Appendix M
Metals Analysis

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PURPOSE OF ANALYSIS

The purpose of DEQ's analyses is to identify sources of iron, manganese, and arsenic that contribute to water quality criteria exceedances, specifically in the Pudding River (for iron and manganese) and Zollner Creek (iron, manganese, and arsenic). For these analyses, DEQ relied on U.S. Geological Survey (USGS) data from studies done between 1991 and 2001and DEQ data collected between 1991 and 2006.[1] DEQ surface water data comes from bimonthly sampling of 4th field watershed monitoring stations, and smaller-scale studies of Zollner Creek. DEQ's recent (2005 and 2006) surface water data collection represents various conditions in the Pudding River portion of the watershed, from heavily agricultural, to urban, to background.

Dissolved metals results are more common in both DEQ and USGS data sets, and are generally presented separately from total metals results. Total metals analyses may better reflect contribution of anthropogenic activities (e.g. land use that contributes to erosion and increased surface runoff to streams). DEQ samples collected in 2005 and 2006 were analyzed for total recoverable metals concentrations. In the following analyses, DEQ has treated total metals results as equivalent to total recoverable metals results and combined the results under the heading "total."

Several techniques are used to evaluate the metals concentrations and distributions. Box and whisker plots (as described in Appendix F) identify seasonal and longitudinal patterns and display concentration variability. Load duration curves (as described in Appendix F) represent the relationships between pollutant loading and stream flow. DEQ followed the methodology as described in the Appendix F(Section: Load Duration Curves) to estimate stream flow when measured flow was not available. If several samples were collected at times when neither measured nor estimated stream flow was available, DEQ plotted the measured concentration with an average subbasin-wide exceedance probability, as described in Appendix G (Section: Flow and Precipitation Relationships). The non-parametric Wilcoxon-Mann-Whitney test[2] identifies significant differences or similarities between means of different data sets, such as iron concentration in groundwater and surface water.

IRON

The greatest total and dissolved iron concentrations are associated with precipitation events and higher stream flows. Median concentrations calculated from samples collected during winter months exceed those from samples collected June – September. Iron concentrations do not indicate any temporal patterns over the period of data collection, but analyses indicate stronger differences between winter and summer samples at a site at approximately river mile 21 than at the mouth of the Pudding River.

The data indicate that the dissolved iron concentrations in the mainstem Pudding River exceed subbasin-wide dissolved iron concentrations (Table M - 1). This may be related to the low stream flow in the Pudding River in the summer months – a greater percentage groundwater contributing to summer flows. Though the median of total iron concentrations from Pudding River mainstem samples (220 ug/L) is less than the median of total iron concentrations from the sub-basinwide DEQ data set (424 ug/L), the sample size of Pudding River total iron results is small (n = 9). As well, the subbasin-wide calculation includes one sample collected from Zollner Creek with a measured total iron concentration of 11,800 ug/L. The median total iron concentration of the Pudding River samples is less than the median concentration from a site representing predominantly forestry land use, Butte Creek at Butte Creek Road (387 ug/L). Pudding River

[1] DEQ compiled USGS data from that agency's National Water Quality Information System database: http://waterdata.usgs.gov/or/nwis/qw/. DEQ data resides in the Laboratory Storage and Retrieval (LASAR) database, accessible through the internet: http://www.deq.state.or.us/. Data from one DEQ site, Molalla River at Canby, included in the basinwide calculations were collected in 1979, 1980, and 1990.

[2] Aroner, E. (1997) Water Quality/Hydrology Graphics/Analysis System, WQHYDRO, User's Manual.

dissolved iron is somewhat greater than the subbasin-wide average and total iron concentrations somewhat less than subbasin-wide concentrations.

The Zollner Creek data indicate a median total iron concentration (1,135 ug/L) that exceeds the subbasin-wide median total iron concentration (462 ug/L) by almost three times. That comparison is strongly influenced by the one Zollner Creek sample measured at 11,800 ug/L. The Zollner Creek median dissolved iron concentration (43 ug/L) is actually less than the median subbasin-wide dissolved iron concentration (90 ug/L).

Table M - 1: Summary of iron data from samples collected by DEQ and USGS.
MRL = minimum reporting limit.

	Type	Area	Number of Samples		Criteria (µg/L)	Median (µg/L)	Min. (µg/L)	Max. (µg/L)
Iron	dissolved	Subbasin-wide	374	(8<MRL)	300	90	0.05	1,100
	total		40			462	40	11,800
	dissolved	Pudding	166	(1<MRL)		152	0.1	860
	total		10			240	160	1,500
	dissolved	Zollner	84	(2<MRL)		43	0.05	1,100
	total		8			1,135	40	11,800
	total	Butte Creek at Butte Creek Rd.	5			387	184	529

EXCEEDANCES

Approximately 4% of the Pudding River samples analyzed for dissolved iron exceeded the criteria (300 ug/L), as did approximately 40% of the samples analyzed for total iron (though from a smaller data set, n = 10). Table M - 2 shows that each of the exceedances, with two exceptions, occurred within a day of rainfall that exceeded 0.3 inches[3].

The Zollner Creek data set indicates that 1% of the dissolved iron samples exceeded the criteria and 75% of the total iron samples (data set n = 8). With two exceptions, the Zollner Creek exceedances occurred within a day of at least 0.2 inches of precipitation.

Proportions of total and dissolved iron in any one sample may be related to the precipitation that fell during or before that sample's collection. For example, on three occasions (April 27, June 1 and July 27, 1993) the USGS analyzed samples for both total and dissolved iron concentrations in the Pudding River or Zollner Creek. Precipitation fell on April 27 and June 1 and the dissolved concentration was 7% of the total (total iron comprised 93% of the concentration). On July 27, no precipitation fell and the dissolved concentration was 51% of the total (total iron only comprised 49% of the sample concentration). Data from these three sampling events indicates that total iron may comprise most of the instream concentration when a precipitation event occurs. When precipitation is not occurring or has not occurred recently dissolved and total fractions are approximately evenly split.

These data indicate that when exceedances occur, they are usually, but not always, responding to a precipitation event. The exceedances that occur during dry periods may be explained by groundwater input, as discussed in the Sources and Source Categories section of this chapter.

[3] Daily precipitation data recorded at the Silverton, OR gauge: http://www.ocs.oregonstate.edu/index.html

Table M - 2: Summary of exceedances of iron criterion in Pudding River and Zollner Creek and associated precipitation on or the day before the date of sample collection.

Date of Exceedance	Dissolved (D) or Total (T)	Fe (µg/L)	Precipitation (in)
Pudding River Samples			
11/6/1979	T	1,200	0.39 on 11/5
2/7/1980	T	1,380	0.42 on 2/6
11/5/1991	D	320	0.42 (0.76 on 11/4)
2/19/1992	D	510	0.77
12/1/1992	D	310	0.34 (0.97 on 11/30)
11/10/1993	D	350	0
4/27/1993	T	1,500	0.13 (0.32 on 4/26)
10/28/1994	D	370	0.65 (3.1 on 10/27)
1/10/1995	D	310	0.75 (0.63 on 1/9)
4/20/2006	T	1,010	0
Zollner Creek Samples			
2/19/1992	D	1,100	0.77
6/1/1993	T	1,800	0.55 (0.37 on 5/31)
7/27/1993	T	570	0
2/8/2005	T	509	0.21 on 2/7
12/21/2005	T	6,970	0.68 (0.42 on 12/20)
2/28/2006	T	11,800	1.13
4/20/2006	T	424	0

TEMPORAL VARIATION

DEQ reviewed the iron concentrations over time from Pudding River and Zollner Creek sites. The data do not indicate a significant increase or decrease in iron concentrations over the time period for which data are available. Figure M - 1 and Figure M - 2 display the iron concentrations from Pudding River and Zollner Creek samples. Displaying the relatively high iron concentrations measured in Zollner Creek in 2005 (Figure M - 1) masks the variation in the remaining sample results. Figure M - 2 reduces the maximum scale so that variability is more discernable.

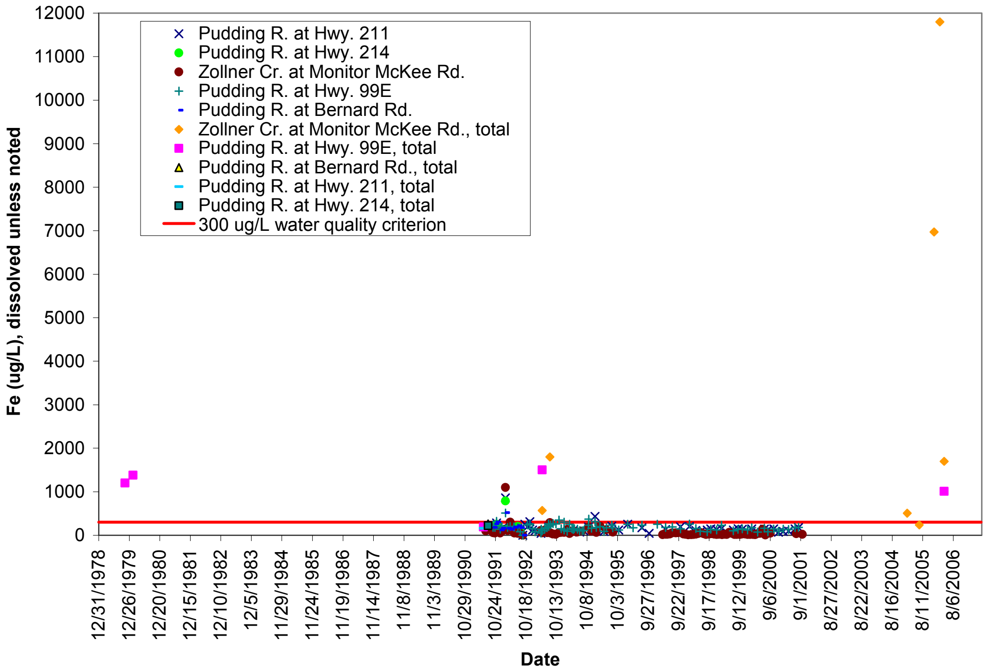

Figure M - 1: Iron concentrations in Pudding River and Zollner Creek.

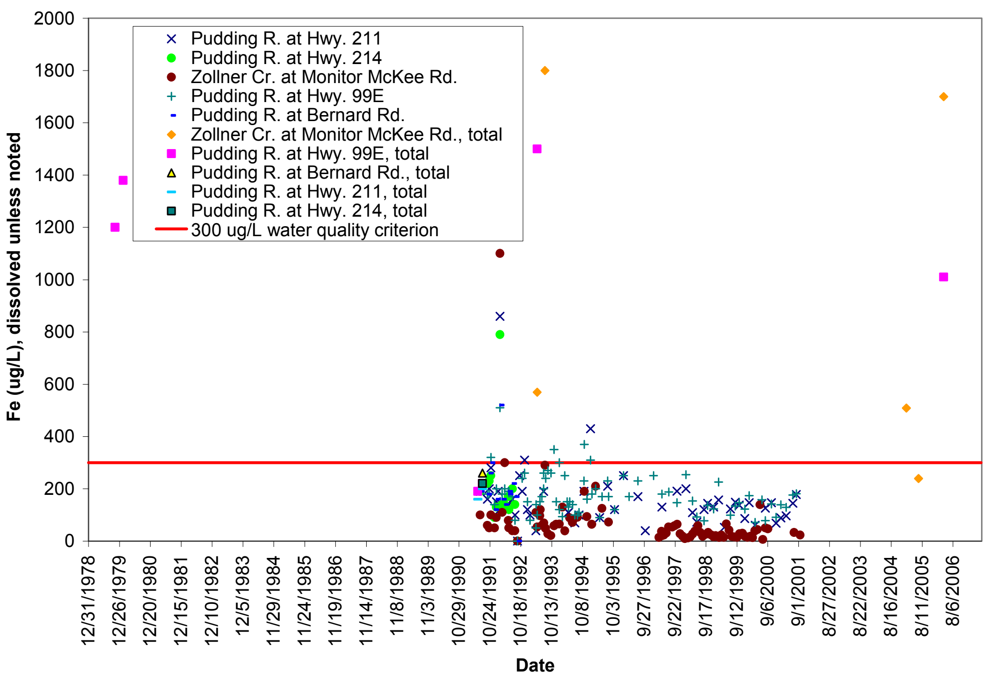

Figure M - 2: Iron concentrations in Pudding River and Zollner Creek, larger scale Y-axis. Two Zollner Creek samples collected in 2005 do not display on this scale. Exceedances occurred at several Pudding River sites on February 19, 1992.

LONGITUDINAL VARIATION

DEQ developed box and whisker plots of the DEQ-collected dissolved iron results to illustrate variability from upstream to downstream locations along the Pudding River. Only the DEQ data set had sufficient samples collected at multiple locations to display longitudinally. The graphical display in Figure M - 3 does not suggest a significant change in the variability or magnitude of dissolved iron concentrations with progression downstream. Sampling on Zollner Creek has been predominantly at one site and did not provide sufficient data for a longitudinal comparison.

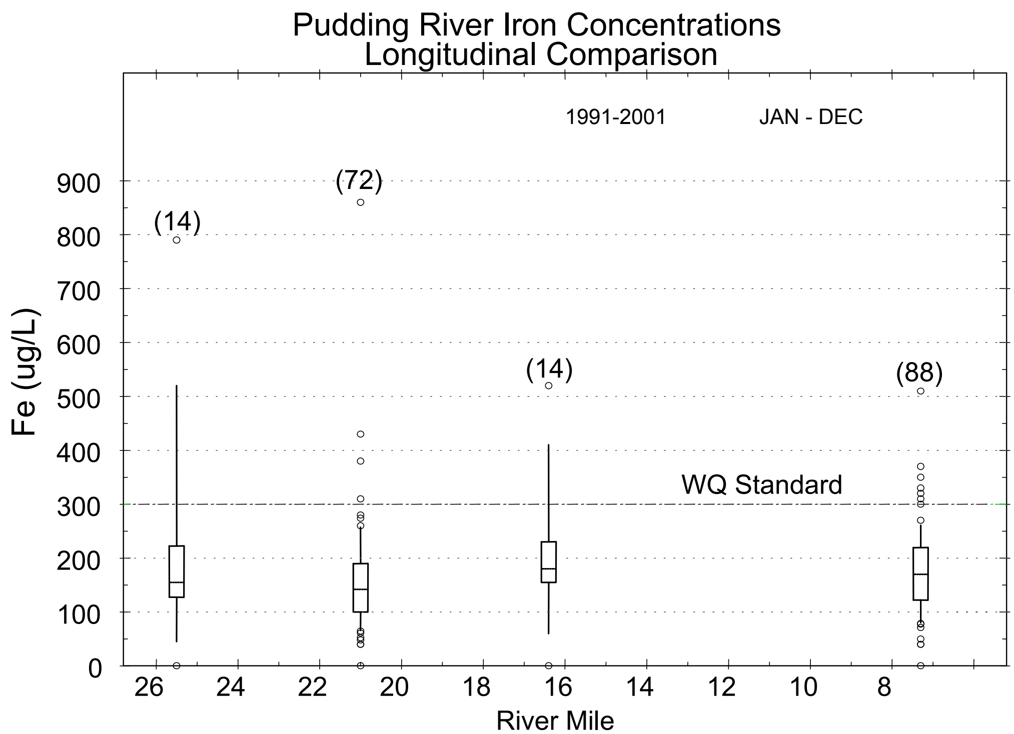

Figure M - 3: Variation in dissolved iron concentrations (DEQ collected data) between and within four Pudding River sites.

SEASONALITY

DEQ used box and whisker plots to discern any relationship between seasons and iron concentrations in the Pudding River and Zollner Creek. Figure M - 4 and Figure M - 5 indicate significant differences in iron concentration among seasons as well as between two sites on the Pudding River. The Pudding River at Woodburn site (Figure M - 4) is located at approximately river mile 21 and the data collected here indicate the median dissolved iron concentration during at least one season is significantly different from at least one of the others (at the 99% confidence level). The first quarter (January through March) yields the highest median concentrations and variation, and the second quarter the lowest median and variation.

Figure M - 5 similarly displays these relationships among seasonal iron concentrations measured in samples collected from the Pudding River at Aurora, approximately river mile 8. While the data suggest a significant difference among seasonal median iron concentrations, the confidence level, 95%, is less than that calculated at river mile 21.

Figure M - 6 shows that Zollner Creek’s data display even less of a tendency toward seasonal differences in dissolved iron concentrations. The median iron concentrations in one season differ from at least one of the others at a 75% confidence level.

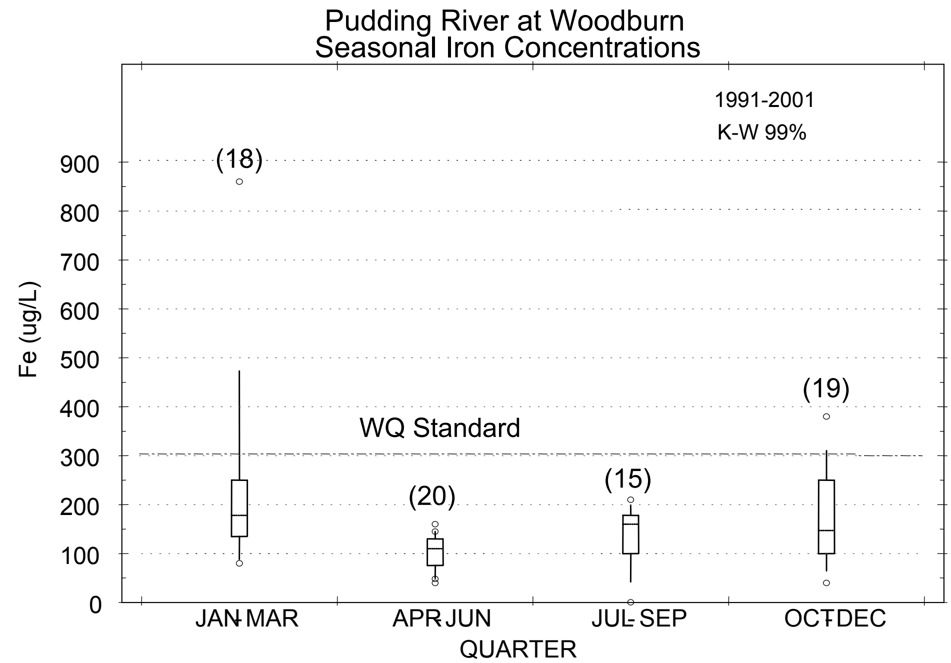

Figure M - 4: Seasonal variation in dissolved iron concentrations measured in samples collected at the Pudding River at Woodburn, river mile 21.

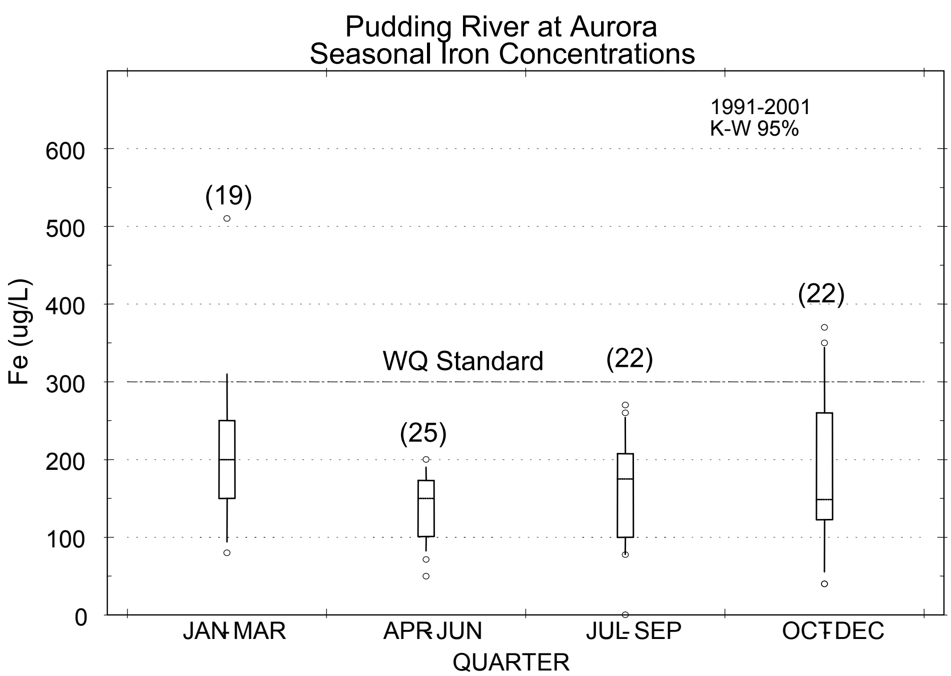

Figure M - 5: Seasonal variation in dissolved iron concentrations measured in samples collected at the Pudding River at Aurora, river mile 8.

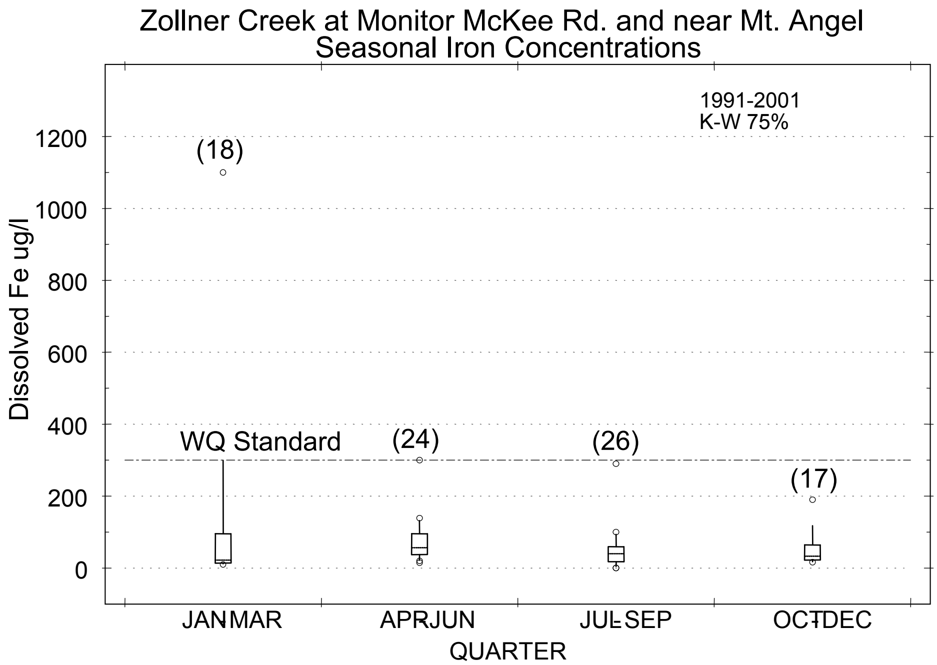

Figure M - 6: Seasonal variation in dissolved iron concentrations measured in samples collected from Zollner Creek.

SOURCES: SURFACE RUNOFF AND EROSION

DEQ plotted the total and dissolved iron concentrations from Pudding and Zollner Creek on load duration curves to view the relationship between iron loading to the stream and stream discharge. Some of the samples had been collected at times when no flow data were available. In those cases, DEQ plotted concentrations against an average basin stream flow exceedance probability calculated from all available flow data on that date. Load duration curves and the derivation of an average exceedance probability are explained in Appendices F and G of this TMDL.

Figure M - 7 illustrates how the iron loading varies with stream flow based on data collected at the Pudding River at Aurora site. Generally, the iron loading is less than what the water quality criteria would allow. The one notable exceedance shown in Figure M - 7 is a sample analyzed for total metals.

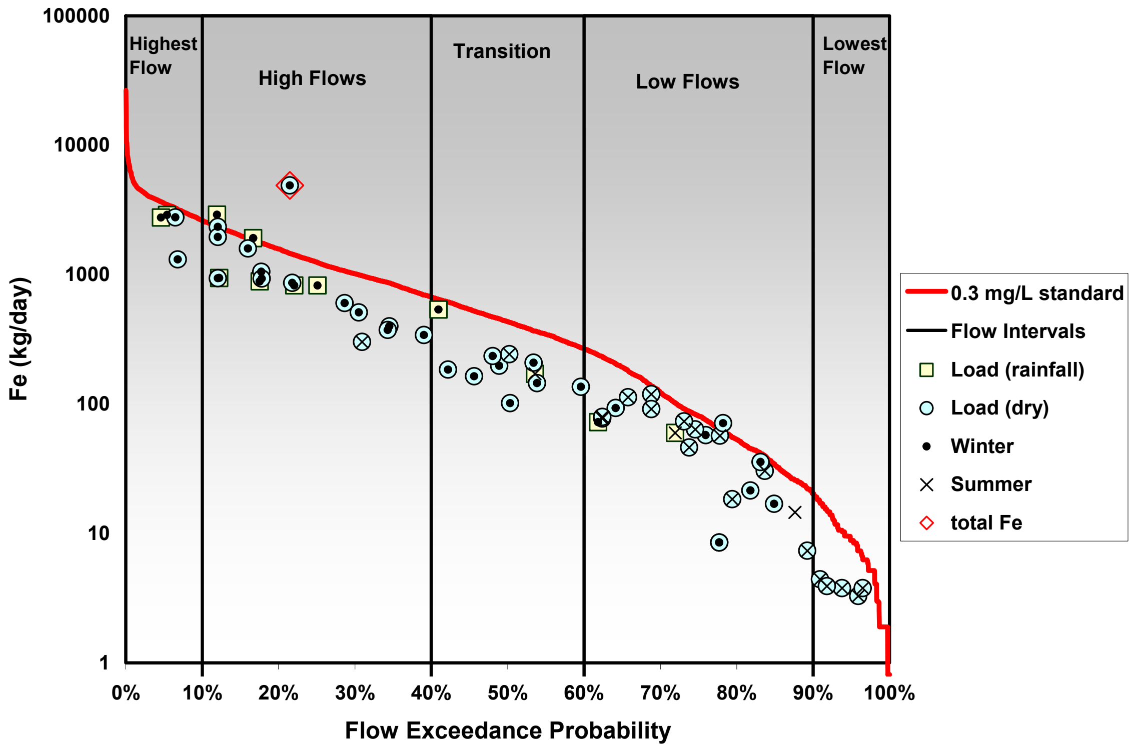

Figure M - 7: Pudding River at Aurora load duration curve based on dissolved concentrations of iron, except where noted.
Data points designated "rainfall" occurred on a day with at least 0.15 inches of precipitation. Data points designated "Winter" occurred October through May.

To derive a broader picture of the conditions under which water quality exceedances occur, DEQ plotted iron concentrations with an average exceedance probability for the basin. This allows the display of data points for which stream flow measurements are not available. Figure M - 8 illustrates that, with one exception, all the water quality exceedances occur at exceedance probabilities less than 50%, i.e. transition to highest stream flows. The four greatest concentrations displayed in Figure M - 8 are represented as "dry" loads because precipitation on the day of sample collection did not equal or exceed 0.15 inches. In three of those four cases, precipitation within the last 24 hours exceeded 0.3 inches. The sample yielding the highest iron concentration (1.5 mg/L, 1,500 ug/L) was collected on a day preceded by six days of precipitation exceeding 0.1 inches each day.

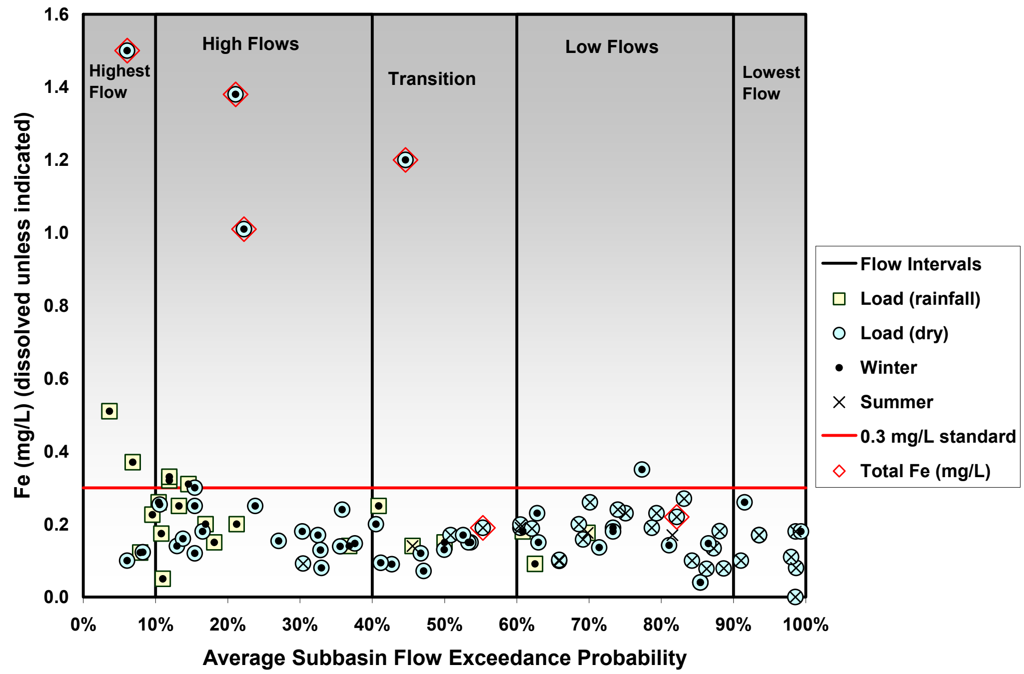

Figure M - 8: Concentration duration curve for Pudding River at Aurora.
Data points designated "rainfall" occurred on a day with at least 0.15 inches of precipitation. Data points designated "Winter" occurred October through May.

Figure M - 9 and Figure M - 10 display similar information for Zollner Creek. Figure M - 9 includes data points for which flow measurements were available or could be estimated. Figure M - 10 includes all data points plotted against the average exceedance probability for the basin. More exceedances occur during transition to high flow periods than low flow periods.

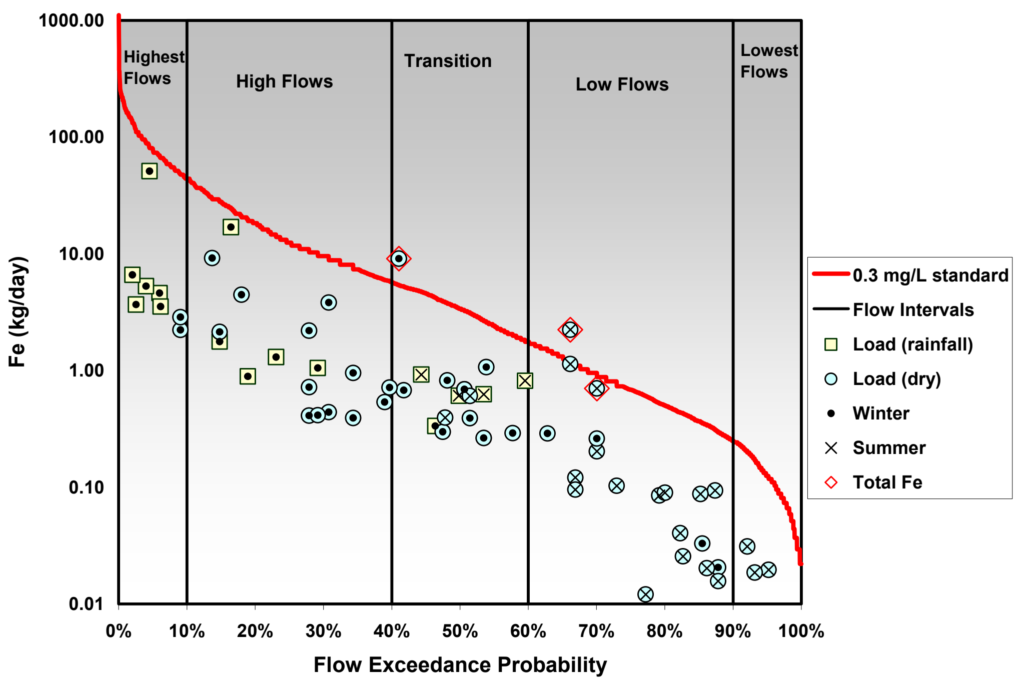

Figure M - 9: Zollner Creek at Monitor Mckee Road load duration curve.

Data points designated "rainfall" occurred on a day with at least 0.15 inches of precipitation. Data points designated "Winter" occurred October through May

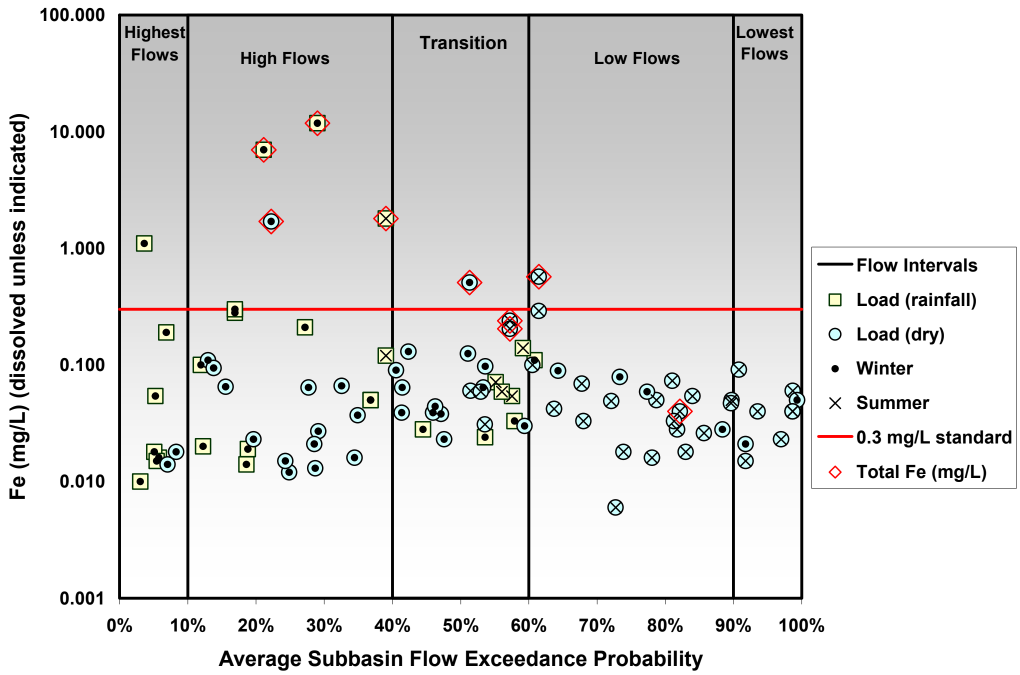

Figure M - 10: Zollner Creek at Monitor-McKee Road concentration duration curve.
Data points designated "rainfall" occurred on a day with at least 0.15 inches of precipitation. Data points designated "Winter" occurred October through May.

SOURCES: GROUNDWATER

Iron concentrations that occur naturally in groundwater from reactions with native soils and bedrock may be responsible for most of the measured iron in surface water in the Pudding River and Zollner Creek. The median dissolved iron concentration in DEQ-collected groundwater samples from the Molalla-Pudding subbasin (Table 6-5, Chapter 6) is 250 ug/L (350 ug/L total iron). Lee and Risley (2002) modeled baseflow, or groundwater contribution to surface flow, in the Pudding River and derived estimates ranging from 72 - 78% for water years 1995 and 1996. Assuming an estimated 75% groundwater contribution to stream flow, one could expect a surface water concentration of approximately 190 ug/L, or 260 ug/L if one calculates based on the median total iron concentration in groundwater.

DEQ used a Wilcoxon Mann-Whitney (WQ Hydro, Aroner, 1997) test to evaluate the likelihood that groundwater iron concentrations and Pudding River or Zollner Creek iron concentrations could be from the same source. The null hypothesis of this test is that the data are from the same population, i.e. the means do not differ. The 2xP value shown on the plots is compared to a pre-determined error level which represents what is an acceptable chance of an incorrect conclusion (known as the significance level, α). For an 80% confidence level, the significance level is 0.20. This indicates that the following is an acceptable chance of error: a 0.10 maximum probability of error in concluding that a the mean of the first data set is greater than the mean of the second data set, and a 0.10 maximum probability of error in concluding that the mean of the first data set is less than the mean of the second data set (for an overall error potential of 0.20). This statistical test is appropriate for data that is not normally distributed, the case for most environmental data where a detection or reporting limit sets a defined minimum concentration (Gilbert, 1987).

The figures in this section compare groundwater and surface water data collected in the same season (summer or winter) and similarly analyzed (i.e. total or dissolved iron). Summer samples were collected June – September and winter samples October – May. Coincidentally, DEQ collected all the winter groundwater samples (in February and March) and USGS collected all the summer groundwater samples (June – September). Since DEQ's study targeted shallower wells, potentially more susceptible to contamination, the higher mean concentration of the winter samples may be attributable to sample design instead of or in addition to season of collection.

The comparison of dissolved iron concentrations in groundwater and those in surface water does not indicate with a high level of confidence that the means of the two data sets differ, either in the winter or summer months. Figure M - 11 displays the spread and mean of dissolved iron concentrations in summer-collected groundwater (USGS only) and the Pudding River (both USGS and DEQ data).

Figure M - 11, since 2xP = 0.4736 is not less than 0.20, it is concluded that there is no statistically significant difference between the means of the two data sets. Even so, the 2xP result of 0.4736 indicates that there is only a 47.3% probability that a difference does not exist in the population. Therefore, a difference is means is possible but not with a high enough confidence level (80%) that this conclusion is accepted.

The data represented in Figure M - 12 indicate that the mean of dissolved iron concentrations in winter-collected groundwater exceeds the mean of surface water dissolved iron concentrations, at the 80% confidence level. Because 2xP = 0.1349, which is less than 0.2, it is concluded that the two data sets have different means. There is a low probability (13.4%) that the two data sets have the same mean.

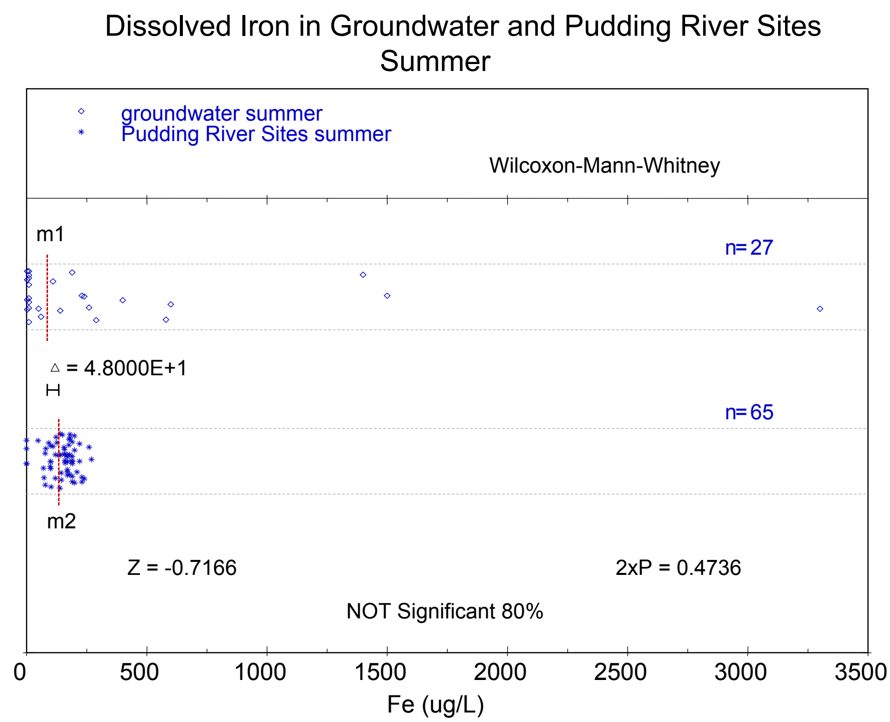

Figure M - 11: Comparison of means between dissolved iron measured in groundwater and Pudding River surface water in the summer months.

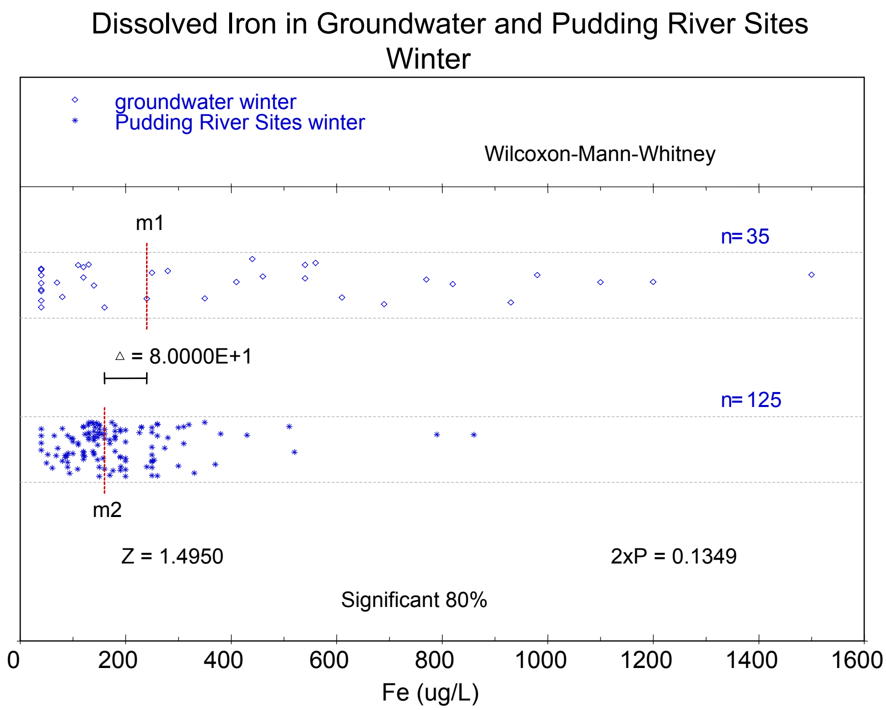

Figure M - 12: Comparison of means between dissolved iron measured in groundwater in the winter months (DEQ data only) and dissolved iron measured in surface water in the winter months at Pudding River sites (both DEQ and USGS data).

Total iron concentrations were not measured in the summer-collected groundwater samples, so only the comparison of winter-collected total iron concentrations in groundwater and surface water are presented in Figure M - 13. Because 2xP = 0.33, which is more than 0.2, it is concluded that the means of the two data sets are not significantly different. There is a relatively high probability (33%) that the two data sets have the same mean. Notably, the data set of total iron measured in winter surface water is small (n = 4).

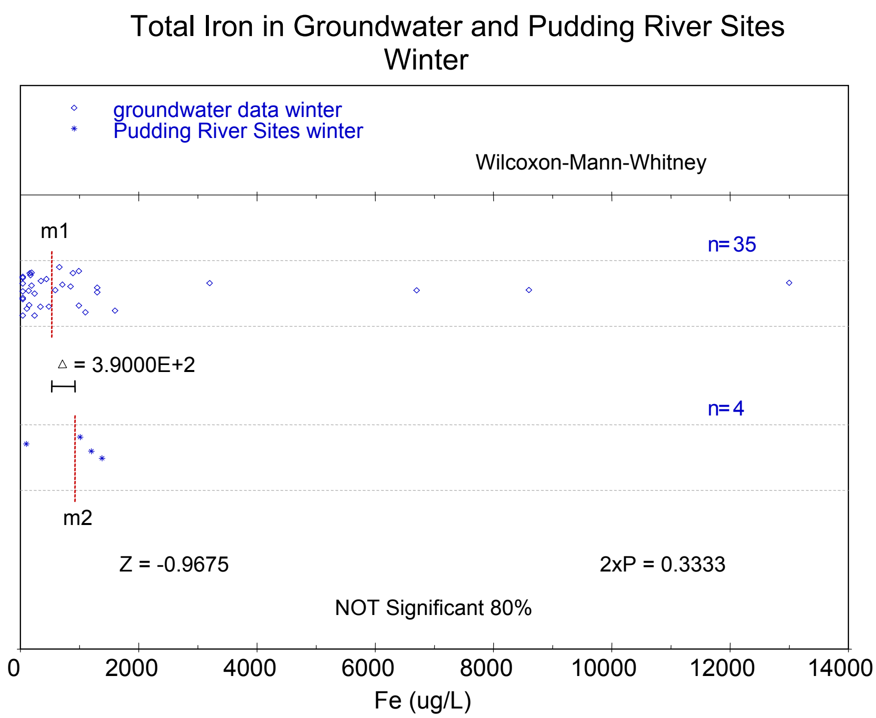

Figure M - 13: Comparison of means between total iron measured in groundwater in the winter months and total iron measured in surface water in the winter months at Pudding River sites (both data sets, DEQ data only).

In summary, iron present in groundwater (i.e. naturally occurring) could be responsible for the dissolved iron concentrations measured in the Pudding River based on a statistical comparison that does not eliminate the null hypothesis – that the two data sets come from the same population. The small total iron data set prevents a definitive conclusion, but the mean of total iron winter-collected surface water data does exceed the mean of winter-collected groundwater total iron concentrations.

The Wilcoxon-Mann-Whitney comparison of Zollner Creek iron concentrations to groundwater iron concentrations yielded variable results. Figure M - 14 compares dissolved iron concentrations in Zollner Creek and groundwater collected in the summer months and illustrates that the groundwater mean concentration is not significantly different from the Zollner Creek mean, based on a 2xP = 0.4641, which is greater than 0.2. There is a relatively high chance (46.4%) that the means of the two data sets are the same (too high to reject the null hypothesis).

Winter-collected dissolved iron concentrations in groundwater significantly exceed the winter-collected dissolved iron surface water concentrations (Figure M - 15). The level of confidence in this conclusion is quite high in that 2xP = 7×10^{-8}. This indicated there is a very low probability (much less than 1%) that the two data sets have the same mean. Figure M - 16, displaying total iron concentrations, indicates a statistically significant difference between two means, but in the opposite direction from the dissolved concentrations: the mean of Zollner Creek total iron concentrations is significantly greater than the mean of total iron groundwater concentrations, at the 95% confidence level. The total iron data set from Zollner Creek is quite small (n = 4) but includes one sample that yielded 11,800 ug/L iron.

In summary, iron concentrations in groundwater (i.e. naturally occurring) would be sufficient to explain dissolved iron concentrations measured in Zollner Creek. The groundwater dissolved iron concentrations are similar to or exceed the surface water dissolved iron concentrations. The significant difference between dissolved groundwater and surface water iron concentrations in the winter may indicate dilution of groundwater input (i.e. dissolved iron) with surface runoff. The small total iron data set from Zollner Creek prevents a definitive conclusion, but the mean of total iron winter-collected surface water data does exceed the mean of winter-collected groundwater total iron concentrations.

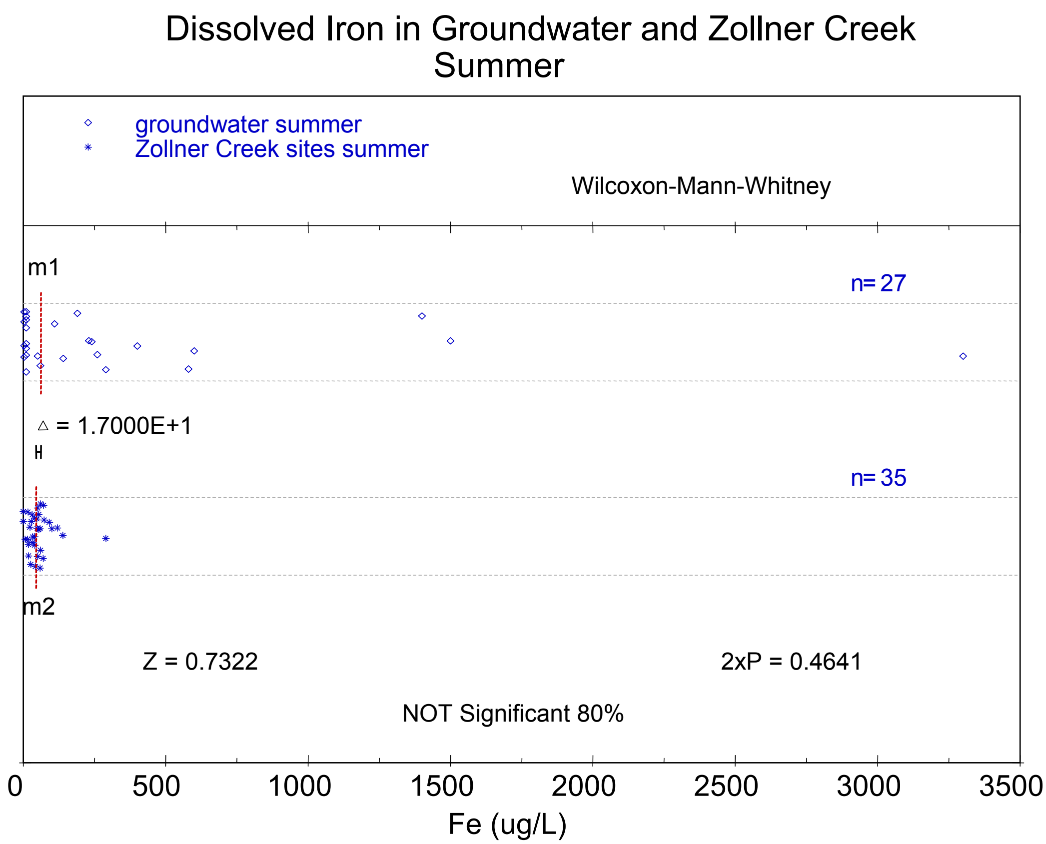

Figure M - 14: Comparison of means between dissolved iron measured in groundwater and Zollner Creek surface water in the summer months.

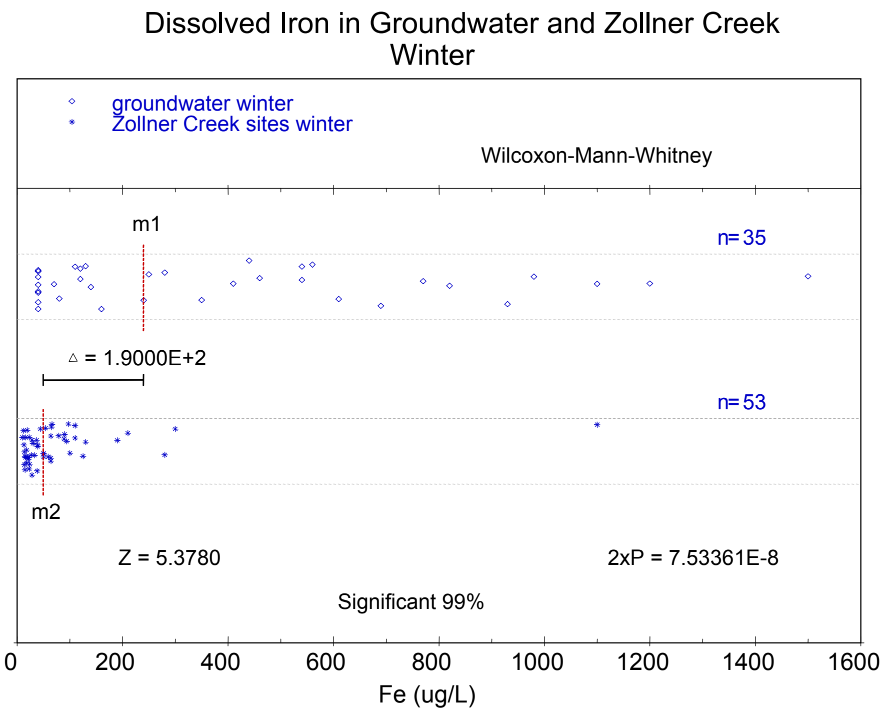

Figure M - 15: Comparison of means between dissolved iron measured in groundwater in the winter months (DEQ data only) and dissolved iron measured in surface water in the winter months in Zollner Creek (both DEQ and USGS data).

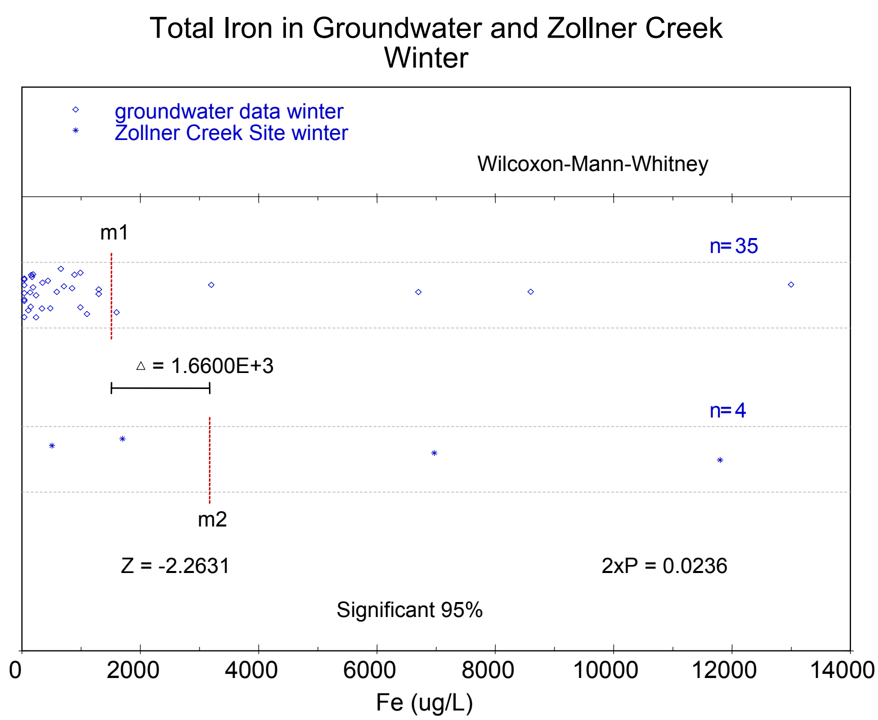

Figure M - 16: Comparison of means between total iron measured in groundwater in the winter months and total iron measured in surface water in the winter months in Zollner Creek (both data sets, DEQ data only).

MANGANESE

OVERVIEW OF DATA

Table M - 3 shows that the median total manganese concentration from the Pudding River (40 ug/L) agrees with the sub-basinwide median, and is approximately one third the Zollner Creek median (118 ug/L). The total manganese Pudding concentration exceeds the median total manganese concentration at a site with predominantly forestry land use (Butte Creek at Butte Cr. Rd) (12 ug/L), though all of the total manganese data sets are small (≤10). Pudding River and sub-basinwide median dissolved manganese concentrations closely agree. The median Zollner Creek dissolved manganese concentration (74 ug/L) exceeds the sub-basinwide median by more than three times.

Some sites in the basin often yield dissolved manganese concentrations near or below detection. Sites with the lowest measured manganese concentrations are Little Abiqua Creek near Scotts Mills, (USGS site), Butte Creek at Butte Creek Road, and Molalla River at Knights Bridge Road.

Table M - 3: Summary of manganese data from samples collected by DEQ and USGS.
MRL = minimum reporting limit.

Manganese	Type	Area	Number of Samples		Criteria (µg/L)	Median (µg/L)	Min. (µg/L)	Max. (µg/L)
	dissolved	Sub-basinwide	375	(39<MRL)	50	20	0.01	482
	total	Sub-basinwide	40	(6<MRL)		40	5.1	434
	dissolved	Pudding	166	(1<MRL)		26	0.07	190
	total	Pudding	10			40	30	70
	dissolved	Zollner	84			74	0.09	482
	total	Zollner	8			118	40	434
	Butte Creek at Butte Creek Rd.		5			12	5.1	26.3

EXCEEDANCES

USGS and DEQ data collected between 1979 and 2006 indicate consistent manganese water quality criterion exceedances in Zollner Creek and occasional exceedances in the Pudding River. Approximately 10% of the combined USGS and DEQ Pudding River samples analyzed for dissolved manganese (17 out of 166 samples) and 10% of those analyzed for total manganese (1 out of 10 samples) yield concentrations that violate the criterion. Approximately 88% of the samples collected from Zollner Creek and analyzed for dissolved manganese (62 out of 84 samples) and 88% of the samples analyzed for total metals (7 out of 8 samples), violate the criterion.

TEMPORAL VARIATION

A review of the USGS and DEQ data collected at Pudding River and Zollner Creek sites does not reveal a trend in manganese concentrations over time. Both agencies collected most of the available data between 1990 and 2001. Most of the results displayed in Figure M - 17 are from dissolved analyses, but results from total analyses are indicated. Both total and dissolved results violate the water quality criterion on occasion.

On three occasions, April 27, June 1 and July 27, 1993, the USGS collected samples for both total and dissolved manganese concentrations in the Pudding River or Zollner Creek, as they did for iron. DEQ calculated the ratio of dissolved to total concentrations and found the results more variable than the dissolved to total iron ratios. Precipitation fell on April 27 and June 1; On April 27 the dissolved manganese concentration in a sample collected from the Pudding River at Aurora was only 18% of the total; On June 1, the dissolved manganese concentration in a sample collected from Zollner Creek was 64% of the total. On July 27, a day when no precipitation fell, the dissolved manganese concentration was 94% of the total in a sample collected from Zollner Creek. While three samples is a small data set from which to draw conclusions, the higher percentages of the dissolved manganese fraction (compared to the dissolved/total iron ratios) and the greater variability in the ratios may suggest that the groundwater contribution to manganese measured in Pudding and Zollner Creeks is greater than the groundwater contribution to iron concentrations.

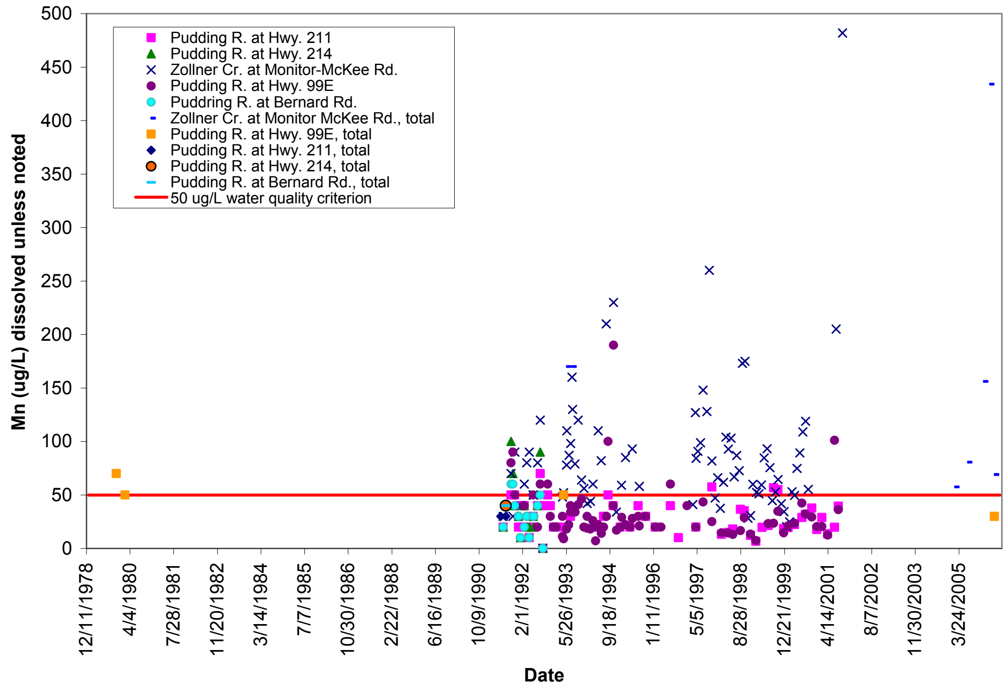

Figure M - 17: Manganese concentrations from Pudding River and Zollner Creek sites.

LONGITUDINAL VARIATION

A review of the variability in dissolved manganese concentrations measured at four sites along the Pudding River (Figure M - 18) does not suggest a significant change with progression downstream. Sampling on Zollner Creek has been predominantly at one site and did not provide sufficient data for a longitudinal comparison.

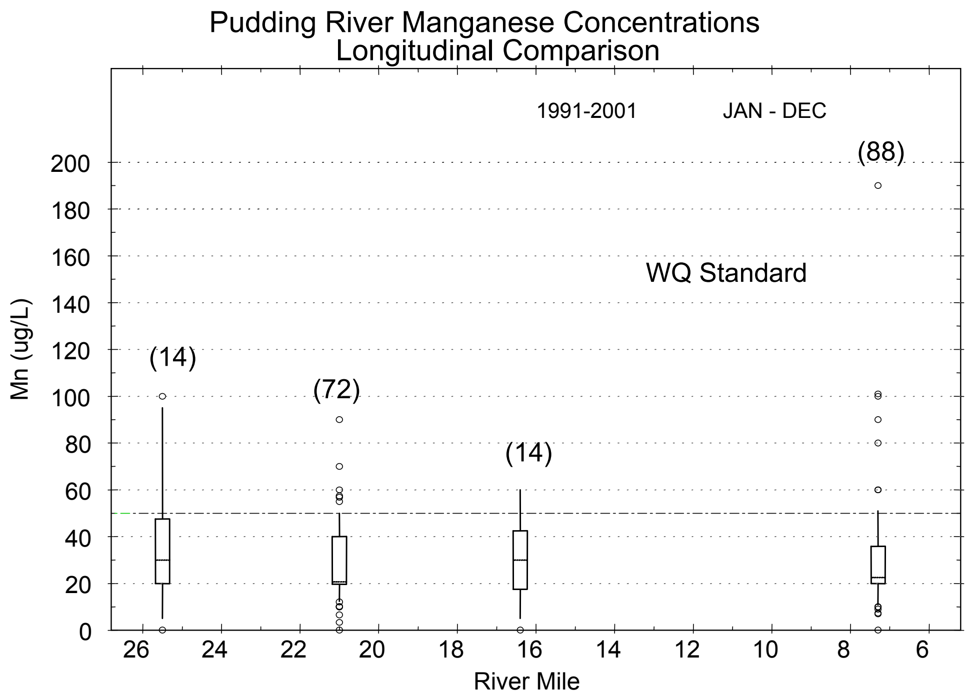

Figure M - 18: A longitudinal comparison of dissolved manganese concentrations from DEQ collected data between 1991 and 2001.

SEASONALITY

Dissolved manganese concentrations tend to be greater in the summer and fall months. Figure M - 19 and Figure M - 20illustrate seasonal differences at two sites on the Pudding River: Woodburn/Hwy 211 at approximately river mile 21 and Aurora/Hwy. 99 E at approximately river mile 8. Both sites demonstrate a significant seasonal difference in median concentrations, although, unlike the seasonal differences in iron concentrations, first and second quarter medians are similar to each other, as are the third and fourth quarter medians. The confidence level in the seasonal difference is greater (99% confidence level) at the more upstream site (Woodburn), compared with the lower site (95% confidence level).

Seasonal variability is also statistically significant in Zollner Creek (Figure M - 21). The median concentrations are similar in the second and third quarters, but the summer months correspond to greater variability and greater measured concentrations overall.

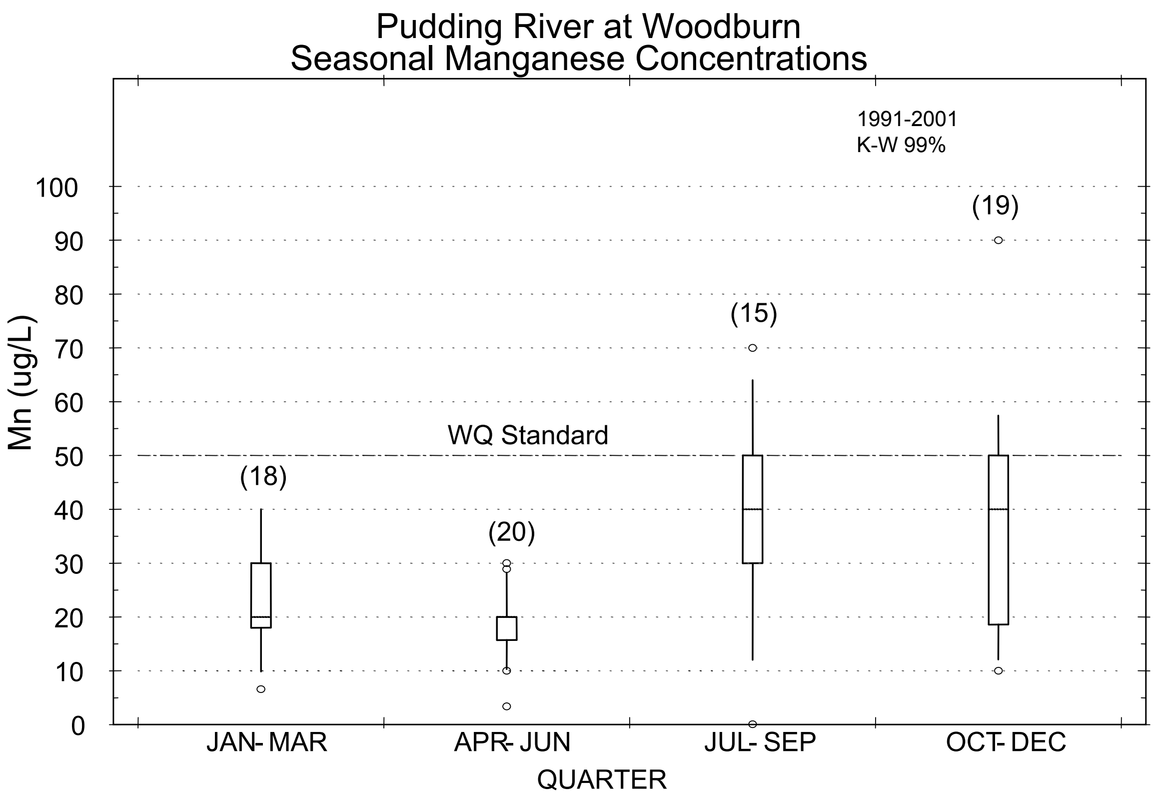

Figure M - 19: Seasonal variability in dissolved manganese concentrations measured in samples collected from the Pudding River at Woodburn/Hwy. 211.

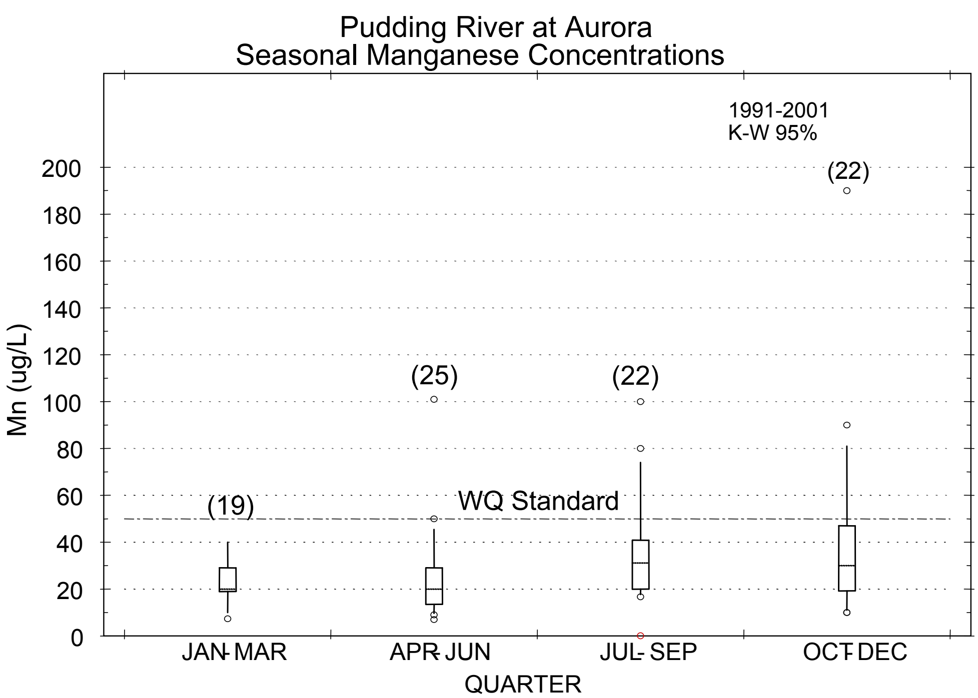

Figure M - 20: Seasonal variability in dissolved manganese concentrations measured in samples collected from the Pudding River at Aurora/Hwy. 99E.

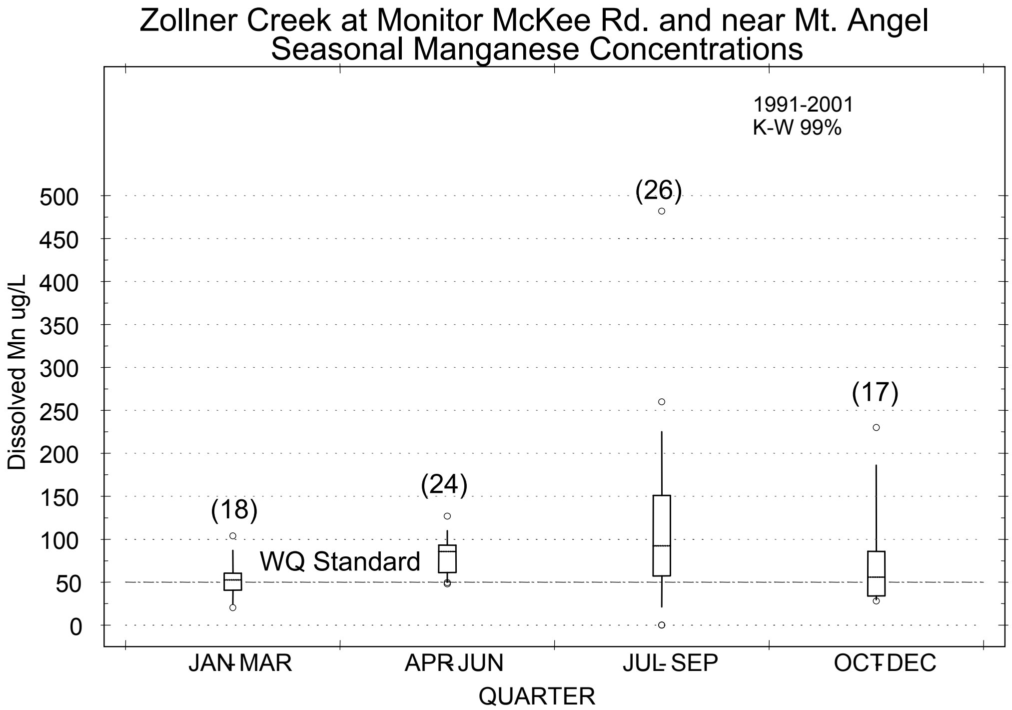

Figure M - 21: Seasonal variability in dissolved manganese concentrations measured in samples collected from Zollner Creek at Monitor McKee Bridge/USGS gauge.

SOURCES: SURFACE RUNOFF AND EROSION

Figure M - 22and Figure M - 23 display manganese loading and concentrations, respectively, from the Pudding River at Aurora across a range of flow conditions. If flow had been measured on the date the sample was collected, the load is plotted in Figure M - 22. As done with the iron data, if no flow data were available, DEQ plotted manganese concentrations against an average basin stream flow exceedance probability calculated from all available flow data on that date (Figure M - 23).

The few exceedances noted in Figure M - 22 occur over the full range of flow conditions, precipitation, and seasons. Plotting all the available data as concentration with an average exceedance probability (Figure M - 23) indicates more exceedances under low flow conditions, although the highest concentration measured also corresponds with high flow conditions.

Load and concentration duration plots of Zollner Creek manganese data show that virtually all samples collected at low flows violate the criterion and most of the samples collected during transition and high flows. Figure M - 24 shows that approximately half of the exceedances occur in summer and approximately half occur under a dry load (less than 0.15 in/day rain). This indicates a greater relative percent of exceedances occurring during the summer, since approximately the same number of exceedances occurred in four months as the remaining eight months of the year[4]. About 75% of the exceedances occur during low or transitional flows (greater than 40% exceedance probability). A similar distribution of exceedances plots on the Zollner Creek concentration duration curve (Figure M - 25). Most concentrations plot above the manganese criterion, a higher relative percent occur in the summer months, and approximately three times as many exceedances occurring under "dry" conditions as "wet" conditions.

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[4] The DEQ and USGS combined data sets includes samples collected in every month, approximately evenly distributed throughout the year.

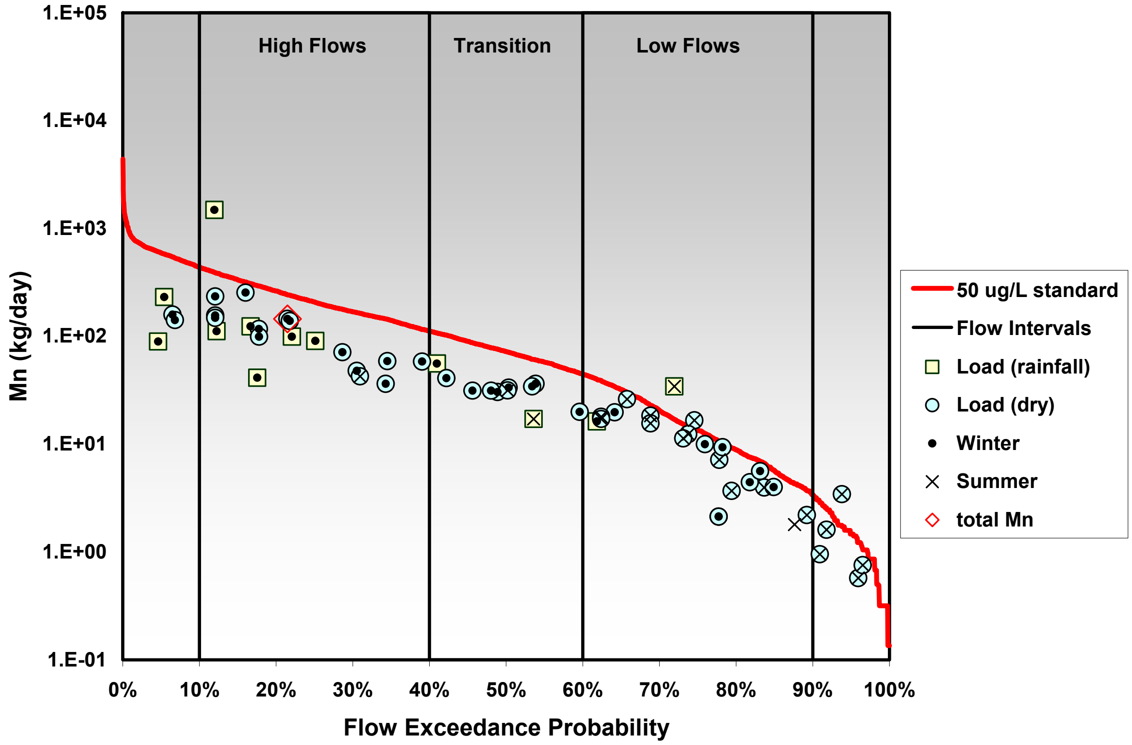

Figure M - 22: Pudding River at Aurora load duration curve based on dissolved concentrations of manganese, except where noted.

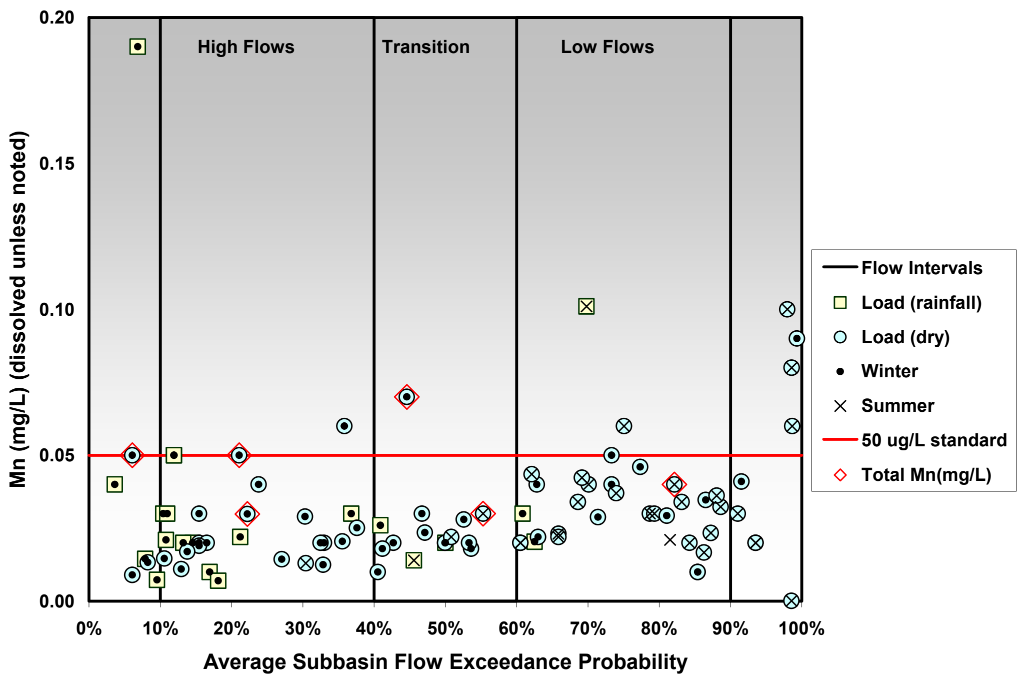

Figure M - 23: Concentration duration curve for Pudding River at Aurora.

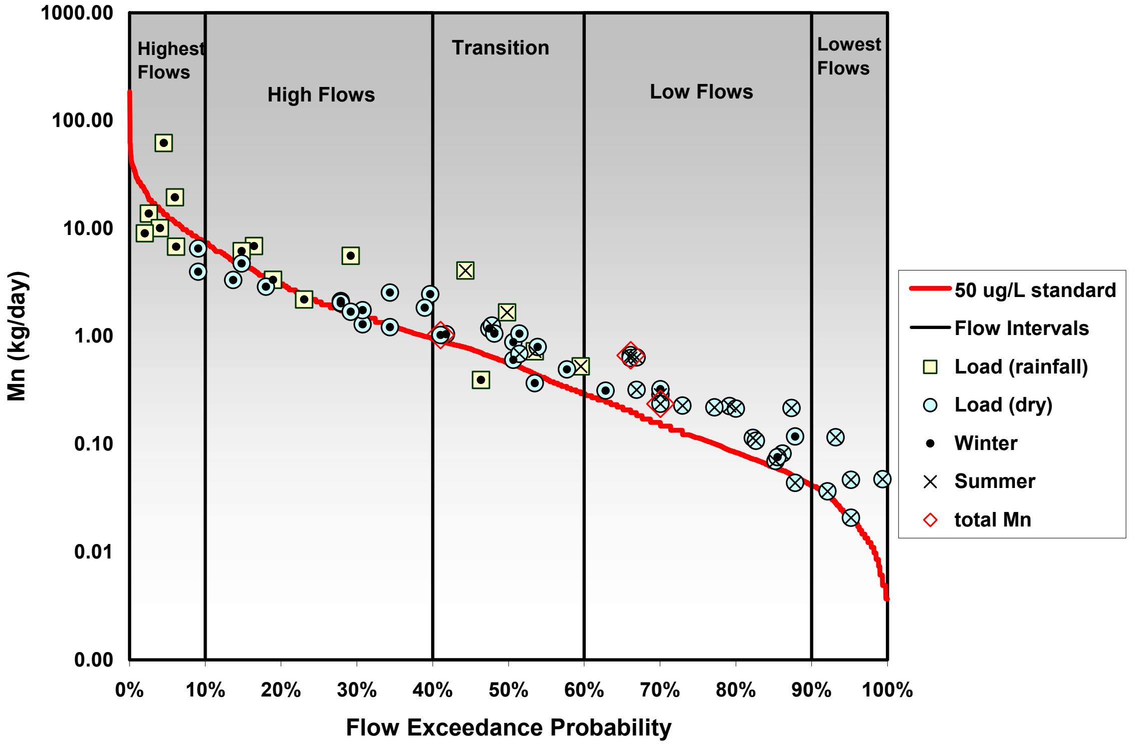

Figure M - 24: Zollner Creek load duration curve.

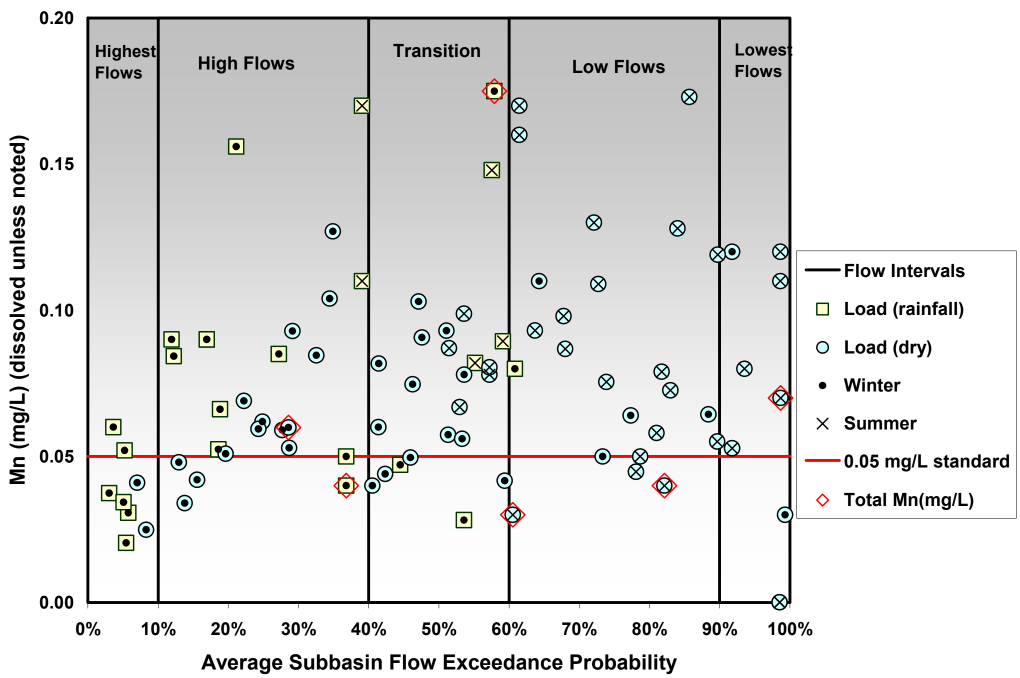

Figure M - 25: Zollner Creek concentration duration curve.

SOURCES: GROUNDWATER

Naturally occurring groundwater manganese concentrations would be sufficient to explain the manganese concentrations measured in Pudding River and Zollner Creek surface water. The median dissolved manganese concentration in DEQ-collected groundwater samples from the

Molalla-Pudding subbasin (from Table 6-5 in Chapter 6) is 300 ug/L (330 ug/L total manganese. Assuming an estimated 75% groundwater contribution to stream flow (Lee and Risley, 2002), one could expect a surface water concentration of approximately 225 ug/L, or 248 ug/L if one calculates based on the median total manganese concentration in groundwater.

DEQ used a Wilcoxon Mann-Whitney (WQ Hydro, Aroner, 1997) test to evaluate the likelihood that groundwater manganese concentrations and Pudding River or Zollner Creek manganese concentrations could be from the same source. DEQ performed the test on several paired data sets, separating dissolved from total concentrations and summer from winter surface water concentrations. Summer samples were collected June – September and winter samples October – May. The null hypothesis of this test is that the data are from the same population, i.e. the means do not differ. The 2xP value shown on the plots is compared to a pre-determined error level which represents what is an acceptable chance of an incorrect conclusion (known as the significance level, α). For an 80% confidence level, the significance level is 0.20. This indicates that the following is an acceptable chance of error: a 0.10 maximum probability of error in concluding that a the mean of the first data set is greater than the mean of the second data set, and a 0.10 maximum probability of error in concluding that the mean of the first data set is less than the mean of the second data set (for an overall error potential of 0.20). This statistical test is appropriate for data that is not normally distributed, the case for most environmental data where a detection or reporting limit sets a defined minimum concentration (Gilbert, 1987).

The mean dissolved manganese concentration in groundwater collected during the summer months is not significantly different from the mean of dissolved manganese concentrations in Pudding River samples collected during the summer (Figure M - 26) at the 80% confidence level. This conclusions is based on 2xP = 0.884, which is greater than 0.2. This indicates there is a relatively high chance (88.4%) that the two data sets have the same mean.

Dissolved manganese concentrations in groundwater collected during winter months significantly exceeds dissolved manganese concentrations in surface water collected during the winter (Figure M - 27). The 2xP value in Figure M - 27 is much less than 0.01. This means there is a very small chance (much less than 1%) that the two means are the same.

Total manganese concentrations in groundwater collected during winter months also exceed surface water total manganese concentrations, but the data set of surface water samples analyzed for total manganese is too small (n = 4) to draw a definitive conclusion (Figure M - 28). A 2xP value less than 0.05 indicates a small chance (less than 5%) that the two data sets have the same mean.

Groundwater manganese concentrations, both dissolved and total, exceed manganese concentrations measured in Pudding River samples in the winter months. Summer dissolved manganese concentrations in groundwater and the Pudding River are not significantly different at the . This implies that groundwater is a major source of manganese to surface water, and is diluted when stream flow and surface runoff increase.

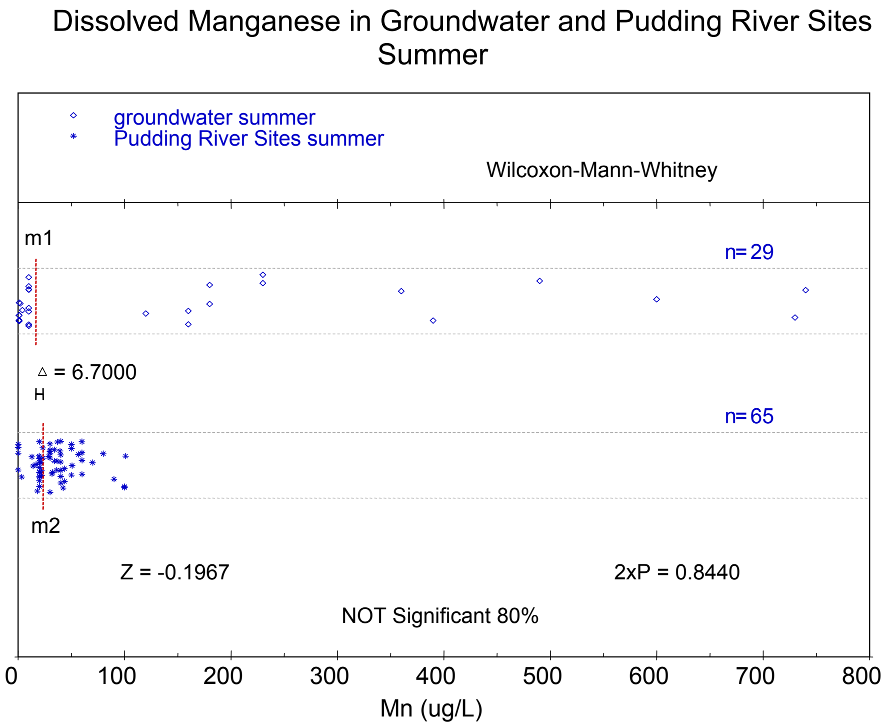

Figure M - 26: A comparison of dissolved groundwater manganese concentrations to those measured in the Pudding River in the summer months.

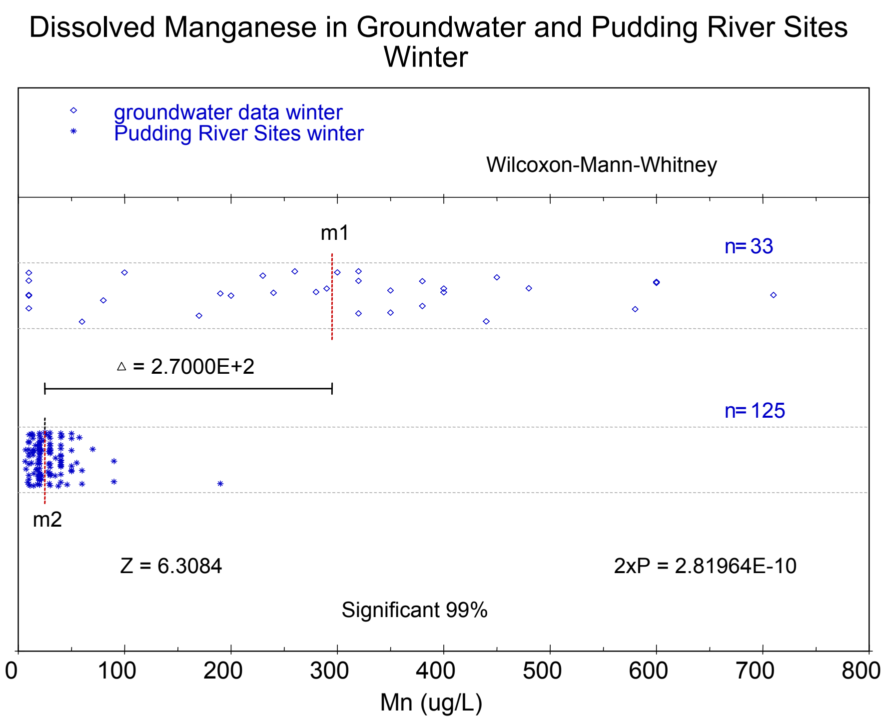

Figure M - 27: A comparison of dissolved groundwater manganese concentrations to those measured in the Pudding River, both in the winter months..

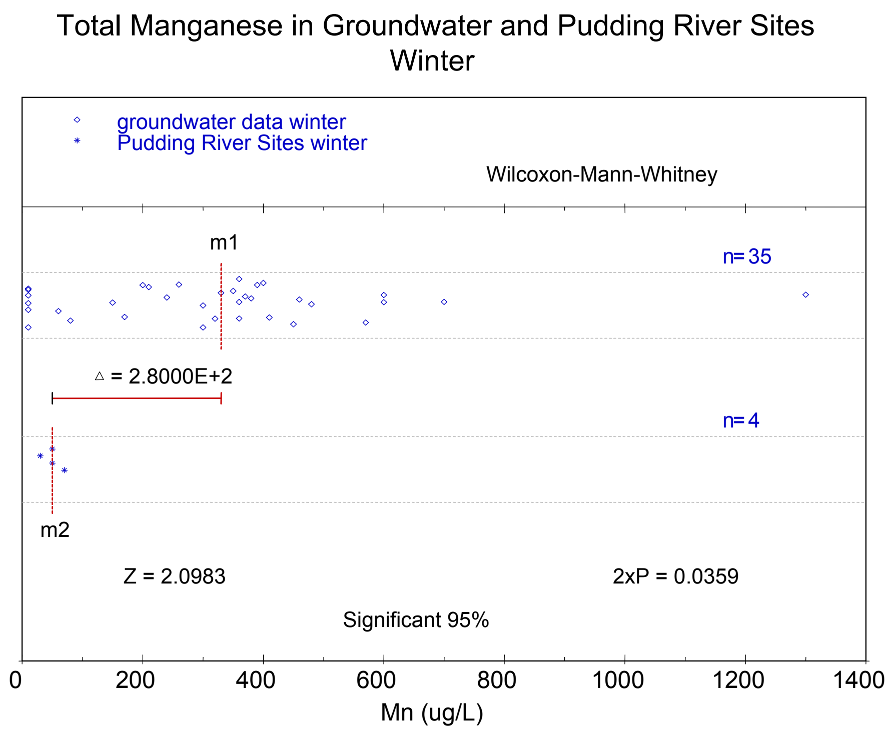

Figure M - 28: A comparison of total groundwater manganese concentrations to those measured in the Pudding River, both in the winter months.

A comparison of manganese concentrations in Zollner Creek to groundwater concentrations reveals a similar pattern. Again, the difference between mean dissolved manganese concentrations in summer collected groundwater and surface water is not statistically significant at the 80% confidence level (Figure M - 29). There is a relatively high probability (46.2%) that the two data sets have the same mean. The mean of winter dissolved manganese concentrations in groundwater exceeds Zollner Creek dissolved manganese concentrations with a high level of confidence (Figure M - 30). There is a small chance (less than 1%) that the two data sets have the same mean.

A comparison of total manganese concentrations in winter-collected groundwater and winter-collected Zollner Creek samples is not conclusive because of a small total manganese data set for Zollner Creek. Figure M - 31 (2xP = 0.3568) indicates the mean manganese concentration in groundwater cannot be distinguished from the mean of surface water concentration with an 80% confidence level. There is a relatively high probability (35.7%) that the two data sets have the same mean.

In summary, manganese concentrations in groundwater (i.e. naturally occurring) would be sufficient to explain dissolved and total manganese concentrations measured in Zollner Creek. The groundwater dissolved manganese concentrations are similar to or exceed the surface water dissolved manganese concentrations. The significantly greater winter dissolved manganese concentrations measured in groundwater imply that surface water dissolved manganese concentrations are diluted from surface runoff. Unlike the pattern of total iron in surface water exceeding total iron in groundwater in the winter months (implied by small Zollner Creek data set), total manganese concentrations do not appear to be significantly different between groundwater and surface water.

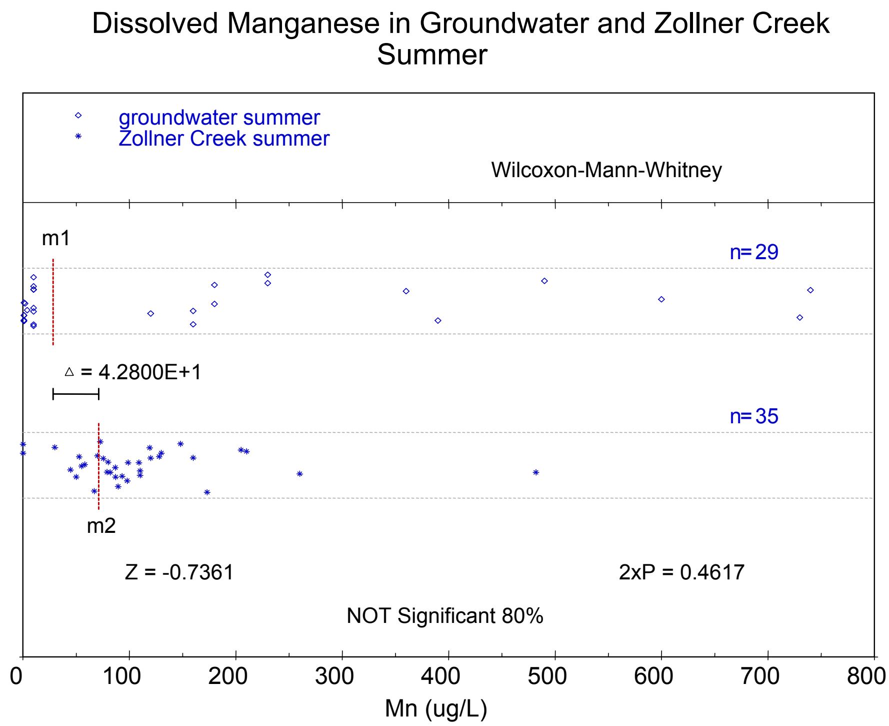

Figure M - 29: A comparison of dissolved manganese concentrations in groundwater to dissolved manganese concentrations measured in Zollner Creek at Monitor-McKee Rd./USGS gauge in the summer.

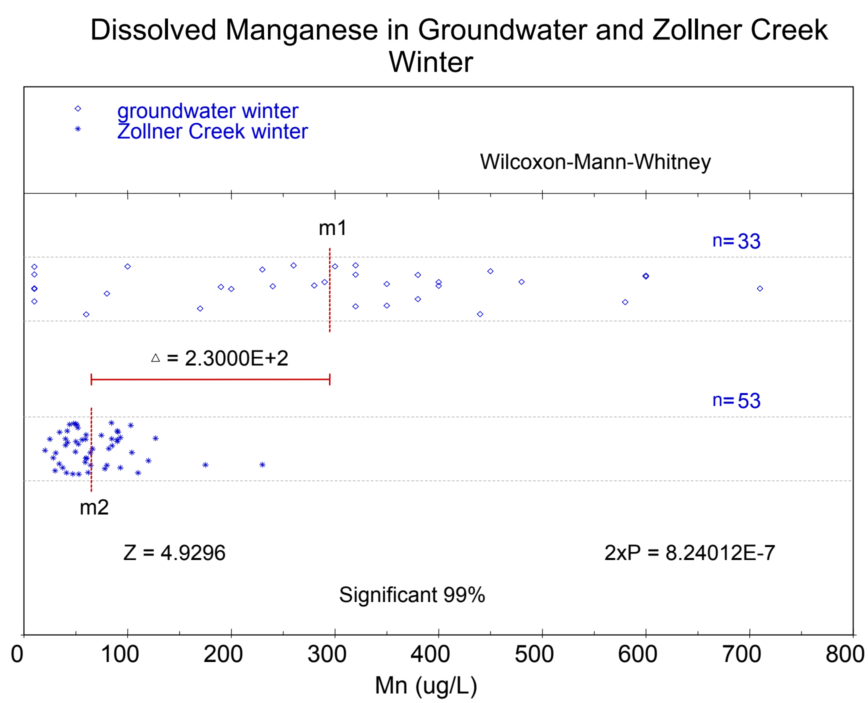

Figure M - 30: Dissolved manganese measurements in Zollner Creek compared with dissolved manganese concentrations in groundwater, both data sets from winter months.

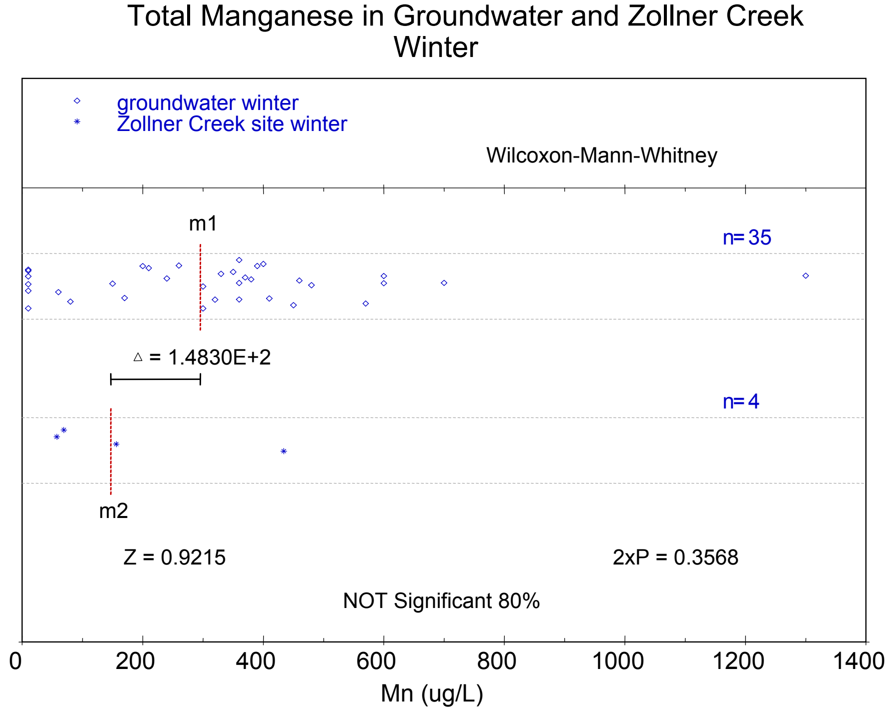

Figure M - 31: A comparison of total groundwater manganese concentrations to those measured in the Zollner Creek, both in the winter months.

ARSENIC

A thorough analysis of arsenic in Zollner Creek is limited by the number of detectable concentrations measured (Table M - 4). A review of the USGS and DEQ data collected between 1990 and 2006 from Zollner Creek produces three detections of 1 ug/L, with unfiltered and filtered samples yielding identical concentrations. Both DEQ and USGS sample sets are quite small (n < 10), so a larger sample set may have revealed more detectable concentrations. Still, samples in the combined data sets were collected in different seasons, at both high and low stream flow, and under wet and dry conditions, and DEQ considers them to be representative of arsenic concentrations in Zollner Creek. Because the method reporting limits exceed the water quality criteria by a factor of 1000, any detection is a exceedance.

Table M - 4: Summary of arsenic data from DEQ and USGS samples.
MRL = minimum reporting limit. *Based on 5 samples below MRL of 3 and 10 ug/L being set at 3 or 10 ug/L for calculation.

	Type	Area	Number of Samples		Criteria (µg/L)	Median (µg/L)	Min. (µg/L)	Max. (µg/L)
Arsenic	dissolved	basinwide	6	(1<MRL)	0.0022	**1**	<1	5
	total		39	(30<MRL)		**4.3**	<1	12
	dissolved	Zollner	3			**1**	1	1
	total		7	(5 <MRL)		**3***	1	1

Figure M - 32 plots all available surface water arsenic data from the combined USGS and DEQ data sets with Zollner Creek arsenic concentrations. The Senecal Creek sample may reflect contamination from the adjacent Marion County landfill. DEQ collected samples in August and November of 2005 in Mill Creek as part of a mixing zone study, and detectable concentrations ranged from 3.9 to 11.9 ug/L. The relatively higher arsenic concentrations measured in Mill

Creek are probably not explained by wastewater treatment plant since the concentration upstream of the treatment plant at time exceeded the downstream sample. The arsenic concentrations measured in Zollner Creek are not significantly different from other concentrations measured in the subbasin.

Zollner Creek arsenic concentrations also do not differ significantly from, and the detectable concentrations are less than median groundwater concentrations (from Table 6-5, Chapter 6). The median groundwater concentrations from DEQ and USGS data sets range from 1.5 to 6.5 ug/L.

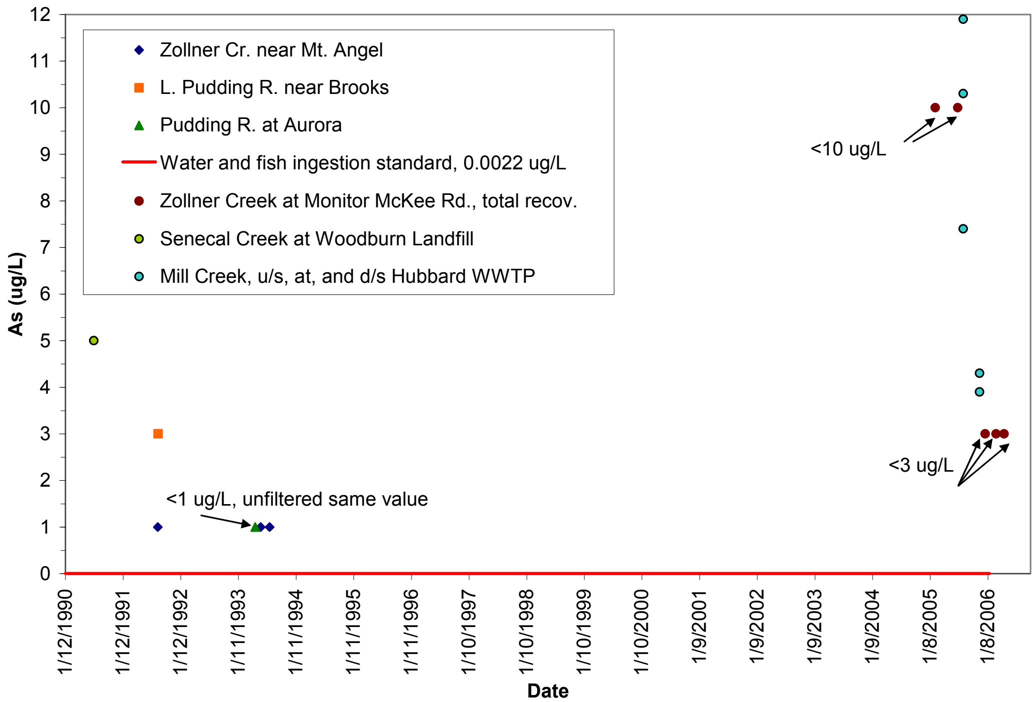

Figure M - 32: All available DEQ and USGS arsenic data from surface water samples in the Molalla-Pudding Subbasin.