Friends of Corte Madera Creek Watershed
P.O. Box 415 • Larkspur • California 94977
info@friendsofcortemaderacreek.org (415) 456-5052 www.friendsofcortemaderacreek.org

Memorandum
Iron and Manganese Levels in Ross Creek, Summer 2011

December 2011

1. Introduction

Ross Creek begins below the dam forming Phoenix Lake, Marin County and flows 1.5 miles to its confluence with San Anselmo Creek to form Corte Madera Creek. In winter and early spring, most of the water in the creek comes over the dam's spillway, but in summer and fall, the creek is fed, at a modest rate, from groundwater inputs and by a leaky low-level release valve at the base of the dam. The water from the low-level release valve emerges from a concrete vault at the base of the dam. Figure 1 shows the locations of the vault, spillway, and dam.

During low summer flows, the upstream 100 to150 feet of the creek contains water that is cloudy and scum covered, rocks in the water are covered with orange deposits and filaments, and at times floccules of orange material are suspended in the slow-moving water. Further downstream, the orange material is absent, but the rocks are covered with thin black deposits. We suspected that these materials might be having a significant effect on the creek's aquatic life. In an attempt to determine the composition of these materials, and thus their possible effects, samples were taken at four locations in the creek during the summer of 2011 and analyzed for total iron (Fe) and total manganese (Mn).

Elevated levels of iron and manganese in the water along with the orange and black deposits suggest that iron and manganese bacteria contribute to the observed conditions (Washington County Department of Public Health and Environment Undated, downloaded 2011). Iron bacteria oxidize iron dissolved in water to form ferric hydroxide [$Fe(OH)_3$], which is often accompanied by orange slime. Manganese bacteria work in a similar fashion, by oxidizing manganese in the water; when manganese reacts with oxygen, the residue formed is dark (black or gray) (South Carolina Department of Health and Environmental Control. Undated, downloaded 2011). Iron and manganese bacteria require water containing at least 0.2 milligrams per liter (mg/L) of iron or manganese, pH between 6.0 and 8.0, temperatures of 45-60° F, and a source of carbon such as calcium carbonate (water hardness) or dissolved carbon dioxide. They also require some oxygen. These conditions are found in Ross Creek during the summer (Washington County Department of Public Health and Environment, undated, downloaded 2011). Direct oxidation of iron and manganese can also occur, but the orange filaments suggest that iron bacteria may be significant contributors.

1.1 Iron in Surface Waters

Excess waterborne iron may be toxic to fish due to the formation of iron 'flocs' on the gills, resulting in gill clogging and disturbed respiration (Bury *et al.* 2002). Peuranen *et al.* (1994) reported damage to gills (staining and fusion of the lamellae) from Fe concentrations of 200 μg/l. Formation of iron precipitates suffocates eggs, induces avoidance behaviors in fish, and degrades the quality of benthic habitats (Vuori 1995).

The EPA chronic criterion for iron in fresh surface waters is 1,000 μg/l. This refers to the average concentration for 96 hours (4 days) this criterion should not be exceeded more than once every three years (EPA 2011). There is no EPA criterion for acute levels of iron. The Canadian Water Quality Guidelines for the Protection of Aquatic Life call for Fe content to be less than 300 μg/l (CCME 2007). We have not found a statement as to whether this is an acute or a chronic criterion.

1.1 Manganese in Surface Waters

Tests reported by Howe et al. (2004) document mortality of half of the coho salmon (*Oncorhynchus kisutch*) exposed for 96 hours to 2400 μg of manganese per liter. Significant embryonic mortality was observed in rainbow trout (*Oncorhynchus mykiss*) eggs exposed to 1000 μg manganese sulfate per liter for 29 days and increased mortality of rainbow trout at a hatchery was found to be positively correlated with manganese concentrations ranging from <500 to 1000 μg/l (Howe *et al.* 2004).

The Province of British Columbia has established two criteria for Mn, one for chronic harm and the other for acute harm. Because Mn is more harmful in soft water than in hard, the criteria are expressed as functions of two variables, the hardness of the water and Mn concentration. The EPA has no published standards for Mn in streams.

To protect freshwater aquatic life from **chronic** effects, the average concentration of total manganese in mg/l[1] should not exceed the value as given by the following relationship:

Average Mn Concentration (mg/l) less than or equal to 0.0044 H + 0.605

To protect freshwater aquatic life from **acute and lethal** effects, the maximum concentration of total manganese in mg/L at any time should not exceed the value as determined by the following relationship:

Maximum Mn Concentration (mg/l) less than or equal to 0.01102 H + 0.54

In these relationships, the quantity H represents water hardness measured in units of mg/l expressed as $CaCO_3$. Table 1 presents some calculated Mn values at different H values.

Table 1: Examples of the Recommended British of Columbia Guidelines to Protect Freshwater Aquatic Life from the Toxic Effects of Manganese

Water Hardness as $CaCO_3$	Guideline (total Mn in mg/l)
Maximum Concentration	**Acute Guideline**
25 mg/L	0.8
50 mg/L	1.1
100 mg/L	1.6
150 mg/L	2.2
300 mg/L	3.8

[1] 1 mg/l = 1000 μg/l

Table 1: Examples of the Recommended British of Columbia Guidelines to Protect Freshwater Aquatic Life from the Toxic Effects of Manganese (continued)

30-day Mean Concentration	Chronic Guideline
25 mg/L	0.7
50 mg/L	0.8
100 mg/L	1.0
150 mg/L	1.3
300 mg/L	1.9

2. Setting and Methods

In the summer months, Ross Creek receives water from two sources, the leaky low-level valve at the base of the Phoenix Lake Dam and groundwater inputs. The concrete vault was designed to dissipate excessive turbulence when the valve is open. The water leaving the vault is clear, but the wetted surfaces of the exterior of the vault are covered with orange deposits. This water comes from the bottom of the lake (at a depth of 35-40 feet). Between the vault and the next sampling location 45 feet downstream, the stream flow is increased by water seeping from the bottom of the dam. There are additional groundwater inputs downstream. A small perennial stream enters Ross Creek between the third and fourth sampling stations. When the first samples were taken on 6/30/2011 water was flowing briskly over the spillway; by 7/17/11, the flow over the spillway was a trickle; and flow had ceased by the time the sample was taken on 7/23/11.

Samples were collected at four locations, covering some 1,600 feet of Ross Creek (see Figure 2, at the end of the memo). At the vault, samples were taken from the water flowing over edge of the concrete vault (see Figure 3). At the other three sampling locations, water was taken from the creek. The flow in the creek was so low that all the samples were necessarily taken near to the surface of the stream. The condition of the water at RC1 on 9/23/11 is shown on Figure 4.

3. Results

The analytical results for the samples are presented in Table 2 and Figures 5 and 6. The Fe content of the water from all sample locations significantly exceeded the Canadian standards' upper limit of 300 m/l. However, these results show concentrations of Fe and Mn varying substantially, with Fe showing the more dramatic fluctuation. There are not enough data to permit any meaningful statistical analysis to be made, but the numbers suggest that the groundwater input picked up between the vault and sampling location RC1, 45 feet downstream, is contributing significant loads of Fe and Mn to the stream flow, which causes the concentrations to become extremely high during the dry summer months. It seems plausible that this groundwater is dominated by seepage through the earthen dam.

The concentrations of Fe decline steadily and fairly quickly as water moves down the creek, but the Fe still remains well above the Canadian guidelines. The background Fe concentration at Creek Park, located on San Anselmo Creek, upstream of the confluence of San Anselmo Creek and Ross Creek, is lower than that in Ross Creek, but not radically so and it also exceeds the Canadian standard. The Mn declines, but not consistently. The Mn levels in San Anselmo Creek are well below those in Ross Creek.

These results suggest that the biota in the creek would benefit if the current levels of Fe and Mn were reduced, certainly in summer and possibly year round. These conclusions would be more robust if the sampling program were extended for at least one more summer and water hardness were tested. It would be useful to know the flow at each site, to evaluate the relative contribution of flow from different sources.

Table 2: Results of 2011 Fe and Mn Testing

		Water over spillway?	Vault	RC1	RC1.25	RC1.5	SA Creek at Creek Park
Latitude			37.955862	37.955746	37.955742	37.959020	
Longitude			-122.574989	-122.574541	-122.573616	-122.572293	
Dist from Vault (ft)			-	45	525	1,600	N/A
Fe (µg/l)	6/30/11	Yes	9,700	1,500	780	670	560
Fe (µg/l)	7/23/11	No	9,300	160,000	1,400	990	
Fe (µg/l)	8/29/11	No	18,000	150,000	9,900	1,500	
Mn (µg/l)	6/30/11	Yes	2,300	290	210	Not Detected	37
Mn (µg/l)	7/23/11	No	2,200	5,400	350	140	
Mn (µg/l)	8/29/11	No	7,200	5,700	5,800	200	

Note:
6/27/11 spillway flowing briskly
7/8/11 moderate flow over spillway
7/17/11 spillway at a trickle

Exceeds EPA standards for Fe causing chronic harm (1000 µg/l)
Exceeds Canadian standards for Fe (300 µg/l)
Exceeds British Columbia standards for Mn causing chronic harm at H = 50 mg/l $CaCO_3$ (800 µg/l)

4. Conclusions

a. The measured Fe and Mn concentrations in Ross Creek within ~1,600 feet of the dam forming Phoenix Lake are undesirably high. They trend to a level about double that recommended for Fe in Canada.

b. The rough background concentration of Fe, as measured at in a single sample taken from San Anselmo Creek upstream of its confluence with Ross Creek, is close to double the Canadian recommended upper limit, but within the EPA standards. This value may be a typical Fe concentration for natural streams in Marin County, but that needs to be confirmed by additional sampling.

c. At relatively high concentrations, Fe can scavenge oxygen from water, depending on the initial oxidation state of the Fe ions. The same is true of Mn. These effects could be significant as both Fe and Mn have ionic forms that are soluble at low oxidation states and are susceptible to further oxidation at ambient temperatures. Fe and Mn are almost certainly harmful to fish in other ways at the concentrations found in upper Ross Creek in the summer. This is troubling because Ross Creek has a population of *O. mykiss*. The perennial reach of Ross Creek, located in the upper portion of the creek, is only about twice the length of the reach sampled. The downstream reach of the creek dries in the summer, typically between mid-May and mid-June, depending on the timing and amount of rainfall. Simply put, much of Ross Creek where there is perennial flow has Fe and Mn levels likely to be harmful to salmonids; where the water quality would likely be good enough to support salmonids in the summer, the stream is dry.

d. If and when the water release mechanism for the dam at Phoenix Lake is reconstructed, considerations of fish protection should guide efforts to reduce the levels of heavy metals (including Fe and Mn, of course) in Ross Creek.
e. The sampling results obtained on Ross Creek in the summer of 2011 are of interest and utility but are very sparse. Efforts should be made continue them in 2012 and preferably longer.

5. References Cited

British Columbia. 2008. *Ambient Aquatic Life Guidelines for Iron*. Overview Report. Water Stewardship Division, Ministry of Environment, Province of British Columbia, March 2008.

British Columbia. 2001. *Ambient Aquatic Life Guidelines for Manganese*. Overview Report. Water Stewardship Division, Ministry of Environment, Province of British Columbia, January 2001.

Bury, N.R., P.A. Walker, and C. Glover. 2002. Nutrient uptake in teleost fish. *Journal of Experimental Biology*. v. 206, 11-23.

Canadian Council of Ministers of the Environment (CCME) 2007. Canadian water quality guidelines for the protection of aquatic life. This document is available on the CCME Internet site (http://www.ccme.ca/assets/pdf/aql_summary_7.1_en.pdf).

Dalzell, D.J.B. and N.A.A. MacFarlane. 1999. The toxicity of iron to brown trout and effects on the gills: a comparison of two grades of iron sulphate. *Journal of Fish Biology*, Volume 55, Issue 2, pages 301–315, August 1999.

EPA. 2011. http://water.epa.gov/scitech/swguidance/standards/current/index.cfm#nonpriority

Howe, P.D., H.M. Malcolm, and D. Dobson. 2004. *Manganese and its Compounds: Environmental Aspects*. Concise International Chemical Assessment Document 63. World Health Organization. Geneva, Switzerland.

Peuranen, S., P.J. Vuorinen, and A. Hollander, 1994. The effects of iron, humic acids and low pH on the gills and physiology of brown trout (*S. trutta*). *Ann. Zool. Fennici*, 31: 389–396

South Carolina Department of Health and Environmental Control. Undated. Iron and Manganese. http://www.scdhec.gov/environment/water/dwor/docs/Iron&Magn.pdf

United States Environmental Protection Agency (EPA). 2002. *National recommended water quality criteria*. This document is available on the EPA Internet site (http://www.epa.gov/waterscience/pc/revcom.pdf).

Vuori, K. 1995. The Direct and indirect effects of iron on river ecosystems, *Ann Zool. Fennici* v. 32 p. 317-329.

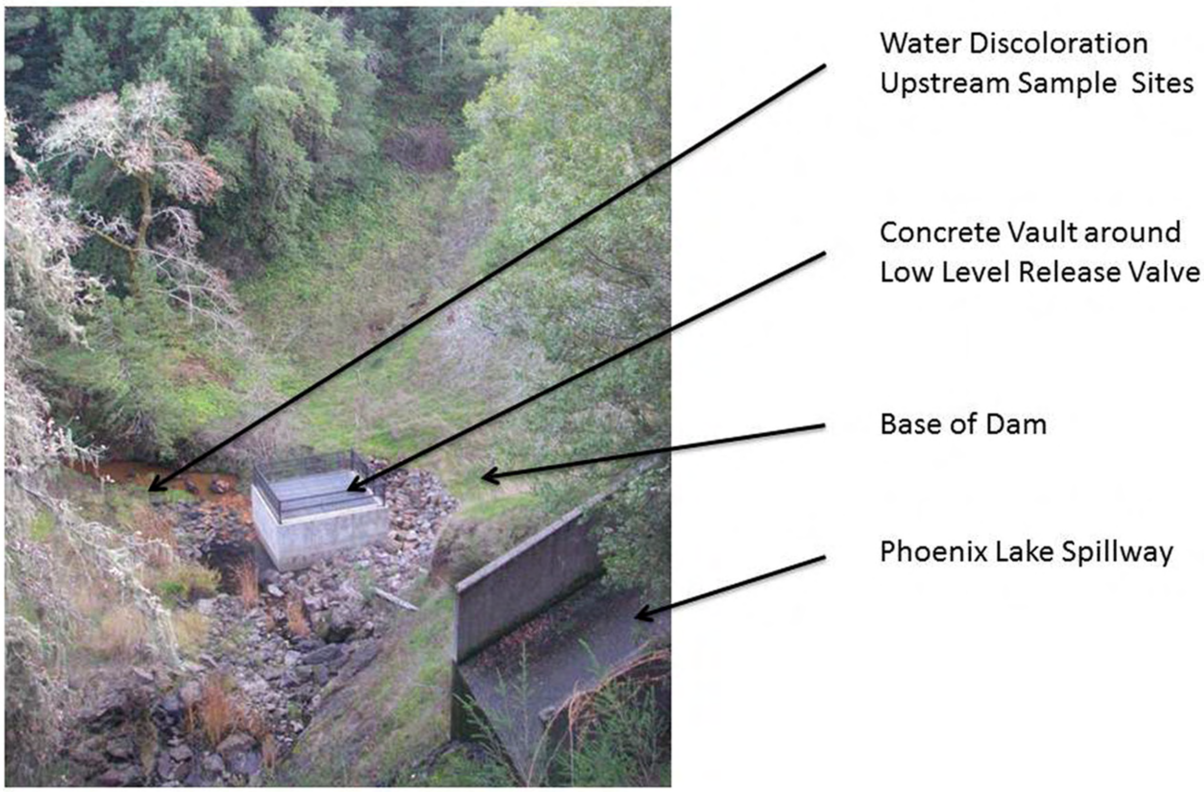
Washington County, Minnesota. Undated. Fact Sheet: Iron Bacteria. http://www.co.washington.mn.us/_asset/7j10tw/ENV-IronBacteria.pdf

Acknowledgements

Destiny Elston, a student at UC Santa Cruz, took the samples, made sure they were delivered to the lab for analysis, and did preliminary research on the effects of iron and manganese on salmonids. Thank you Destiny, for your excellent work.

Gerhard Epke reviewed the draft and provided valuable comments. He also took the photo in Figure 1.

Figure 1: View of Ross Creek headwaters from Phoenix Lake Road



Source: Gerhard Epke

Figure 2: Map of Sampling Sites

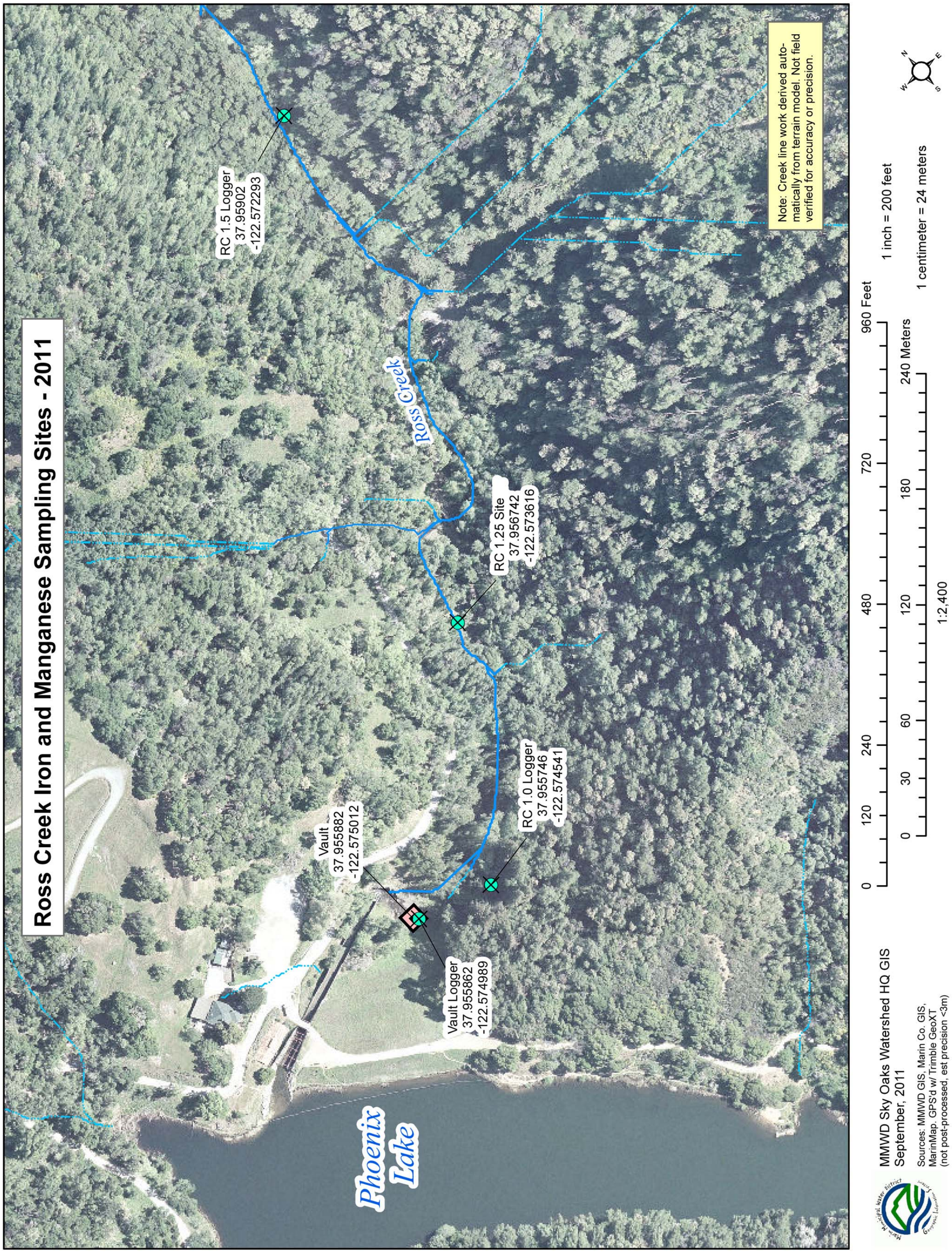


Figure 3: Vault on 9/23/11

Figure 4: Site RC1 on 9/23/11

Photos by Sandra Guldman

Figure 5: Iron in Ross Creek

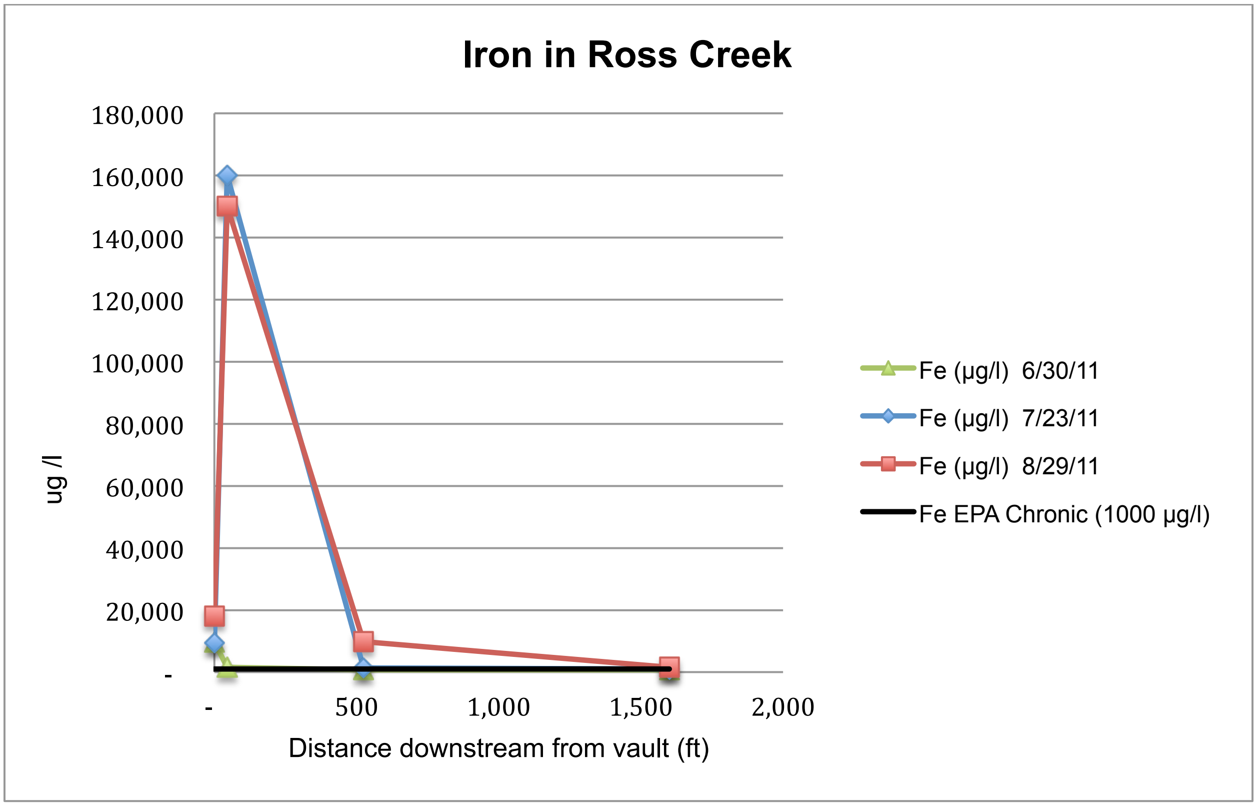


Figure 6: Manganese in Ross Creek