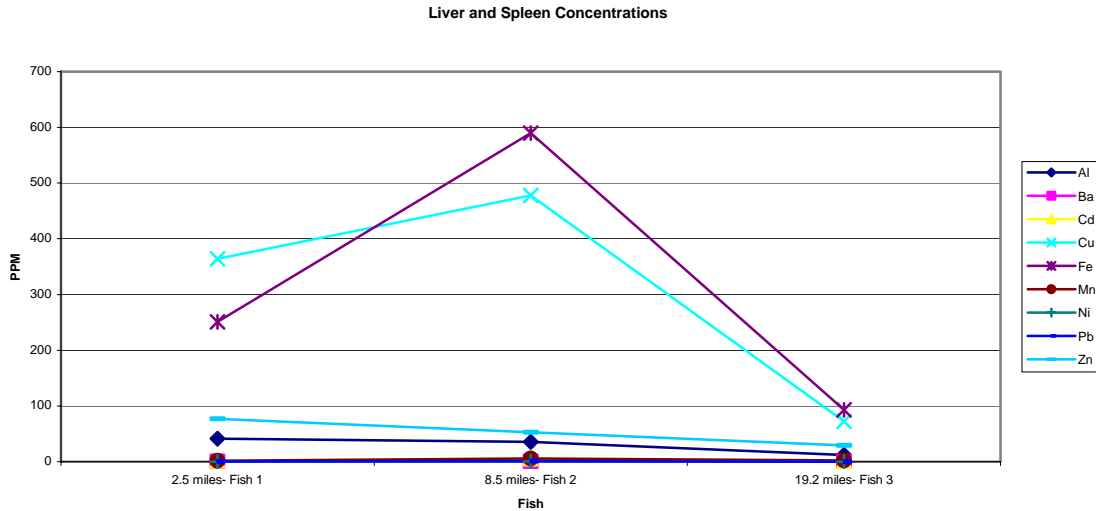


Fig. 4 – Brown trout combined liver and spleen concentrations at 2.5, 8.5, and 19.2 miles below the Eagle mine effluent.

Conclusions

Based on the results of this data it becomes clear that the Battle Mountain mining district above Minturn is continuing to have an impact on the aquatic systems of Eagle River. Our analysis recorded levels of zinc and manganese that are chronic toxins to brown trout. This toxic plume extended well below Minturn, but not beyond the confluence with Gore Creek. Metals dissolved in the water hold the greatest immediate threat to the aquatic life but metals in the sediment also present long-term risk. A slight lowering of the pH of the river may be enough to bring these metals back into solution and contaminate the river. The sediment also exchanges with organisms living upon it, and bioconcentration effects may take place that vary with the species. Although the number of fish samples analyzed in this study is small, their value when interpreting the health of the river points to the value of periodic analysis of fish specimens for indicating the long-term health of the river as the fish act to better integrate the levels. They also demonstrate that the residual effects on the fish can extend further downstream than might at first be predicted from either the water or sediment concentrations.

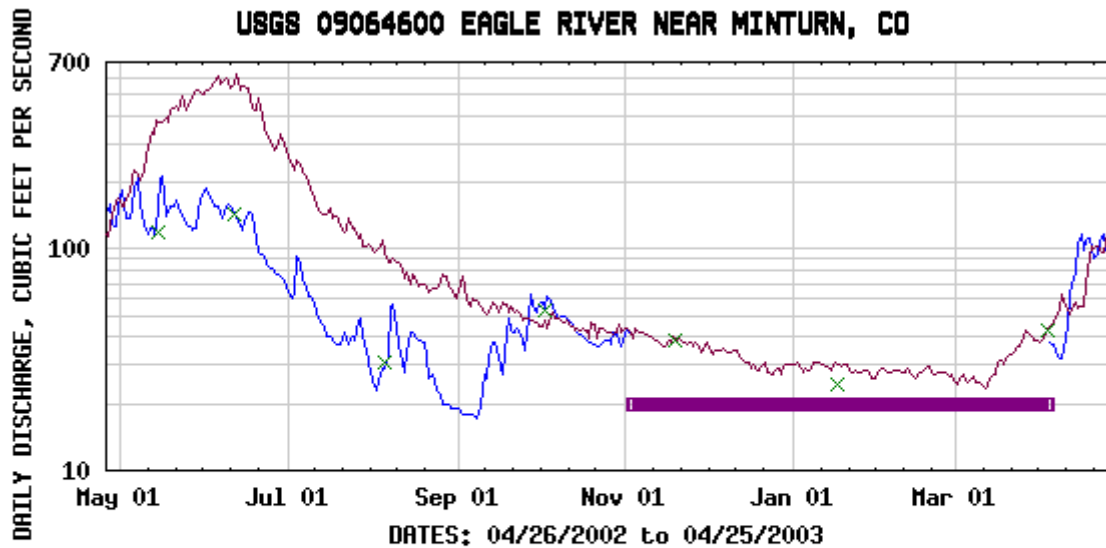
Appendix 1

	Time	Flow/CFS	Average
1. USGS Water gauge below the town of Minturn (8.5 miles downstream)	8:45am	41	69.4
2. Above Minturn, Old Cemetery Rd. Bridge (5.8 miles downstream)	9:20am	41*	69.4
3. Foot of Battle Mountain, ¼ mile down from HW 24 bridge (2.5miles downstream)	9:45am	41*	69.4
4. USGS Water gauge below town of Redcliff (2.1 miles upstream)	10:15am	15.4	28.9
5. First Creek above Redcliff (4.1 miles upstream)	12:15am	ICE	---
6. Below Eagle/Gore confluence (9.4 miles downstream)	4:10pm	46.0	126.1
7. Eagle Creek, Below Camp Hale (5.6 miles upstream)	10:38am	5.7	---
8. Eagle River above Gore Confluence (9 miles downstream)	4:15pm	41*	69.4
9. Avon Water Treatment center (14 miles downstream)	4:30pm	70.0	195
10. USGS Water gauge Avon Bob's Bridge (15 miles downstream)	4:45pm	3.3	5.89
11. USGS Water gauge Edwards Lake Creek (19.2 miles downstream)	5:00pm	13.10	20.5
12. USGS Water gage Gore Creek Mouth	5:10pm	4.95	56.7
		*Approx	

Source: <http://water.usgs.gov/>



USGS 09064600 EAGLE RIVER NEAR MINTURN, CO



EXPLANATION

- DAILY MEAN DISCHARGE
- MEDIAN DAILY STREAMFLOW BASED ON 11 YEARS OF RECORD
- × MEASURED DISCHARGE
- Flow at station affected by ice

Provisional Data Subject to Revision

Appendix 2

**Water Samples- Eagle
River**

(Concentration in ppm)

<i>Miles:</i>	19.200	15.000	14.000	9.400	9.000	8.500	5.800	2.500	-2.100	-4.100	-5.600
Al	0.250	0.189	0.187	0.153	0.172	0.175	0.136	0.091	0.173	0.159	0.093
Ba	0.060	0.065	0.063	0.036	0.035	0.038	0.039	0.044	0.082	0.063	0.008
Cd	0.011	0.013	0.013	0.009	0.010	0.008	0.007	0.006	0.008	0.007	0.006
Cu	0.013	0.012	0.011	0.006	0.012	0.008	0.004	0.004	0.006	0.003	0.006
Fe	0.016	0.015	0.020	0.073	0.079	0.082	0.055	0.055	0.013	0.007	0.337
Mn	0.090	0.163	0.211	0.368	0.365	0.426	0.567	0.514	0.003	0.002	0.067
Ni	0.036	0.030	0.029	0.028	0.025	0.020	0.019	0.009	0.024	0.019	0.018
Pb	0.171	0.129	0.142	0.121	0.111	0.091	0.075	0.058	0.087	0.095	0.104
Zn	0.034	0.074	0.051	0.278	0.227	0.261	0.313	0.379	0.015	0.008	0.040

Appendix 3

**Concentration in Sediment
(ppm)**

Miles from Mine Effluent

Ext.1-Clays	9.4	8.5	5.8	2.5	-2.1	-4.1
Al	38.6	69.5	38.1	81.8	58.2	76.6
As	8.9	15.5	9.9	18.6	13.0	17.1
Ba	4.7	2.7	8.9	7.0	3.0	2.8
Cd	1.0	1.7	1.1	2.1	1.5	1.9
Cu	0.3	0.5	0.4	0.9	0.5	0.5
Fe	1.1	1.9	1.4	2.3	1.7	1.2
Mn	10.4	0.8	224.3	1.3	1.0	0.7
Ni	2.9	5.2	3.2	6.6	4.4	5.8
Pb	12.0	20.9	13.2	1.8	18.1	24.2
Zn	4.2	5.2	2.1	3.0	1.0	4.3
Ext.2-Carbonates	9.4	8.5	5.8	2.5	-2.1	-4.1
Al	35.6	45.2	50.1	43.8	32.5	45.5
As	20.6	32.9	25.8	45.2	32.4	39.8
Ba	28.1	24.0	49.4	35.7	15.4	19.0
Cd	1.3	1.7	3.1	0.8	0.7	1.4
Cu	0.4	1.9	2.1	1.3	-0.7	1.2
Fe	140.0	40.7	786.6	71.0	47.8	64.6
Mn	1426.2	40.5	1463.1	147.7	18.3	64.5
Ni	2.4	1.4	3.1	1.7	1.5	1.5
Pb	14.7	5.5	18.1	11.6	7.1	10.4
Zn	1426.2	432.5	1463.0	43.0	5.9	303.1
Ext.3-Oxides	9.4	8.5	5.8	2.5	-2.1	-4.1
Al	63.4	154.4	145.9	264.5	38.9	26.1
As	63.1	91.7	66.6	127.5	86.4	108.9
Ba	16.8	15.5	40.7	55.5	19.5	4.2
Cd	1.8	62.1	2.9	7.2	2.0	1.9
Cu	0.0	35.1	5.9	0.0	0.0	0.0
Fe	1647.3	6556.6	1669.4	16137.7	5009.0	353.1
Mn	912.2	776.2	1793.7	1658.8	151.1	6.5
Ni	2.6	5.0	4.2	8.7	2.2	1.4
Pb	38.2	40.5	74.3	79.0	20.8	19.3
Zn	128.6	474.7	335.0	817.5	25.0	2.9

Ext.4-Organic	9.4	8.5	5.8	2.5	-2.1	-4.1
Al	623.9	644.5	414.8	259.8	1551.9	563.6
As	26.1	69.4	35.5	45.9	54.0	37.9
Ba	18.9	40.9	32.0	13.7	74.9	6.6
Cd	1.6	56.5	2.1	3.0	2.7	0.7
Cu	11.0	30.7	20.1	16.3	25.3	1.1
Fe	1426.3	2292.5	1463.1	2886.9	2118.0	838.4
Mn	255.1	591.7	1463.1	144.6	161.7	6.9
Ni	3.9	6.8	4.6	3.3	8.5	1.6
Pb	76.2	76.7	103.7	42.8	59.6	6.4
Zn	138.1	459.6	209.2	184.3	69.4	5.7

Ext.5-Minerals	9.4	8.5	5.8	2.5	-2.1	-4.1
Al	505.8	398.0	579.8	2683.4	833.3	286.6
As	14.7	25.5	8.3	120.1	24.2	16.5
Ba	4.5	5.2	8.5	419.5	17.6	2.4
Cd	0.9	0.9	1.2	30.9	1.3	0.4
Cu	1.8	2.3	5.3	110.1	4.3	0.1
Fe	1426.3	2292.5	1463.1	2051.2	2118.0	541.8
Mn	41.6	43.0	139.8	2886.9	26.4	2.5
Ni	2.7	2.0	3.4	38.1	4.5	1.2
Pb	20.2	13.6	25.7	366.9	15.9	3.2
Zn	29.9	42.9	63.0	1351.0	17.6	2.3

References

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- ¹ R. W. Walker and M. B. Kennedy, *Mines and Minerals of the Great American Rift (Colorado – New Mexico)*, Van Nostrand Reinhold Co., NY pp 262-265 (1983).
- ² M. H. Dodson, Asst. Admin., Five-Year Review Report for Eagle Mine Superfund Site, Eagle County, Colorado, Region VIII U.S. EPA, Denver, Colorado (2000). Accessed (April 27, 2003) at: <http://www.epa.gov/region8/superfund/sites/co/eaglmine.html>, (The following file is the full report. Note: This is a very large, 10 MB file!) <ftp://ftp.epa.gov/r8/FiveYearRev/EagleMine5yrScan.pdf>
- ³ Woodling, John and Jenifer Ketterlin. “Annual Biological Monitoring of the Eagle Mine Superfund Site; Eagle County, Colorado in 2001.” Department of Natural Resources (2003).
- ⁴ Masses estimated from log-log plot based on literature values for length and mass. E. Lydersen, N. Rukka, J. Jensen, B. Kjelsberg, B. Tornsjø, R. Vogt, L. A. Vollestad, and A. Poleo, “Seasonal variation in mortality of brown trout (*Salmo trutta*) in an acidic aluminum-rich lake,” *J. of Limnology*, **61**(1): 61-68 (2002).
- ⁵ D. O. Norris, et al, “Some Aspects of Hepatic Function in Feral Brown Trout Living in Metal Contaminated Water.” *Comparative Biochemistry and Physiology Part C Toxicology and Pharmacology*. 127C.1 pp 71-78 (Aug., 2000).
- ⁶ A. Tessier, P. G. C. Cambell, and M. Bisson, “A Sequential Extraction Procedure for the Speciation of Particulate Trace Metals” *Analytical Chemistry* **51**(7), 844-851 (1979).
- ⁷ B. Molony, “Environmental requirements and tolerances of Rainbow Trout and Brown Trout With Special Reference to Western Australia.” Department of Fisheries; Government of Western Australia. Fisheries Research Report NO. 130, 2001.
- ⁸ USGS Stream data for sampling sites 09064600 (Eagle river above Minturn, 8/3/98), 09065100 (Cross Creek, 7/31/98), and 08066510 (Gore Creek, 4/26/94).
- ⁹ M. H. Dodson, Asst. Admin., Five-Year Review Report for Eagle Mine Superfund Site, Eagle County, Colorado, Region VIII U.S. EPA, Denver, Colorado (2000).
- ¹⁰ USGS Stream data for sampling sites 09064600 (Eagle river above Minturn, 9/5/96), 09065100 (Cross Creek, 9/5/96), and 08066510 (Gore Creek, 9/28/95).
- ¹¹ J. R. Deacon and V. C. Stephens, *Trace Elements in Streambed Sediment and Fish Liver at Selected Sites in the Upper Colorado River Basin, Colorado, 1995-96*. U.S. Geological Survey, Water-Resources Investigations Report 98-4124, Denver, Colorado (1998).
- ¹² European Commission, Health and Consumer Protection, Scientific Committee on Food, “The Tolerable Upper Level Intake of Manganese,” http://europa.eu.int/comm/food/fs/sc/scf/out80f_en.pdf (2000).
- ¹³ Ibid.