COLORADO
Water Quality Control Division
Department of Public Health & Environment

Colorado's Interim Alert Notification Thresholds for Cement Creek and the Animas River

April 8, 2016 • Official Version
Environmental Data Unit

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DEFINITIONS

Colloidal	A substance consisting of particles that are dispersed throughout another substance.
Dissolved Metals	Metals content that can pass through a 0.45 µm filter.
pH	A measure expressing the acidity or alkalinity of a solution on a logarithmic scale where 7 is neutral, lower values are more acidic, and higher values are more alkaline.
Precipitate	A substance deposited in solid form from a solution.
Sonde	An instrument probe that automatically transmits information about its surroundings, such as under water.
Specific Conductance	A measure of the electric current in the water carried by ionized substances.
Total Metals	Metals content present as both dissolved and particulate in the water.

1. EXECUTIVE SUMMARY

Following the release from the Gold King Mine on August 5, 2015 into Cement Creek and then into the Animas River, there was concern for the risk of heavy metal exposure to agricultural, recreational and water supply users of the river. This concern continues and extends to the approaching spring snowmelt runoff.

On February 5, 2016 the Animas River Team at U.S. Environmental Protection Agency's (EPA) National Exposure Research Lab presented preliminary key findings of the fate and transport study of metals loading in the Animas River from the Gold King Mine release (EPA 2016a). The key tenets of this draft report are only preliminary estimates. However, those findings characterize matter-of-fact details that help explain the fate and transport of chemicals and sediment during and shortly after the release, current conditions, and prospects for the fate and transport of those matrices during the spring runoff.

EPA further reports that a U.S. Geological Survey (USGS) study of acid mine drainage in the Animas River in the 1990's found that increased colloidal and dissolved metal concentrations were common in the river following storms and spring runoff due to acid mine drainage contamination from the complex of abandoned mines in the headwaters (Church et al. 1997). What was clear from this study was that riverbeds accumulate metals from AMD during periods of low flow and release those accumulated metals during periods of high flow.

High flows, expected each spring during snowmelt, and unanticipated precipitation events are both equally capable of releasing accumulated loads of metals. Characterizing relationships between those metals and continuously monitored parameters, such as pH, turbidity or specific conductance, becomes important for addressing associations between elevated metals concentrations and impacts on Colorado's designated uses.

Using existing water quality data from the Upper Animas River basin, the Water Quality Control Division (WQCD) has developed interim notification thresholds for specific conductance and pH at two USGS discharge gages near the Town of Silverton. A specific conductance reading that exceeds 1465 µs/cm at USGS gage 09358550 on Cement Creek at Silverton or a pH that falls below 5.3 at USGS gage 09359020 on the Animas River below Silverton will activate verification site visits.

Exceedences of these interim thresholds will form the basis for preliminary alert notifications, which are intended to communicate water quality risks to the public. Additional water quality data, collected during the spring runoff and fall-winter base flow period, will be used to adaptively adjust or develop new thresholds at three USGS gages total.

2. BACKGROUND

High flows are associated with spring snowmelt runoff as well as unanticipated precipitation events. Both events are equally capable of releasing accumulated loads of metals during turbulent, elevated flows. Characterizing correlations between those metals and instantaneous measurements, such as pH, turbidity or specific conductance, becomes important for addressing links between elevated metals concentrations and impacts on Colorado's designated uses, such as recreation and water supply.

Using existing water quality data from Cement Creek, Mineral Creek, the Animas River, and other local waterbodies, the WQCD has completed a preliminary correlation analysis between instantaneous measurements and total and dissolved metals. These findings are presented below.

3. THRESHOLDS – CEMENT CREEK IN SILVERTON

Introduction

The WQCD focused on dissolved lead as the most serious concern to public health in Cement Creek. This was based on three key factors: 1) an adequate amount of data to develop a relationship, 2) potential health effects from short-term or long-term exposure, and 3) its close proximity to residents, including children, from the Town of Silverton.

According to the National Primary Drinking Water Regulations, which are the legally enforceable standards that apply to public water systems, lead has an action level or maximum contaminant level (MCL) of 15 ppb[1]. Prolonged exposure through ingestion or physical contact may result in delayed physical or mental development in children and kidney problems or high blood pressure in adults (EPA 2016b).

Data Treatments

- Paired data was pooled from Cement Creek, Mineral Creek and the Animas River, above and below the Town of Silverton, to develop a correlation between dissolved lead and specific conductance. The paired data was collected by WQCD staff between August 5, 2015 (Gold King Mine spill) and February 23, 2016. The data is available in Appendix A.

- It is well know that conductivity of all solutions change as the solutions' temperature changes. However, since the paired data was collected more recently, specific conductance data was "temperature compensated" to 25 ^{o}C. Newer water quality probes are capable of using temperature and raw conductivity values associated with each determination to generate a specific conductance value compensated to a default temperature. This data was appropriately compensated.

- The WQCD substituted left-censored data values with half the reported method detection limit. Left censoring is where a data point is below a certain value but it is unknown by how much. Use of left-censored data may bias estimates of central tendency if the number of observations is low (Newman, 1995), but in this case the increase in observations diminished the bias.

Scatterplot and Regression Analysis

A linear model was developed using regression analysis. The R-squared value shows that specific conductance explains 71% of the variance in dissolved lead, indicating that the model fits the data reasonably well. The p-value of 0.00 indicates that the relationship between dissolved lead and specific conductance is statistically significant at an α-level of 0.05.

[1] Parts per billion

Water quality data and regression analysis results are located in Appendix A.

Notification Threshold

Additional regression analysis between specific conductance and other dissolved metals has demonstrated reasonable correlations from which we can conclude that measurements of specific conductance in cold, low ionic-strength waters can provide good estimates of total dissolved solids (Thomas, 1986).

Increasing specific conductance values are a signal that total dissolved solids all together are increasing. Although other correlations could be used as the basis for developing an alert notification threshold, the WQCD considers a single threshold benchmark beneficial because it removes potential confounding factors and reduces the incidence of contradictory notifications. Multiple benchmarks could potentially undermine the effectiveness of the notification system and unnecessarily heighten public health concerns.

In accordance with this consideration, a specific conductance that exceeds 1465 µs/cm at USGS gage 09358550 on Cement Creek at Silverton will activate a verification site visit.

Notification threshold = 1465 µs/cm Spec. Conductance

The verification site visit will involve directly measuring specific conductance with a handheld, multi-parameter water quality sonde. If the specific conductance value continues to exceed the notification threshold then an alert notification will be issued to collaborating emergency response agencies.

4. THRESHOLDS – ANIMAS RIVER NEAR SILVERTON

Introduction

Development of notification thresholds at this location was based largely on the fate and transport characterization of chemicals and sediment during and shortly after the release, current conditions, and prospects for the fate and transport of those matrices during the high flow events. This characterization articulates a sequence of metals accumulation and release based on multiple environmental factors, including cyclical flows.

Central to this characterization is the sequence of chemical transformations that played out during and after the spill event. This narrative indicates that as the plume entered the Animas River, the mixing of highly acidic water from Cement Creek with more basic water in the Animas River significantly lowered acidity and triggered a chemical transformation of dissolved metals to colloidal particles and then to solid precipitate. EPA estimates that the majority of the total metal load was deposited in the Animas River riverbed (EPA 2016a). A firsthand observation by WQCD staff since then indicates that much of the precipitated matter was deposited in the Animas River immediately downstream of Cement Creek.

The WQCD anticipates that high flows will release the metal precipitates or solids in sediment that were deposited in the Animas River between Cement Creek and the WQCD's monitoring station (#82) just below Mineral Creek. Developing a correlation here will provide a key benchmark threshold at a point where the metals transformation from total particulate matter to a dissolved fraction will be most active.

Data Treatments

- Paired specific conductance and metals data was pooled from WQCD station #82 to develop preliminary correlations. The paired data was collected by multiple agencies between 1970 and 2016 and was readily available in WQCD's local database. This data is presented in Appendix B.

- Specific conductance data was temperature compensated to 25 ^{o}C.

- Paired pH and metals data was pooled from the entire Upper Animas River basin to develop additional correlations. The data was collected by the WQCD between August 10^{th} and 18^{th} of 2015. This data is available in Appendix B.

- Since pH is temperature dependent, only water quality data collected during the month of August was used to eliminate any potential bias.

- The WQCD substituted left-censored data values with half the reported method detection limit.

Scatterplot and Regression Analysis

Correlations between specific conductance and available total and dissolved metals were tested using scatterplot and regression analysis.

The most encouraging correlations occurred between specific conductance and dissolve iron (Fe) and manganese (Mn). R-squared values showed that specific conductance explained 71% and 82% of the variance in dissolved iron and manganese, respectively, indicating that the models fit the data very well. Each had p-values of 0.00, which indicated that the relationships were statistically significant at an α-level of 0.05.

Correlation relationships between pH and available dissolved metals were also tested using additional scatterplot and regression analysis. Relationships were statistically significant at an α-level of 0.05. The purpose for this analysis is explained in the Discussion section below.

Water quality data and regression analysis results are located in Appendix B.

Discussion

The preliminary results of regression analysis between specific conductance and Fe and Mn led the WQCD to further examine how the chemical relationship between Fe/Mn and acid mine drainage works. EPA indicates that when the Gold King Mine spill plume flowed from Cement Creek into the Animas River, the pH of the plume was raised above 3 due to exposure to the Animas River's well-oxygenated waters. As a result, the river became cloudy and turbid due to the oxidation of iron and manganese to the $Fe3+$ and $Mn4+$ states, which formed colloidal particles and then precipitated as solids. This resulted in the notable yellow-orange solid synonymous with the plume, known as "yellow boy" (Alcorn, 2007). This account is consistent with EPA's fate and transport analysis that indicated nearly all dissolved metals from the Gold King Mine spill was transformed to a solid precipitate by the time it reached the San Juan River in New Mexico.

Metals are partitioned between solid and liquid phases and within each phase, further partitioning occurs as determined by ligand concentrations and ligand bond strengths. In solid phases, surface water particulates are partitioned into six fractions, which include dissolved, exchangeable, and iron-manganese oxide. Metals partition differently among these fractions and may be affected strongly by variations in pH and other environmental factors (Elder, 1989). Since rates of oxidation are not rapid, reduced forms can persist for some time in aerated waters (Sawyer and McCarty, 1967).

The dissolved fraction consists of carbonate complexes, whose abundance increases with pH. Metals in solution, including metal cation/anion complexes, and hydrated ions whose solubility is affected strongly by pH tend to increase with decreasing hydrogen ion activity (Elder, 1989).

Although high levels of dissolved iron and manganese do not pose any known adverse health risks, the presence of the iron-manganese fraction indicates that others metals are adsorbed to iron-manganese particulate matter. Thus, pH becomes an important factor governing metal speciation and bioavailability in aqueous solutions. Because the hydroxide ion is directly related to pH, the solubility of those metal hydroxide minerals increases with decreasing pH, and more dissolved metals become potentially available for incorporation into biological processes as pH decreases. (John and Leventhal, 1995).

This description is supported by recent water quality data collected at site #82 that point to decreasing pH and increasing dissolved manganese and total iron concentrations, as well as dissolved aluminum, copper, nickel and zinc.

Notification Threshold

Bioavailability of metals released from mineral deposits is complex and dependent on many interrelated chemical, biological and environmental processes (John and Leventhal, 1995). However, the preliminary analysis of the fate and transport of metals in the Upper Animas River basin provides a meaningful baseline from which to proceed with establishing an interim alert notification. Regression analysis using pH and other dissolved metals has demonstrated a relatively convincing association that when pH is lowed somewhere around 5.3-5.0 or below more dissolved metals will become potentially available, which could put downstream agricultural, recreational and water supply users at risk for exposure to heavy metal toxicity.

The WQCD recommends a cautious approach to setting the initial notification threshold at this site. In accordance with this recommendation, a pH that falls below 5.3 at USGS gage 09359020 on the Animas River below Silverton will activate a verification site visit.

Notification threshold = 5.3 pH

The verification site visit will involve directly measuring pH with a handheld, multi-parameter water quality sonde. If the pH value continues to exceed the threshold then an alert notification will be issued to collaborating emergency response agencies.

5. NEW AND MODIFIED THRESHOLDS

The WQCD will continue to collect instantaneous measurements and grab samples at USGS stations 09358550 and 09359020 into the near future. Additional field and laboratory data will be used to fine-tune the interim notification thresholds.

The WQCD will also collect instantaneous measurements and grab samples on the Animas River in Durango at USGS station 09361500. If deemed necessary, a notification threshold(s) will be developed exclusive to this location.

All notification thresholds may be subject to adjustment or termination at any time based on new data, evolving health risk analysis, new circumstances that may arise, or specific observations or events witnessed by local emergency response agencies.

6. REFERENCES CITED

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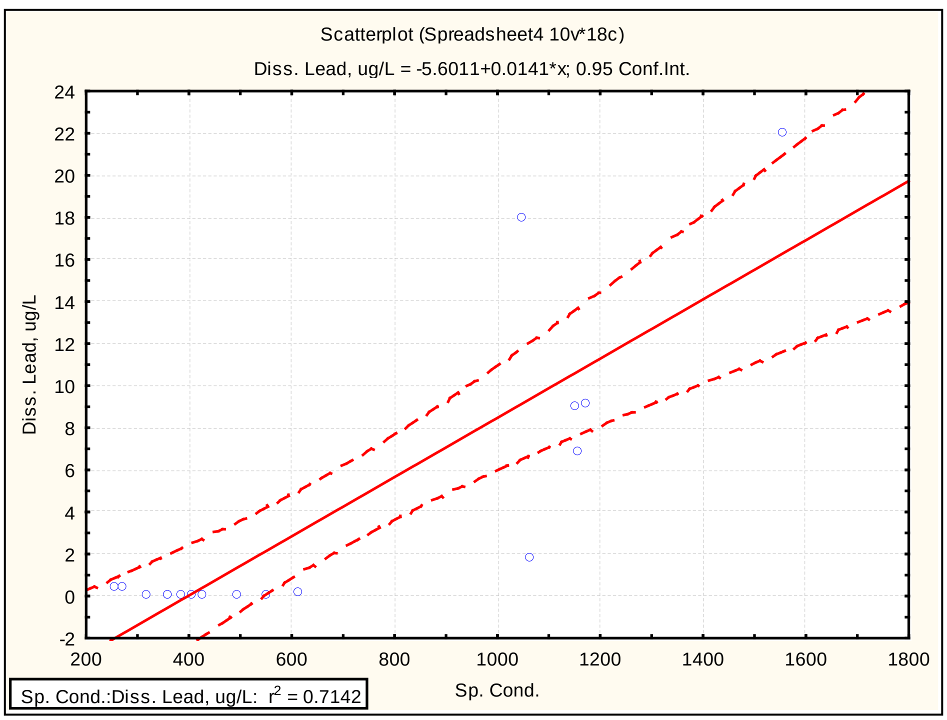
APPENDIX A – CEMENT CREEK DATA AND REGRESSION GRAPH

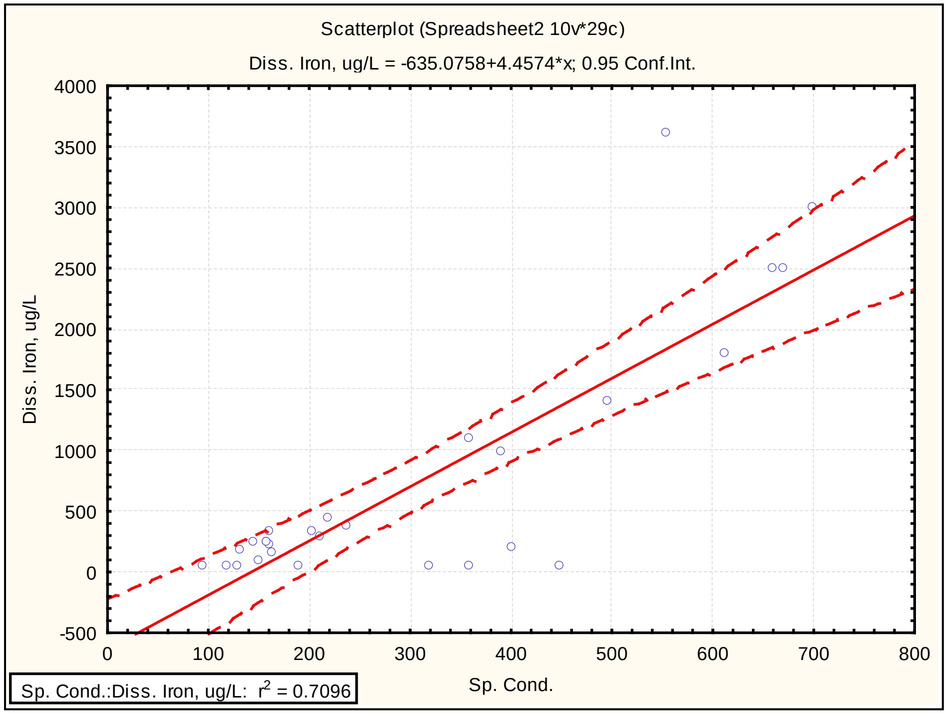
Station	Description	Lat	Long	Date	Time	Sp. Cond.	Lead, Dissolved (ug/L)
9488	Animas River above Cement Creek	37.81109	-107.65932	8/11/2015	9:35	496.7	0.065
9487	Animas River above Mineral Creek	37.80402	-107.66477	8/11/2015	10:20	554	0.065
82	Animas River near Silverton	37.79700	-107.66940	8/11/2015	11:05	612.5	0.21
AN72	Animas River at gage	37.78977	-107.66755	8/11/2015	13:10	1173	9.1
9456	Cement Creek below Gold King Mine	37.89397	-107.64786	8/15/2015	9:53	1155.6	6.9
9458	Cement Creek above Gold King Mine	37.89605	-107.64696	8/15/2015	10:09	1152.5	9
9488	Animas River above Cement Creek	37.81109	-107.65932	8/15/2015	11:05	259.08	0.37
CEM49	Cement Creek above Animas River	37.80999	-107.66069	8/15/2015	11:46	405.09	0.0385
9487	Animas River above Mineral Creek	37.80402	-107.66477	8/15/2015	12:20	358.05	0.0385
9447	Mineral Creek above Animas River	37.80282	-107.67282	8/15/2015	12:44	361.74	0.0385
AN72	Animas River at gage	37.78977	-107.66755	8/15/2015	13:08	1557	22
82	Animas River near Silverton	37.7902	-107.66757	10/13/2015	10:45	1066	1.8
82	Animas River near Silverton	37.7902	-107.66757	12/1/2015	10:45	274.8	0.39
82	Animas River near Silverton	37.7902	-107.66757	2/23/2016	9:45	1050	18
CEM49	Cement Creek above Animas River	37.80999	-107.66069	10/13/2015	13:00	428.7	0.0385
CEM49	Cement Creek above Animas River	37.80999	-107.66069	12/1/2015	12:30	318.6	0.0385
CEM49	Cement Creek above Animas River	37.80999	-107.66069	2/23/2016	23:45	384.2	0.0385



APPENDIX B – UPPER ANIMAS RIVER BASIN DATA AND REGRESSION GRAPHS

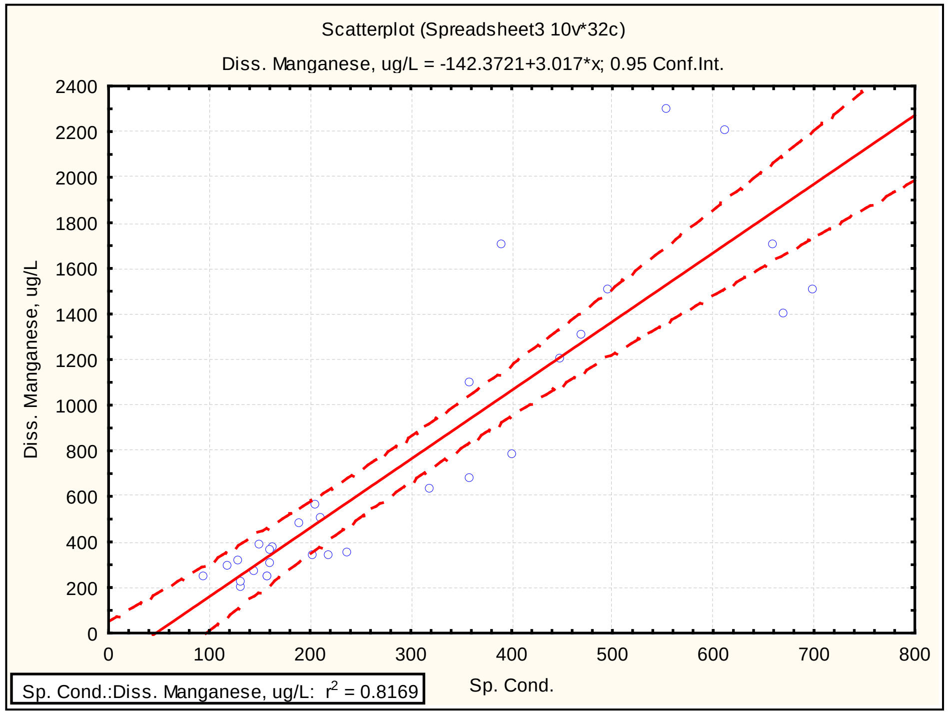
Specific Conductance and Dissolved Iron Regression Analysis

Station	Description	Date	Sp. Cond.	Dissolved Iron (ug/L)
82	Animas River near Silverton	6/9/1988	120	50
82	Animas River near Silverton	3/7/1989	450	50
82	Animas River near Silverton	4/24/1989	190	50
82	Animas River near Silverton	6/29/1989	150	100
82	Animas River near Silverton	5/30/1989	96	50
82	Animas River near Silverton	4/19/1990	320	50
82	Animas River near Silverton	5/2/1990	360	50
82	Animas River near Silverton	3/5/1990	400	200
82	Animas River near Silverton	6/14/1990	130	50
82	Animas River near Silverton	4/30/1992	220	440
82	Animas River near Silverton	4/18/2000	359	1100
82	Animas River near Silverton	6/5/2000	159	240
82	Animas River near Silverton	3/21/2001	660	2500
82	Animas River near Silverton	5/16/2001	161	230
82	Animas River near Silverton	3/13/2002	699	3000
82	Animas River near Silverton	5/15/2002	238	370
82	Animas River near Silverton	3/10/2003	672	2500
82	Animas River near Silverton	5/20/2003	203	340
82	Animas River near Silverton	4/5/2004	390	990
82	Animas River near Silverton	6/21/2004	164	160
82	Animas River near Silverton	5/26/2005	133	180
82	Animas River near Silverton	6/9/2005	158	240
82	Animas River near Silverton	5/24/2006	145	250
82	Animas River near Silverton	6/21/2006	212	280
82	Animas River near Silverton	5/15/2007	161	340
82	Animas River near Silverton	10/13/2015	496.7	1400
82	Animas River near Silverton	12/1/2015	554	3600
82	Animas River near Silverton	2/23/2016	612.5	1800



Specific Conductance and Dissolved Manganese Regression Analysis

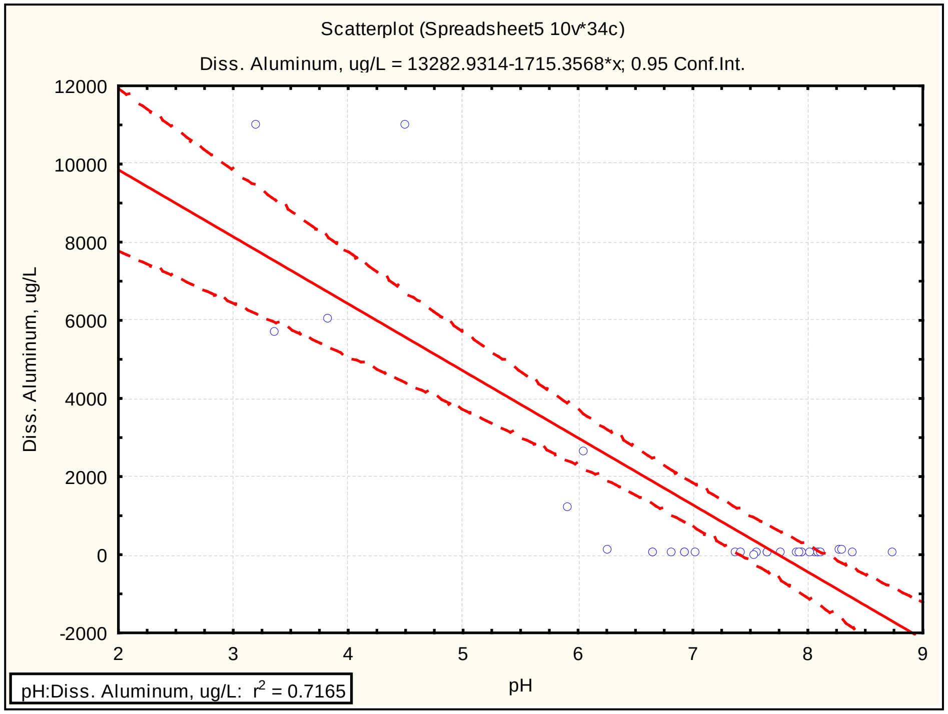
Station	Description	Date	Sp. Cond.	Dissolved Manganese (ug/L)
82	Animas River near Silverton	6/9/1988	120	290
82	Animas River near Silverton	3/7/1989	450	1200
82	Animas River near Silverton	4/24/1989	190	480
82	Animas River near Silverton	6/29/1989	150	390
82	Animas River near Silverton	5/30/1989	96	250
82	Animas River near Silverton	4/19/1990	320	630
82	Animas River near Silverton	5/2/1990	360	680
82	Animas River near Silverton	3/5/1990	400	780
82	Animas River near Silverton	6/14/1990	130	320
82	Animas River near Silverton	4/30/1992	220	340
82	Animas River near Silverton	4/15/1999	470	1300
82	Animas River near Silverton	5/20/1999	207	560
82	Animas River near Silverton	6/17/1999	131	200
82	Animas River near Silverton	4/18/2000	359	1100
82	Animas River near Silverton	6/5/2000	159	240
82	Animas River near Silverton	3/21/2001	660	1700
82	Animas River near Silverton	5/16/2001	161	300
82	Animas River near Silverton	3/13/2002	699	1500
82	Animas River near Silverton	5/15/2002	238	350
82	Animas River near Silverton	3/10/2003	672	1400
82	Animas River near Silverton	5/20/2003	203	340
82	Animas River near Silverton	4/5/2004	390	1700
82	Animas River near Silverton	6/21/2004	164	370
82	Animas River near Silverton	5/26/2005	133	220
82	Animas River near Silverton	6/9/2005	158	240
82	Animas River near Silverton	5/24/2006	145	270
82	Animas River near Silverton	6/21/2006	212	500
82	Animas River near Silverton	5/15/2007	161	360
82	Animas River near Silverton	10/13/2015	496.7	1500
82	Animas River near Silverton	12/1/2015	554	2300
82	Animas River near Silverton	2/23/2016	612.5	2200

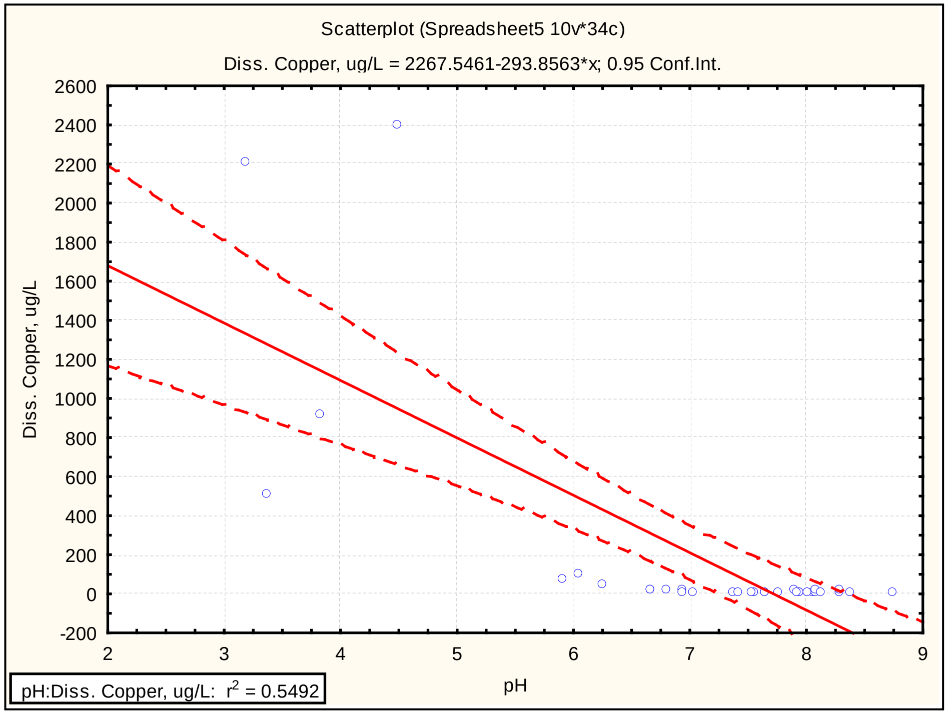


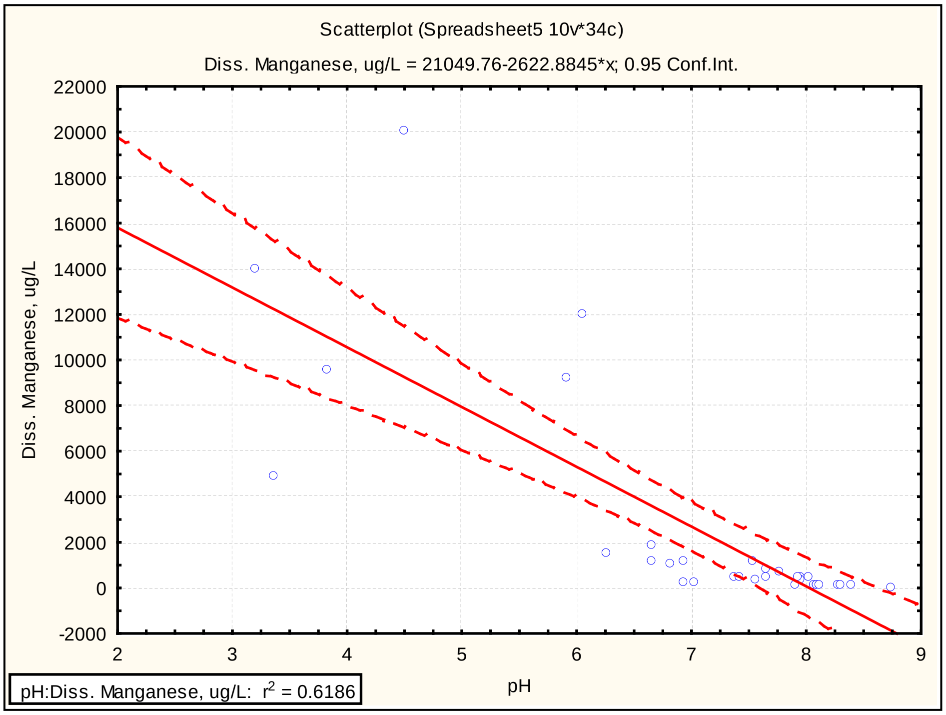
pH and Dissolved Metals Regression Analysis

Station	Description	Latitude	Longitude	Date	Time	PH	Diss. Aluminum (ug/L)	Diss. Copper (ug/L)	Diss. Manganese (ug/L)	Diss. Nickel (ug/L)	Diss. Zinc (ug/L)
66	Animas River at Bondad	37.05095	-107.87509	8/10/2015	13:05	8.74	34	1.95	20	0.55	1.15
9423A	Animas River at 9th St bridge	37.27366	-107.88544	8/10/2015	14:20	8.07	25	1.95	110	0.55	28
9421	Animas River at Lightner Creek	37.26825	-107.88613	8/10/2015	15:15	8.09	25	1.95	120	0.55	39
9488	Animas River above Cement Creek	37.81109	-107.65932	8/11/2015	9:35	7.77	33	1.95	740	0.55	240
9487	Animas River above Mineral Creek	37.80402	-107.66477	8/11/2015	10:20	6.66	56	11	1800	8.5	990
82	Animas River near Silverton	37.79700	-107.66940	8/11/2015	11:05	6.81	12	11	1000	5	550
AN72	Animas River at gage	37.78977	-107.66755	8/11/2015	13:10	6.94	9.6	13	1100	2.75	560
9438	Animas River above James Ditch	37.44422	-107.80399	8/12/2015	11:59	7.37	68	1.95	420	2.75	110
9438A	James Ditch at intake	37.44362	-107.80498	8/12/2015	12:06	7.42	48	1.95	420	2.75	110
9438A	James Ditch at intake	37.44360	-107.80493	8/12/2015	12:13	7.56	22	1.95	370	2.75	47
9438A	James Ditch at intake	37.44359	-107.80497	8/12/2015	12:29	7.66	26	1.95	430	2.75	36
9438B	James Ditch at James Ranch	37.42678	-107.81502	8/12/2015	13:42	8.28	77	1.95	140	2.75	5.3
81	Animas River at Bakers Bridge	37.45844	-107.79976	8/12/2015	14:40	8.02	48	1.95	430	0.55	90
9438A	James Ditch at intake	37.44352	-107.80501	8/12/2015	15:20	7.95	58	1.95	440	2.75	120
9423A	Animas River at 9th St bridge	37.27366	-107.88544	8/13/2015	8:50	7.91	68	14	98	0.55	26
9421	Animas River at Lightner Creek	37.26825	-107.88613	8/13/2015	9:35	8.09	38	14	110	0.55	39
9420	Animas River below Durango WWTF	37.25933	-107.87778	8/13/2015	10:35	8.3	130	19	100	0.55	32
9456	Cement Creek below Gold King Mine	37.89397	-107.64786	8/15/2015	9:53	3.2	11000	2200	14000	37	11000
9458	Cement Creek above Gold King Mine	37.89605	-107.64696	8/15/2015	10:09	5.91	1200	73	9200	15	5100
9488	Animas River above Cement Creek	37.81109	-107.65932	8/15/2015	11:05	7.66	60	1.95	760	0.55	270
CEM49	Cement Creek above Animas River	37.80999	-107.66069	8/15/2015	11:46	3.38	5700	500	4900	12	3500
9487	Animas River above Mineral Creek	37.80402	-107.66477	8/15/2015	12:20	6.26	77	48	1500	3	1000
9447	Mineral Creek above Animas River	37.80282	-107.67282	8/15/2015	12:44	7.03	38	1.95	250	1.4	140
AN72	Animas River at gage	37.78977	-107.66755	8/15/2015	13:08	6.67	21	14	1200	2.6	620
9420	Animas River below Durango WWTF	37.25933	-107.87778	8/15/2015	18:19	8.39	38	1.95	83	2.75	47
9423A	Animas River at 9th St bridge	37.27456	-107.88427	8/15/2015	19:00	8.12	34	1.95	99	0.55	67
9426	Animas River at Trimble Bridge	37.38474	-107.83748	8/15/2015	20:00	6.93	27	1.95	260	0.55	140
81	Animas River at Bakers Bridge	37.45852	-107.79969	8/15/2015	20:43	7.95	62	4.4	370	1.2	120
9458	Cement Creek above Gold King Mine	37.89605	-107.64696	8/18/2015	10:15	6.06	2600	94	12000	25	6700
9485	Animas River above Elk Creek	37.72196	-107.65468	8/18/2015	10:15	7.54	1	1.95	1100	2.7	490

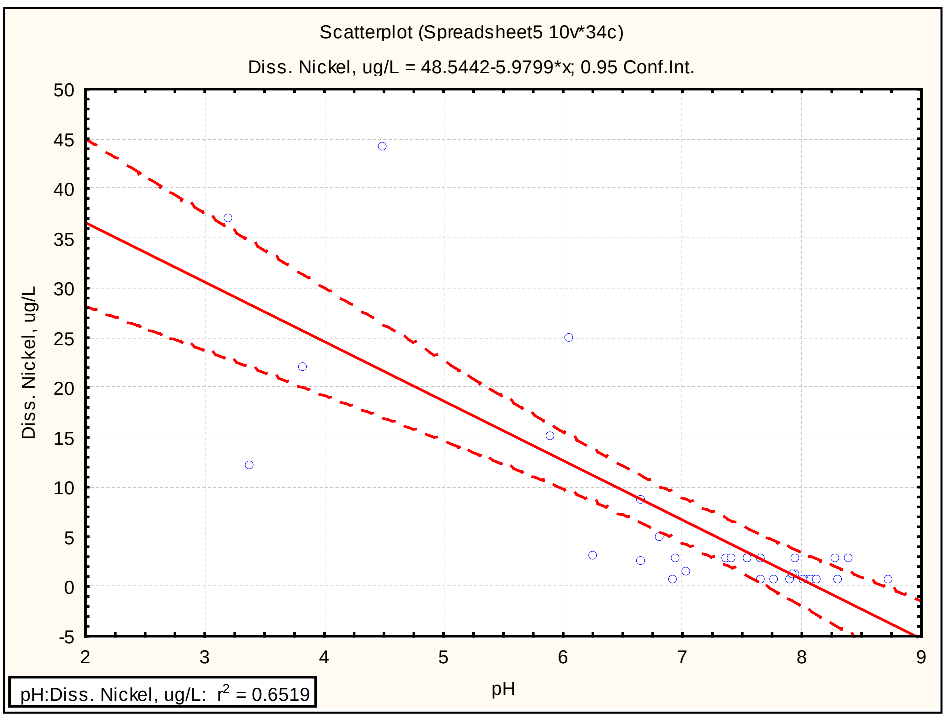
Station	Description	Latitude	Longitude	Date	Time	PH	Diss. Aluminum (ug/L)	Diss. Copper (ug/L)	Diss. Manganese (ug/L)	Diss. Nickel (ug/L)	Diss. Zinc (ug/L)
9456	Cement Creek below Gold King Mine	37.89397	-107.64786	8/18/2015	10:45	4.5	11000	2400	20000	44	13000
9454	Cement Creek at Ski Resort	37.88480	-107.66526	8/18/2015	12:20	3.83	6000	910	9500	22	6100
81	Animas River at Bakers Bridge	37.45852	-107.79969	8/18/2015	14:20	7.93	23	1.95	440	1.2	110



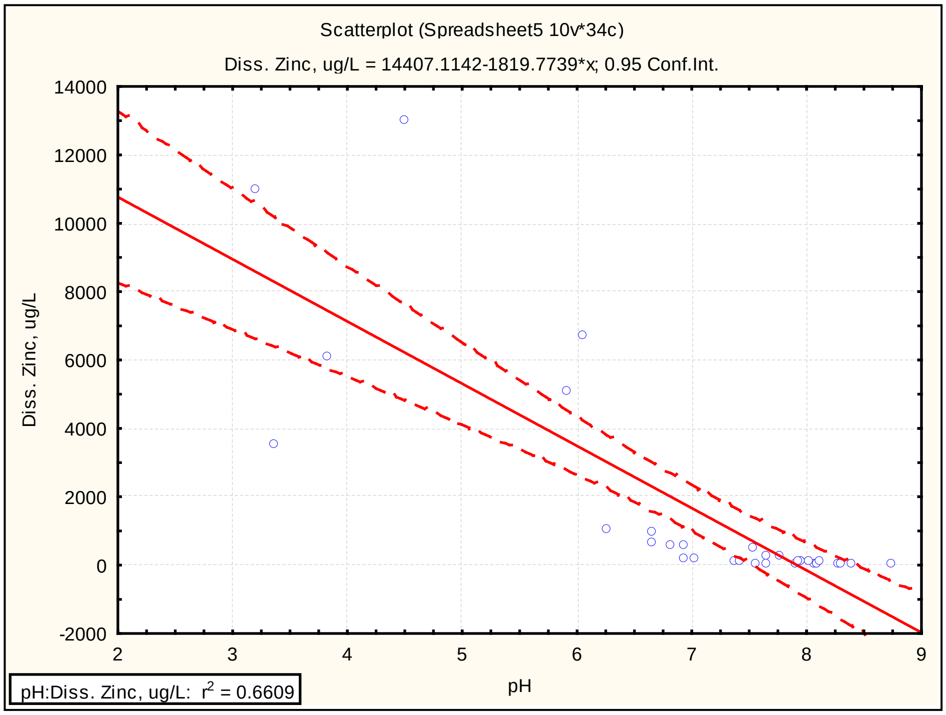




Scatterplot (Spreadsheet5 10v*34c)
Diss. Manganese, ug/L = 21049.76-2622.8845*x; 0.95 Conf.Int.
Diss. Manganese, ug/L
pH
pH:Diss. Manganese, ug/L: r2 = 0.6186



Scatterplot (Spreadsheet5 10v*34c)
Diss. Nickel, ug/L = 48.5442-5.9799*x; 0.95 Conf.Int.
Diss. Nickel, ug/L
pH
pH:Diss. Nickel, ug/L: r2 = 0.6519



Scatterplot (Spreadsheet5 10v*34c)
Diss. Zinc, ug/L = 14407.1142-1819.7739*x; 0.95 Conf.Int.
Diss. Zinc, ug/L
14000
12000
10000
8000
6000
4000
2000
0
-2000
2
3
4
5
6
7
8
9
pH
pH:Diss. Zinc, ug/L: r2 = 0.6609