Chapter 6
Iron, Manganese, Arsenic

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INTRODUCTION

The iron total maximum daily load (TMDL) for the Molalla-Pudding Subbasin has been developed within hydrologic units 1709000902 (Butte Creek/Pudding River), 1709000903 (Rock Creek/Pudding River), 1709000904 (Senecal/Mill Creek) and 6th field hydrologic units associated with the Little Pudding River watershed and tributaries on the west side of the upper Pudding River. The TMDL addresses segments of the following streams identified as water quality limited on the 303(d) list: Pudding River and Zollner Creek. Required TMDL components from OAR 340-042-0040 as well as a summary of the treatment of other parameters are listed in Table 6 - 1.

Table 6 - 1: Iron TMDL components and treatment of other parameters.

Name and Location of Waterbodies OAR 340-042-0040(4)(a)	Perennial and intermittent streams, as identified in OAR 340-041- 0340; Figures 340A & 340B, streams in the Molalla-Pudding Subbasin, HUCs 1709000902, 1709000903, 1709000904 and the 6th field HUCs 170900090108, 170900090109 and 170900090110.
Pollutant Identification OAR 340-042-0040(4)(b)	*Pollutants:* Iron, manganese, arsenic. DEQ proposes delisting for arsenic and manganese based on evidence they are present in surface water at natural concentrations.
Water Quality Standards and Beneficial Use Identification OAR 340-042-0040(4)(c) OAR 340-041-0033(1) OAR 340-041-0033(2)	(1) Narrative Criteria: Toxic substances may not be introduced above natural background levels in the waters of the State in amounts, concentrations, or combinations that may be harmful, may chemically change to harmful forms in the environment, or may accumulate in sediments or bioaccumulate in aquatic life or wildlife to levels that adversely affect public health, safety or welfare, aquatic life, wildlife or other designated beneficial uses. (2) Numeric Criteria: Levels of toxic substances may not exceed the criteria listed in Table 20 which were based on criteria established by EPA and published in Quality Criteria for Water (1986), unless otherwise noted. Human Health Criteria are 300 micrograms per liter for iron, 50 micrograms/liter for manganese, and 2.2 nanograms/liter for arsenic (0.0022 micrograms/liter). Iron and Manganese water quality criteria fall under Secondary Standards – based on taste, odor, color, and staining properties of water, rather than toxicity. The Oregon Environmental Quality Commission approved new toxics criteria in May 2004 which includes a revision of the arsenic criteria in Table 33A , but these values are not yet approved by EPA. For this TMDL, DEQ uses the more conservative of the criteria in Table 20 and Table 33A. Beneficial Uses: Human Health -- Water and Organism Ingestion. Public and Private Domestic Water Supply .
TMDL Loading Capacity OAR 340-042-0040(4)(d) Excess Load OAR 340-042-0040(4)(e) Sources or Source Categories OAR 340-042-0040(4)(f)	Loading Capacity: Loading capacity was developed only for iron since DEQ proposes delisting for arsenic and manganese. The loading capacity was determined through the development of load duration curves that determine the load that will achieve the human health criteria . Excess Load: The difference between the actual pollutant load and the loading capacity of a waterbody. Iron excess load was calculated for five flow intervals across all flow conditions. Sources: Iron, manganese, and arsenic are all naturally occurring substances in rocks and soils, particularly those deriving from volcanic sources. Runoff and erosion of soils may cause these metals to be present in surface water at higher than natural concentrations. Industrial and agricultural activities (e.g. mining, wood preserving, and historic pesticide manufacturing and use) may add arsenic to groundwater and surface water.
Wasteload Allocations OAR 340-042-0040(4)(g) Load Alloacations OAR 340-042-0040(4)(h) Surrogate Measures OAR 340-042-0040(5)(b) *40 CFR 130.2(i)*	Waste Load Allocations (Point Sources): Since DEQ's analysis does not indicate that point sources contribute to iron exceedances, DEQ allots wasteload allocations for iron to point sources that cover their current conditions of discharge. Load Allocations (Non-Point Sources) and Surrogate Measures The load allocation for iron is expressed as a percent reduction based on flow, ranging from 54% to 79% for the Pudding River and its tributaries and 19% to 96% for Zollner Creek. The load allocations apply to all land uses (urban, agricultural, forestry).
Seasonal Variation OAR 340-042-0040(4)(j) *CWA §303(d)(1)*	Violations of water quality standards occur throughout the year and under both low flow and high flow conditions.
Margins of Safety OAR 340-042-0040(4)(i) *CWA §303(d)(1)*	*Margins of Safety:* No numeric margin of safety is developed in this TMDL, although conservative assumptions and procedures result in an implicit margin of safety. For percent reduction calculations, DEQ used the 90th percentile of the data which slightly overestimates the needed reduction. Percent reductions are also what is necessary to reduce total iron to the water quality criterion. Data indicate that dissolved concentrations are likely to be significantly less.

Reserve Capacity **OAR 340-042-0040(4)(k)**	DEQ allocates 10% of the loading capacity to reserve capacity in this TMDL. Future permitted sources of iron will be required to meet the water quality criteria or demonstrate they do not cause or contribute to iron water quality violations. Potentially increased non-point source contributions, such as from land development, may not cause total loading to exceed the loading capacity.
Water Quality Management Plan **OAR 340-042-0040(4)(l)**	The Water Quality Management Plan (WQMP) provides the framework of management strategies to attain and maintain water quality standards. Detailed plans and analyses included in specific DMA implementation plans will supplement the WQMP.

NAME AND LOCATION OF WATERBODIES

DEQ and other entities have identified exceedances of iron, manganese and arsenic water quality criteria in the Molalla-Pudding Subbasin, specifically in samples collected from the Pudding River and Zollner Creek. Figure 6 - 1 shows the location of Zollner Creek and the Pudding River within the Molalla-Pudding Sub-Basin. State water quality standards (OAR 340-41-0033 Table 20) include the criteria for these three metals on the table of toxics criteria (Table 20), although the occurrence of these metals may be natural.

DEQ analyzed all available data for these parameters and reviewed the literature to identify the likely sources of iron, manganese and arsenic (Fe, Mn, and As) in surface water in the Molalla-Pudding subbasin and to evaluate the likelihood that they exist at naturally occurring concentrations. DEQ's goal was to determine if the sources were anthropogenic or if anthropogenic activity concentrated natural concentrations in surface water.

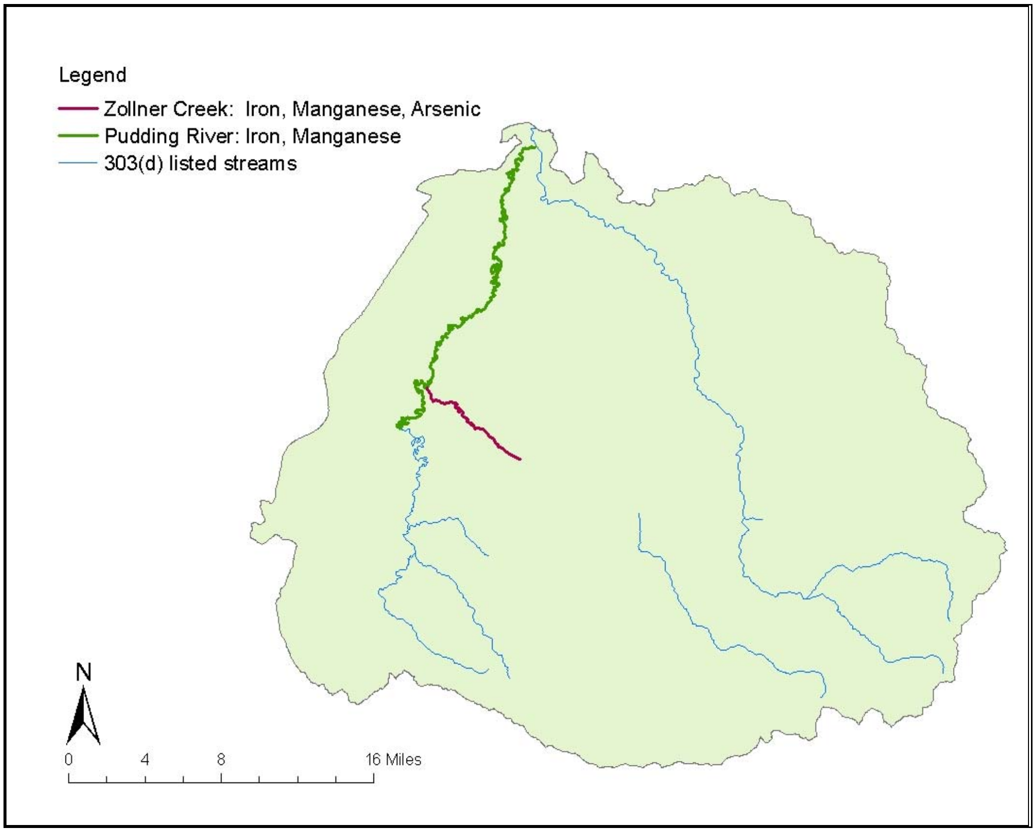

Figure 6 - 1: Zollner Creek and Pudding River reaches listed for exceedance of metals water quality criteria.

POLLUTANT IDENTIFICATION

Iron, manganese, and arsenic are elements that occur naturally in geologic materials. According to the EPA[1] iron and manganese are not considered risks to human health, but can cause taste, odor, color,

[1] http://www.epa.gov/safewater/consumer/2ndstandards.html

and staining problems in domestically used water. The EPA has classified arsenic as a known carcinogen. Arsenic may be present in one or more oxidation states, depending on available oxygen. Trivalent forms of arsenic (inorganic and organic) are more toxic to humans and aquatic organisms and are usually only present under anaerobic conditions. Webb (1966) found that arsenite (a reduced form of arsenic) is approximately 60 times more toxic to humans than arsenate (oxidized arsenic). Ferguson and Gavis (1972) concluded that it is unlikely that consumption of arseno-organic compounds in fish or other organisms will constitute a hazard from arsenic poisoning. Rather, the potential hazard is in the consumption of water containing high concentrations of inorganic arsenite.

WATER QUALITY STANDARDS AND BENEFICIAL USES

BENEFICIAL USES

Oregon Administrative Rules (OAR Chapter 340, Division 41, Table 340A) lists the “Beneficial Uses” occurring within the Molalla-Pudding Sub-Basin (Table 6 - 2). Numeric and narrative water quality standards are designed to protect the most sensitive beneficial uses. Water and Fish Ingestion (arsenic) and Public and Private Domestic Water (iron and manganese) are the most sensitive beneficial uses related to toxics in the Molalla-Pudding Sub-Basin.

Table 6 - 2: Beneficial uses occurring in the Molalla-Pudding River Subbasin (OAR 340 – 41 – 0340). Toxics-Sensitive Beneficial uses are marked in gray. Iron, manganese and arsenic are included in the toxics category.

Beneficial Use	***Occurring***	***Beneficial Use***	***Occurring***
Public Domestic Water Supply	✓	Salmonid Fish Spawning (Trout)	✓
Private Domestic Water Supply	✓	Salmonid Fish Rearing (Trout)	✓
Industrial Water Supply	✓	Resident Fish and Aquatic Life	✓
Irrigation	✓	Anadromous Fish Passage	✓
Livestock Watering	✓	Wildlife and Hunting	✓
Boating	✓	Fishing	✓
Hydro Power	✓	Water Contact Recreation	✓
Aesthetic Quality	✓	Commercial Navigation & Transportation	

WATER QUALITY CRITERIA

Water quality criteria consist of numeric and narrative criteria. Numeric criteria are scientifically derived ambient concentrations developed by U.S. Environmental Protection Agency (EPA) or States for various pollutants of concern to protect human health and aquatic life. Narrative criteria are statements that describe the desired water quality goal. The State of Oregon adopted toxics water quality criteria from EPA guidance (EPA, 1986) to protect the most sensitive beneficial uses of Oregon waterbodies. Those criteria are summarized in Table 20 of OAR 340-041-0033, and fall into two categories – Primary Standards and Secondary Standards. Primary Standards are based on health considerations and are designed to protect people from three classes of pollutants: pathogens, radioactive elements and toxic chemicals. Arsenic is classified under Primary Standards. Secondary Standards are based on taste, odor, color, and staining properties of water. Iron and manganese are both classified under the Secondary Standards.

Iron and manganese are not toxic at concentrations listed in Table 20, but the aesthetic quality of water for domestic use and drinking is compromised at 300 μg/L for iron and 50 μg/L for manganese. The arsenic criterion is based on a conservative measure of toxicity that accounts for bioaccumulation. The arsenic criterion (2.2 ng/L – nanograms/liter) protects the beneficial use of fish and water consumption and is typically below the detection limit of common laboratory analyses.

In 1992, EPA set the fish consumption criteria at 0.14 μg/L and fish consumption/water ingestion criteria at 0.018 μg/L. These arsenic water quality criteria represent a one in one million (10^{-6}) cancer risk level from inorganic arsenic exposure. As a relative comparison, arsenic concentrations derived from unpolluted oceanic air masses average 0.019 μg/L (Welch *et al* 1988). The EPA Office of Water also has a drinking water standard, or maximum contaminant level (MCL), effective since January 2006 of 10 μg/L.

The Oregon Environmental Quality Commission approved new toxics criteria in May 2004, including revisions of the Fe, Mn, and As criteria, but EPA has not yet approved those criteria because of on-going litigation regarding the fish consumption criteria. The 2004 proposed criteria clarify that Fe and Mn exceedances would be based on dissolved concentrations. The As criteria for water and fish ingestion would increase to 0.018 μg/L and reference the inorganic form of As only. Until the 2004 proposed criteria are approved, DEQ continues to use the criteria in Table 20 for federal Clean Water Act purposes, including TMDLs.[2]

Additional conditions in the State water quality standards pertinent to this TMDL are:

> **OAR 340-41-0033(1)**: Toxic substances may not be introduced above natural background levels in waters of the state in amounts, concentrations, or combinations that may be harmful, may chemically change to harmful forms in the environment, or may accumulate in sediments or bioaccumulate in aquatic life or wildlife to levels that adversely affect public health, safety, or welfare or aquatic life, wildlife, or other designated beneficial uses;
>
> **OAR 340-41-0033(3)**: To establish permit or other regulatory limits for toxic substances for which criteria are not included in Tables 20, 33A, or 33B, the department may use the guidance values in Table 33C, public health advisories, and other published scientific literature. The department may also require or conduct bio-assessment studies to monitor the toxicity to aquatic life of complex effluents, other suspected discharges, or chemical substances without numeric criteria.

In assessing toxics exceedances, DEQ designated Category 5 waterbodies (i.e. those requiring a TMDL) with a minimum sample set of two and a minimum of two (2) exceedances of the most stringent applicable toxics criteria. DEQ used water and fish ingestion criteria where fishing and water supply were listed as beneficial uses. One can review DEQ's assessment methodology at this location: (http://www.deq.state.or.us/wq/assessment/rpt02.htm).

DEQ placed Zollner Creek on the 1998 303(d) list for exceedances of the iron, manganese, and arsenic criteria. The U.S. Geological Survey (USGS) supplied the data for Zollner Creek from 1993 project work. DEQ placed the Pudding River from the mouth to river mile 35.4 on the 2004/2006 303(d) list for iron and manganese exceedances based on analysis of samples collected from two sites that DEQ regularly monitored between 1994 and 2001. Table 6 - 3 summarizes exceedances of metals criteria in the Molalla-Pudding Sub-Basin.

Table 6 - 3: Pudding River samples collected by DEQ and ODA between 1994 and 2001. Zollner Creek samples collected by USGS in June and July 1993.

<table>
<tr><th colspan="6">Toxics (Metals) Criteria and Exceedances</th></tr>
<tr><th colspan="3"></th><th colspan="2">Pudding River</th><th>Zollner Creek</th></tr>
<tr><td rowspan="2">Manganese</td><td rowspan="2">50 μg/L (total)</td><td rowspan="2">OAR Table 20, 1986 U.S. EPA Guidelines</td><td>3 out of 37 samples</td><td>River Mile 7.3</td><td rowspan="2">2 out of 2 (170 μg/L) Analysis for total Mn.</td></tr>
<tr><td>4 out of 35 samples</td><td>River Mile 21</td></tr>
<tr><td rowspan="2">Iron</td><td rowspan="2">300 μg/L (total)</td><td rowspan="2">OAR Table 20, 1986 U.S. EPA Guidelines</td><td>2 out of 37 samples</td><td>River Mile 7.3</td><td rowspan="2">2 out of 2 (570 – 1800 μg/L) Analysis for total Fe.</td></tr>
<tr><td>1 out of 35 samples</td><td>River Mile 21</td></tr>
<tr><td>Arsenic</td><td>2.2 ng/L (total)</td><td>OAR Table 20, 1986 U.S. EPA</td><td colspan="2"></td><td>2 out of 2 samples (1 μg/L).</td></tr>
</table>

[2] With approval of new toxics criteria in Tables 33A – C, iron and manganese water and fish ingestion standards would be based on dissolved rather than total concentrations. The Pudding River and Zollner Creek listings are currently based on total concentrations.

		Guidelines		

SOURCES OR SOURCE CATEGORIES

Iron and manganese concentrations in surface and groundwater commonly exceed water quality standards. Iron and manganese occur naturally in volcanic rocks, associated soils, and alluvial sediments of volcanic origin.

Micronutrient soil additions to agricultural crops may include iron and manganese, but these are not typically needed to increase production of most common crops grown in the Molalla-Pudding subbasin: grass seed, hays and forage, and Christmas trees (Hart, *et al*., 2004).

Arsenic is also a naturally occurring metal, particularly in volcanic rocks and sediments, but several industrial and agricultural activities may add arsenic to groundwater and surface water. Mining, wood preserving, and (historic) pesticide manufacturing and use may release arsenic into the environment. Only very limited quantities of arsenic-containing pesticides are still manufactured and used under strict limitations in the U.S., but lead arsenate pesticides may have historically been used in the Molalla-Pudding Subbasin. Arsenic may also be a contaminant in phosphorus fertilizers (Chang, et al., 2004).

Wood preserving facilities may use a copper-chromium-arsenic compound. Ten businesses related to lumber and wood products reside in the Molalla Pudding basin[3]. Two have conducted wood treating on site, but apparently not with copper-chromium-arsenic compounds.

DEQ's Facility Profiler database does not list any metal mining facilities in the watershed, although 15 operations related to rock and gravel mining operate in the Molalla-Pudding Subbasin. Arsenic is a potential contaminant of concern associated with auto wrecking yards (heavy metals contamination in used motor oil). Nineteen auto repair facilities are located in the Molalla-Pudding subbasin, and three are involved in DEQ's Cleanup program. None of these three have documented arsenic contamination in soils or groundwater.

Four sites in the Molalla-Pudding Subbasin appear in DEQ's cleanup database that have demonstrated iron, manganese or arsenic contamination (Table 6 - 4). While the cleanup sites listed in Table 6 - 4 may be contributing locally to groundwater and surface water contamination, they do not explain metals concentrations measured in Zollner Creek (none of these facilities is located in the Zollner Creek watershed) or the Pudding River sampling locations upstream of the cleanup sites.

[3] Descriptions of facilities holding permits can be found on DEQ's Facility Profiler database: http://deq12.deq.state.or.us/fp20/

Table 6 - 4: Sites identified in DEQ's Environmental Cleanup Site Information database, in the Molalla-Pudding subbasin having documented or suspected iron, manganese, or arsenic contamination.

Facility	Location	Groundwater Contaminants	Actions and Status
North Marion Disposal Facility (ECSI 1633)	17827 Whitney Lane, Woodburn	As: 170 µg/L Mn: 11,500 µg/L Fe: 24,000 µg/L (concentrations in leachate can reach >500,000 µg/L Fe, >50,000 µg/L Mn, >300 µg/L As)[4]	Remedial Action ongoing; Senecal Creek potentially hydraulically connected to Willamette Silt aquifer
Sanitary Service Co. Landfill (ECSI 1318)	3250 Deer Park Dr. SE, Salem	Fe: 1,400 µg/L (leachate seeps)	No current investigation or monitoring.
Molalla Pit Landfill (ECSI 163)	S. Soda Springs Rd., Molalla	Fe: 180,000 µg/L Mn: 2,200 µg/L	Closest creek is Rock Creek. No further action required 3/8/1994.
Torgeson Rural Residential Properties (ECSI 4076)	26940 and 26926 S. Bolland Rd., Canby	As is a potential contaminant of concern but not detected above 20 µg/L	Former auto wrecking yard near Gribble Creek. Investigation on-going.

Locations in the subbasin where DEQ has collected samples analyzed for metals are pictured in Figure 6 - 2. Table 6 - 5 summarizes the distribution of concentrations measured. As an estimate of instream concentrations of the metals coming from predominantly forested land, DEQ reviewed the data collected from a site (Butte Creek at Butte Creek Road) upstream of agricultural and urban activities. The differences between the samples from the predominantly forested site and the subbasin as a whole, suggest that a substantial portion of the iron and manganese (perhaps 30 – 80%) measured in Molalla-Pudding subbasin streams may be present before streams pass through agricultural and urban land uses. Interpretation of the arsenic results is more difficult because the method detection limit was higher for the Butte Creek and Butte Creek Road samples than for other samples collected. For iron and manganese, subbasin wide median concentrations exceed the median concentrations from the predominantly forested site, and the analysis in Appendix M examines the conditions under which these metals may concentrate in surface water.

[4] Woodburn Landfill groundwater and leachate data compiled from DEQ's ECSI database (http://www.deq.state.or.us/lq/ECSI/ecsi.htm) and DEQ's Laboratory Storage and Retrieval (LASAR) database, accessible through the internet: (http://www.deq.state.or.us/lab/lasar.htm).

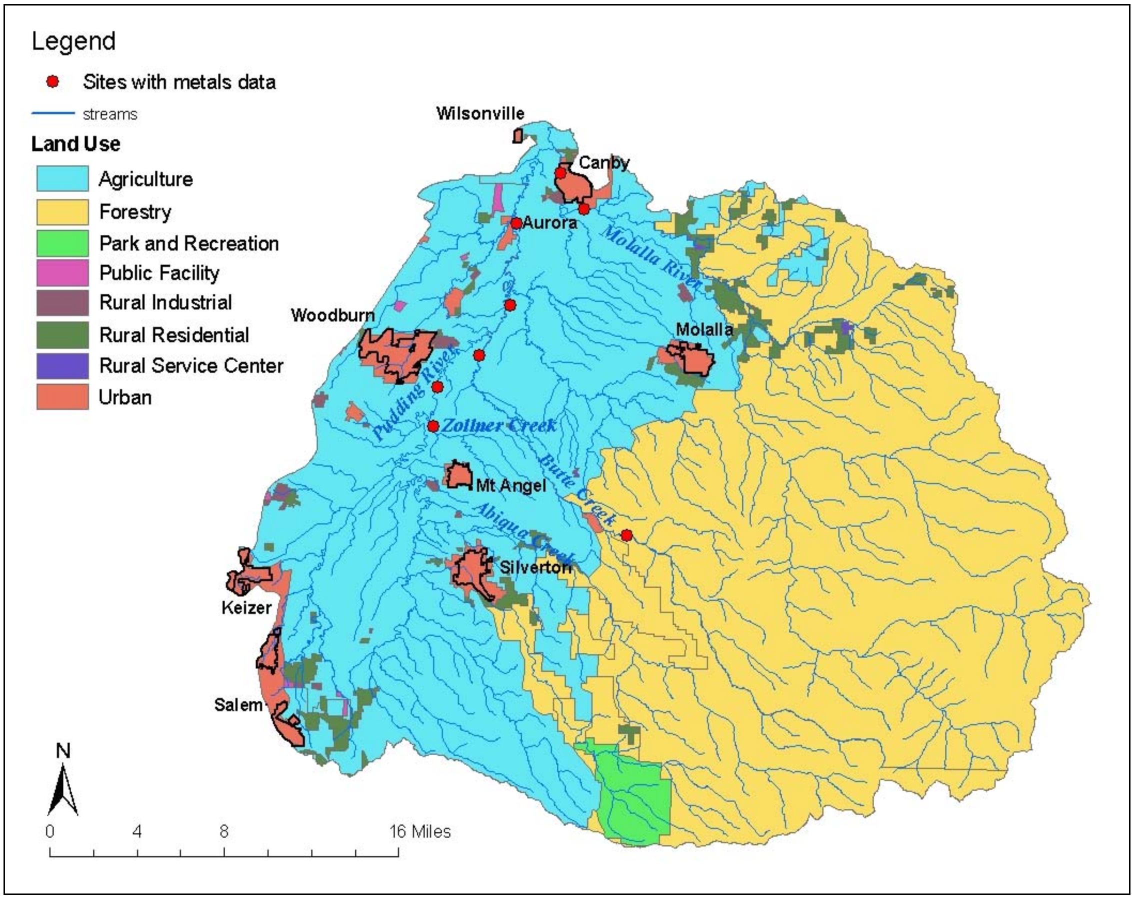

Figure 6 - 2: Molalla-Pudding Subbasin land use and location of samples analyzed for metals.

Table 6 - 5: Summary of metals concentrations in samples collected in the Molalla—Pudding Subbasin. Sample size indicated by "n." Calculations include assumption that concentrations below the method reporting limit are at the method reporting limit, unless no samples yielded a concentration above the reporting limit. No Butte Creek at Butte Creek Rd. samples yielded As concentrations exceeding the method reporting limits of 10 or 3 µg/L.

	Median Fe(T) (µg/L)	**25th percentile Fe (T) (µg/L**	**Median Mn (T) (µg/L)**	**25th percentile Mn (T) (µg/L**	**Median As (T) (µg/L**	***25th percentile As (T) (µg/L**
Butte Creek at Butte Creek Rd. (n=5)	387	210	12	7	<10	<10
Molalla-Pudding Subbasin-wide	462 n=40	208 n = 40	40 n = 40, 6 qualified	25 n = 40, 6 qualified	4.3 n = 39,30 qualified	3 n = 39, 30 qualified

IRON, MANGANESE, AND ARSENIC IN ROCKS AND SOILS

Juan (1994) found that natural background iron concentrations in Washington State soils average between 25.0 and 58.7 mg/g. In Clark County, across the Columbia River from Oregon, iron concentrations in soils average 36.1 mg/g. Manganese concentrations in volcanically derived soils generally range between 200 μg/g and 1000 μg/g (Alloway, 1990). Juan (1994) found that natural background manganese concentrations in Washington State soils average between 700 and 1500 μg/g. Natural soil arsenic concentrations in Washington State average between 5.1 and 9.3 μg/g and in Clark County, 5.8 μg/g (Juan 1994). Based upon an average of sites sampled statewide, the State of Oregon reported a range of naturally occurring background concentrations for soil arsenic between 1 and 10 μg/g (Baldwin and McCreary, 1998).

Willamette Silt and Quaternary alluvium cover much of the area around Zollner Creek and the Pudding River, but approximately four miles east of Zollner Creek, exposed marine rocks and volcanics indicate the geologic formations that underlie the Zollner Creek and Pudding River watersheds (Hampton, 1972). The mineralogy of the underlying rock is relevant to the concentrations of Fe, Mn, and As measured in surface water. The marine rocks (Oligocene, 30 – 35 mybp) were deposited in an embayment adjacent to an area of active volcanism and are reworked volcanic rocks (tuff, tuffaceous sandstone, and sandstone). The reworked material is cemented by clay derived from decomposed volcanic glass (Hampton, 1972).

Tributaries entering the Pudding River from the southeast (e.g. Abiqua, Butte, Silver Creeks) flow through these exposed marine rocks as well as Columbia River Basalts and volcanic flows and breccias of the Little Butte Volcanic Series. The Little Butte Volcanic Series includes basalt, basaltic andesite, volcanic conglomerate, and pyroclastic debris extruded in the Cascade foothills in Oligocene time (30 – 35 million years before present, mybp).

Volcanic rocks and sedimentary rocks derived from volcanic materials contain percentages of Fe and the trace elements Mn and As high enough to expect some expression in groundwater and surface water. An average andesite, for example, is between 5 and 10% by weight iron oxide and a basalt about 10% (Klein and Hurlbut, 1985). Manganese is not a major element in the earth's crust (like iron), but is among the most abundant of the minor elements (approximately 0.13% by weight of an average basaltic rock) (Klein and Hurlbut, 1985). An average basalt may contain 2 mg/kg arsenic, and 1,500 mg/kg manganese (Drever, 1988, p. 329).

The most recent geologic mapping of Oregon (Walker and MacLeod 1991) identifies what was previously called the Little Butte Volcanic series as undifferentiated tuffaceous sedimentary rocks, tuffs and basalt, including rhyolitic (silicic) rocks. Hinkle and Polette, 1999, point out than silicic volcanic rocks are commonly associated with high concentrations of arsenic because As can be a component of volcanic glass. Arsenic may also be adsorbed or coprecipitated with iron oxides and absorbed to clay mineral surfaces (Hinkle and Polette, 1999).

In summary, Molalla-Pudding subbasin rocks and derivative soils and alluvium contain iron, manganese, and arsenic. The following section describes how these naturally occurring materials may be expressed in surface and groundwater.

IRON, MANGANESE, AND ARSENIC IN GROUNDWATER AND SURFACE WATER

Chemical weathering of minerals in volcanic rocks will result in the formation of clays (primarily composed of aluminum and silica) and oxides, carbonates, or other compounds deriving from remaining major and trace elements. Weathering products will also depend on factors such as dissolved organic carbon content, pH, and oxidation potential of the groundwater or surface water.

Iron, manganese and arsenic concentrations in groundwater and surface water are often related because arsenic can adsorb on or coprecipitate with iron and manganese and adsorb onto clay mineral surfaces under oxidizing conditions. Arsenic becomes mobile when reducing conditions are sufficient to dissolve iron and manganese but not enough to produce sulfide (Korte, 1991). Anderson and Bruland (1991) noted that in surface waters, greater concentrations of arsenic, iron and manganese occurred in the absence of dissolved oxygen. Within oxygenated zones (groundwater or surface water), arsenic V (arsenate) is stable; under anoxic conditions, arsenic III (arsenite) is stable (Edwards 1994).

Reducing conditions, conducive to mobilizing metals, are more common in groundwater. Table 6 - 6 summarizes the metals concentrations measured in groundwater samples collected in the Molalla-Pudding Subbasin between February and August 1993 (Figure 6 - 3).

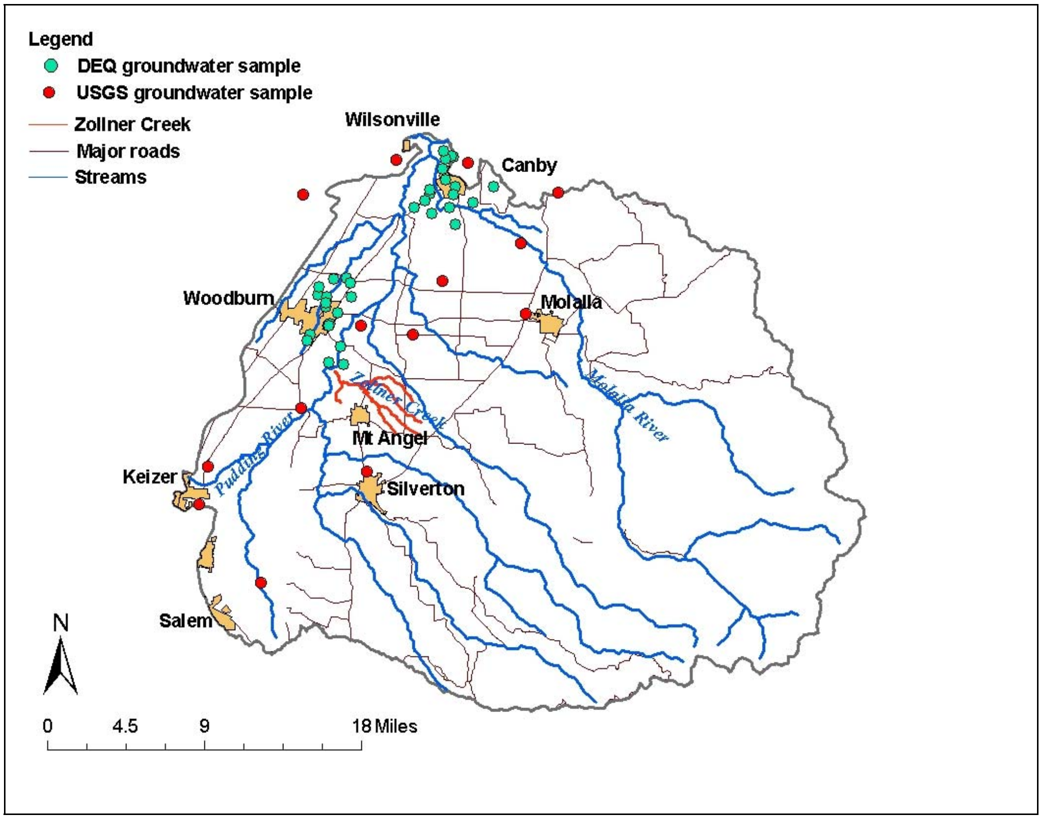

Figure 6 - 3: DEQ and USGS groundwater sampling locations, sampled between February and August 1993. USGS sampling was part of a larger-scale study; DEQ sampling was more targeted to areas of suspected contamination.

The median metals concentrations measured in groundwater sampled by DEQ exceed the median concentrations measured in the USGS samples, but the maximum dissolved metals concentrations were measured in the USGS samples. The differences may be attributed to groundwater samples collected from wells installed in different formations. Measured concentrations of iron, manganese and arsenic varied by as much as hundreds of µg/L. The USGS data set includes 13 samples in which dissolved oxygen was also measured. While the data are insufficient to derive a relationship, iron, manganese and arsenic concentrations in groundwater do tend to be highest at the lowest dissolved oxygen concentrations (Figure 6 - 4through Figure 6 - 6).

Table 6 - 6: Summary of groundwater data collected in the Molalla-Pudding subbasin.
MRL = minimum reporting limit. Concentrations below the method reporting limit were assumed to be at reporting limit for calculations. The data sets are kept separate because DEQ targeted its sampling in shallower wells, more susceptible to contaminants. The USGS sampling was done on a larger scale, more randomly, and in deeper wells.

	Source	Type	Number of Samples		Median (µg/L)	Minimum (µg/L)	Maximum (µg/L)
Arsenic	USGS	dissolved	18	(6 <MRL)	**1.5**	<1	4
		total	2	(1 <MRL)		<1	2
	DEQ	dissolved	18	(6 <MRL)	**6.5**	<5	21
		total	35	(6 <MRL)	**5**	<5	22
Fe	USGS	dissolved	27	(10 <MRL)	**60**	<3	3,300
	DEQ	dissolved	35	(8 <MRL)	**250**	<40	1,500
		total	35	(6 <MRL)	**350**	<40	13,000
Mn	USGS	dissolved	27	(14 <MRL)	**29**	<1	740
	DEQ	dissolved	33	(4 <MRL)	**300**	<10	710
		total	35	(6 <MRL)	**330**	<10	1,300

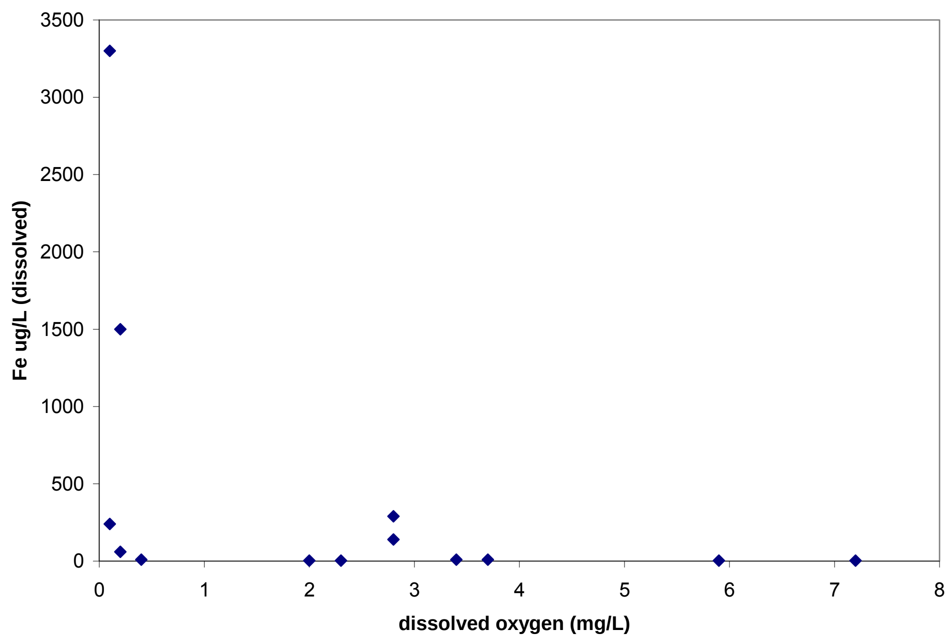

Figure 6 - 4: Dissolved oxygen and dissolved iron concentrations measured in groundwater collected by the USGS from June to August 1993.

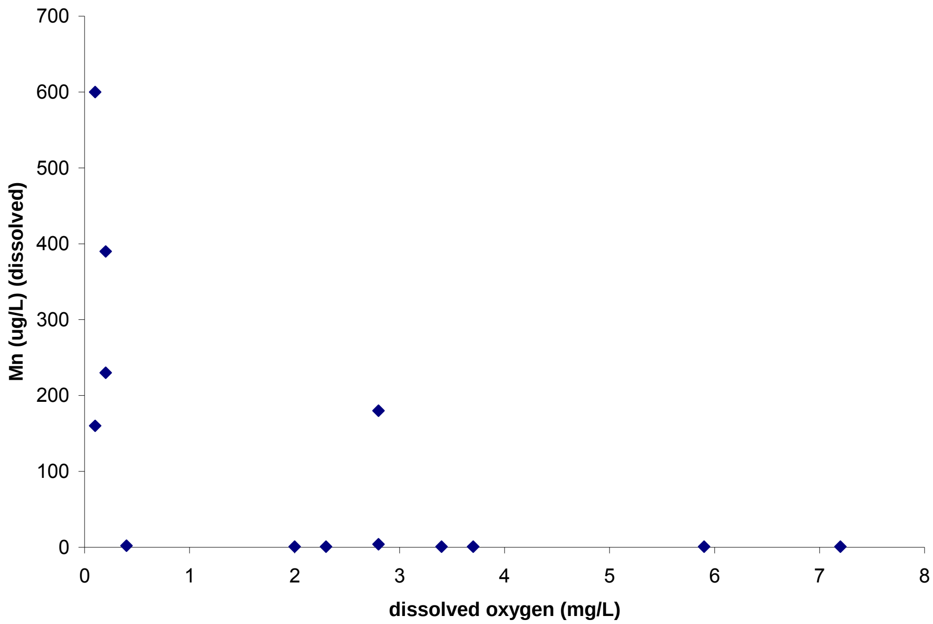

Figure 6 - 5: Dissolved oxygen and dissolved manganese concentrations measured in groundwater collected by the USGS from June to August 1993.

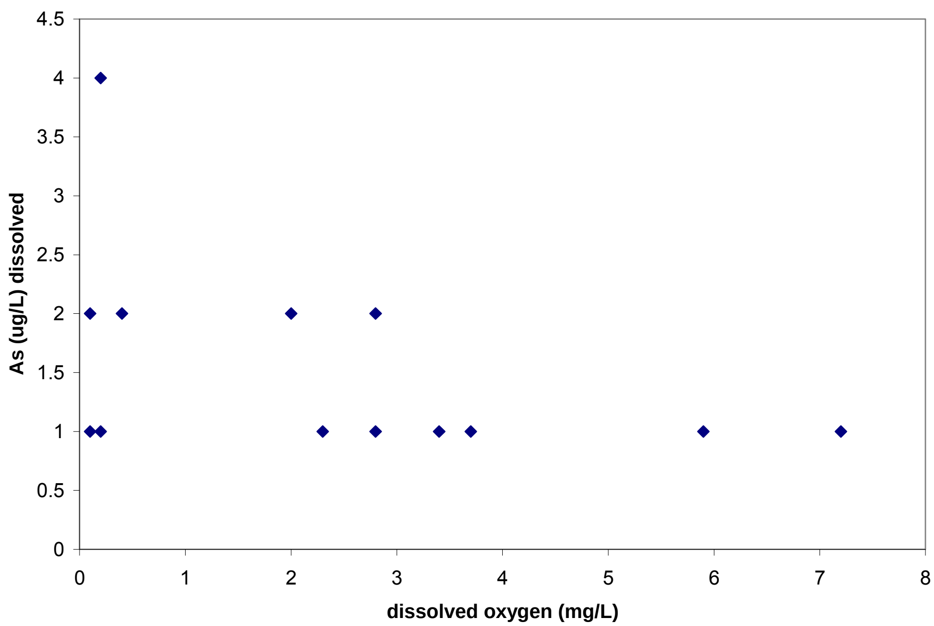

Figure 6 - 6: Dissolved oxygen and dissolved arsenic concentrations measured in groundwater collected by the USGS from June to August 1993.
Seven concentrations less than the method reporting limit (1 µg/L) are represented as 1 µg/L.

In a study of arsenic in groundwater of the Western United States, Welch, *et al*. (1988) noted that elevated arsenic concentrations (greater than 50 µg/L) are commonly associated with alluvial sediments. Hinkle and Polette (1999) observed that arsenic concentrations exceeding the EPA drinking water standard at the time (50 µg/L) are widespread in groundwater throughout the Willamette Basin. Higher As concentrations in Linn and Lane Counties were detected in samples from wells in areas where the Eugene Formation and Little Butte Volcanic series equivalent were exposed at the surface or covered with a thin layer of alluvium, and in alluvial sediments in the Tualatin basin. Concentrations ranged from less than 1 to 2,000 µg/L, with many concentrations substantially exceeding most concentrations recently measured in Zollner Creek. USGS did not find a seasonal pattern in As concentrations generally, but surmised some wells drew from different aquifers at different times of year.

A Washington State Department of Ecology study (Johnson and Golding, 2002) compiled arsenic data collected from surface water sites throughout the state, both reference sites and those more likely influenced by anthropogenic activity. The study found that concentrations of arsenic due to natural sources ranged from 0.2 to slightly more than 1.0 µg/L. The report concluded that arsenic concentrations greater than 2 to 5 µg/L may indicate anthropogenic contamination and recommended delisting 8 of 14 stream segments 303(d) listed for arsenic.

Approximately 21 percent of stream and river samples collected by the USGS in a 1969 nationwide study had arsenic concentrations above 10 μg/L (Welch, *et al*.,1988). No data was given as to the suspected source of surface water arsenic, other than to note that it is “unusual to find high arsenic concentrations in river water without a significant contribution of arsenic from geothermal water or mineralized areas”. Edwards (1994) reported that a random survey of raw drinking water sources in the United States resulted in an average arsenic concentration of 4 μg/L.

While metals concentrations in groundwater vary, probably reflecting flow paths through different geologic formations, the concentrations of iron, manganese, and arsenic measured in Molalla-Pudding subbasin groundwater are not unusual when compared to measurements made nationally, regionally, or within the Willamette Valley. Iron, manganese, and arsenic measured in Pudding-Molalla Subbasin surface water likely originate from natural sources, eroded volcanics and alluvial sediments derived from volcanic rocks. Groundwater concentrations of these metals, though greater than water quality standards, are typical for this type of geologic setting.

CONCLUSIONS FROM IRON ANALYSIS

A detailed analysis of measured iron concentrations and relationships to stream flow, precipitation, and groundwater input is presented in Appendix M. The conclusions in this section are based on the analyses in Appendix M, literature review, and results of other studies in the subbasin (summarized in the Sources and Source Categories section of this chapter).

The source of iron concentrations measured in Pudding River and Zollner Creek is probably natural – i.e. soils and alluvium deriving from volcanic rocks. A comparison of dissolved iron concentrations in surface water and groundwater supports this conclusion: Figures M-11, M-12, M-14 and M-15 in Appendix M show that the means of groundwater dissolved iron concentrations tend to exceed or be statistically similar (at an 80% confidence level) to the means of both Pudding River and Zollner Creek dissolved iron concentrations. Data also indicate that the majority of iron concentrations measured in the Pudding River and Zollner Creek are similar to surface water concentrations measured in other parts of the basin, including measurements from a site with predominantly forestry land use, upstream of the most intensive agricultural and urban activities (Table M-1).

Total iron data sets are generally too small to lead to definitive conclusions. Still, the limited data do indicate either statistically similar or higher mean total iron concentrations in surface water than mean total iron groundwater concentrations (Figures M-13 and M-16). All total iron analyses were performed on surface water samples collected in the winter months(October – May), which corresponds to higher stream flows and precipitation. Zollner Creek total iron concentrations also exceed total iron concentrations measured at the site with predominantly forestry land use. Greater total iron concentrations in surface water and similar or greater dissolved iron concentrations in groundwater may indicate two different sources for dissolved and total iron.

Analyses of samples collected from various sites on the Pudding River and Zollner Creek over approximately twenty years do not reveal any temporal or longitudinal patterns in iron concentrations (Figures M-1, M-2, M-3). A discernable change in iron concentrations over time might indicate a change in land use practices or laboratory analytical technique. Longitudinal variation might highlight spatial differences in land use, pollutant sources, or tributary contributions that influence iron concentrations.

The majority of measured iron concentrations in the Pudding River and Zollner Creek are relatively consistent over time and space; variations tend to be concentration spikes, often related to rainfall events.

The data indicate that exceedances of the water quality criterion tend to occur with precipitation, although this is not universally true (Table M-2). Exceedances based on dissolved concentrations do occur during precipitation events, but rain seems to cause total iron concentrations to exceed the criterion by a much greater degree than do dissolved concentrations. The highest exceedances were measured in samples collected from Zollner Creek following more than 0.6 inches of precipitation in 24 hours and analyzed for total iron. Based on only three events in which samples from the same site were analyzed for both total and dissolved concentrations[5], the difference between the dissolved and total fractions are greater when it's raining.

Seasonality of iron concentrations is slightly more pronounced at river mile 21 on the Pudding River than further down stream (approximately river mile 8) (Figures M-4 and M-5). At both locations, the highest dissolved concentrations were measured in January – March. And the lowest measured in April – June. These observations are based on dissolved iron surface water data and so conclusions about surface contributions are more tenuous. Still, the data do indicate that dissolved concentrations increase during rain events and during high flow events. Zollner Creek iron dissolved concentrations demonstrate less seasonality (Figure M-6) and this may indicate a larger groundwater baseflow component to Zollner Creek flow, compared to baseflow contribution to the Pudding River. A higher percentage of groundwater baseflow in Zollner Creek would be consistent with its small watershed.

A review of calculated Pudding River iron loads (where flow data were available) indicates few exceedances of the water quality criterion, but the exceedances and near exceedances that do occur do so across flow conditions (Figure M-7). A simple plot of concentration and estimated stream flow exceedance probability shows more exceedances and more severe exceedances at high flows (Figure M-8). Where flows are available, Zollner Creek measurements also exceed the iron criterion at low to mid flows (Figure M-9), but more data plotted by concentration reveals more exceedances (mostly total iron) at high flows (Figure M-10). The data displayed in the load duration and concentration duration curves indicate that at higher flows and precipitation, eroding stream banks may contribute sediment to the steam, increasing the total iron concentration.

The overall conclusion from the analysis of iron concentrations in groundwater and surface water, stream flow, and precipitation is that iron, though a naturally occurring material, may be contributed in unnatural concentrations through runoff and erosion.

IRON LOADING CAPACITY

DEQ calculated a loading capacity for iron because the data indicate that anthropogenic activities may increase the concentration of iron in surface water above natural concentrations. The loading capacity is determined by the following equation:

$$LoadingCapacity(\frac{kg}{day}) = 300\frac{ug}{L} * Q\frac{ft^3}{s} * 28.32\frac{L}{ft^3} * 86400\frac{s}{day} * 10^{-9}\frac{kg}{ug}$$

The iron loading capacity for the mainstem Pudding River is the load at a particular flow at which the concentration of iron is 300 µg/L. The loading capacity is determined based on flow measured at Aurora (river mile 8). The loading capacity of Zollner Creek is determined based on the flow as measured near Mt. Angel, at Monitor-McKee Road. The loading capacities of the Pudding River and Zollner Creek will protect the water and fish ingestion beneficial use throughout the watershed. Table 6 - 7 and Table 6 - 8 show the loading capacity under several flow scenarios.

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[5] USGS collected samples from Zollner Creek near Mt. Angel on June 1 and July 27, 1993, and DEQ collected samples from Pudding River at Aurora on April 27, 1993.

Table 6 - 7: Example Flow Based Loading Capacity of the Pudding River

Flow (cfs)	Flow Exceedance Probability	Load to meet criterion of 300 micrograms/l (kilograms per day)
12	95%	8.8
110	75%	80
590	50%	430
1710	25%	1,250
4850	5%	3,560

Table 6 - 8: Example Flow Based Loading Capacity of Zollner Creek.

Flow (cfs)	Flow Exceedance Probability	Load to meet criterion of 300 micrograms/l (kilograms per day)
0.17	95%	0.12
0.93	75%	0.68
4.6	50%	3.4
17	25%	12.4
108	5%	79

IRON EXCESS LOAD

Current pollutant load was estimated by calculating the 90th percentile of the load within each flow interval, based on all samples collected when stream flow data were available. Representing current pollutant load by the 90th percentile of loads in a flow interval is a more conservative estimate than using the median. Loading capacity for each flow interval was calculated with the highest exceedance probability in the flow interval, as a conservative estimate. The difference between the loading capacity and the estimated current pollutant load is an explicit excess load. Table 6 - 9 presents the current pollutant load and excess load for the Pudding River and Zollner Creek.

Additionally, excess load can be represented by the percent reduction necessary to meet water quality standards. DEQ used a surrogate measure (i.e. percent reduction), explained in the load allocations section of this chapter, as a more practical expression of load allocations. The iron load equivalent to the percent reduction that substitutes for a load allocation is an implicit excess load. At present, there is no indication that point source discharges contribute to excess load.

Table 6 - 9: Iron excess load for Pudding River and Zollner Creek.
NA = not applicable because the 90th percentile of iron concentrations in this flow interval is less than the loading capacity.

	Highest Flows 0 - 10% Exceedance Probability	**High Flows** 10 - 40% Exceedance Probability	**Transitional Flows** 40 - 60% Exceedance Probability	**Low Flows** 60 – 90% Exceedance Probability	**Lowest Flows** 90 - 100% Exceedance Probability
Pudding River					
Current load (kg/day)	2854.8	2397.2	242.5	92.7	4.2
Load capacity (kg/day)	2624.3	670.3	267.2	20.4	1.9
Excess load (kg/day)	230.5	1726.9	NA	72.3	2.3
Zollner Creek					
Current load (kg/day)	20.0	5.9	1.0	0.8	0.03
Loading capacity (kg/day)	44.04	5.73	1.76	0.25	0.04
Excess load (kg/day)	NA	0.1	NA	0.6	NA

IRON ALLOCATIONS

DEQ calculated allocations for iron because the data and analysis in Appendix M indicate that anthropogenic activities may increase the concentration of iron in surface water above natural concentrations. Allocations apply year-round because exceedances occur during both summer and winter periods and in all flow regimes. The allocations are designed to protect the sensitive beneficial use, water and fish ingestion.

WASTELOAD ALLOCATIONS

The preceding analysis indicates that the source of iron is likely natural, though water quality exceedances may result from anthropogenic activities that promote bank erosion and storm runoff. At this time, each point source in Table 6 - 10 is allotted an iron wasteload allocation that equals the facility's current conditions. These are point sources that discharge to the Pudding River downstream of river mile 35.4 (the extent of the listing and demonstrated impairment) or a tributary that enters the Pudding River downstream of river mile 35.4. Each facility's WLA also requires that the facility cause no measurable increase in in-stream iron concentrations. Permitted sources in Table 6 - 10 will be required to monitor and submit sufficient data so that DEQ can conduct an effluent characterization for each facility. Eight sampling events for municipal sources and 12 sampling events for industrial sources will constitute sufficient data. Based on the monitoring data, DEQ will evaluate the extent that each permitted source causes or contributes to iron water quality exceedances. If the evaluation indicates a measurable increase in receiving water iron concentrations from the permitted point source activities or processes, DEQ would calculate effluent limits at that time.

Table 6 - 10: Sources permitted to discharge wastewater in the Pudding River downstream of river mile 35.4 or a tributary that enters downstream of river mile 35.4.

Facility Name	Permit Type	Permit Description	Receiving Stream	River Mile	Wasteload Allocation
City of Woodburn Wastewater Treatment Plant	Major NPDES-DOM-C1a	Sewage disposal; 5 MGD or more, less than 10 MGD	Pudding River	21.4	Current conditions
City of Aurora Wastewater Treatment Plant	Minor NPDES-DOM-Db	Sewage disposal; less that 1 MGD with lagoons.	Pudding River	8.8	Current conditions
City of Gervais Wastewater Treatment Plant	Minor NPDES-DOM-Db	Sewage disposal; less that 1 MGD with lagoons.	Pudding River	31.2	Current conditions
City of Mt. Angel Wastewater Treatment Plant	Minor NPDES-DOM-Da	Sewage – less than 1 MGD	Pudding River	34	Current conditions
City of Hubbard Wastewater Treatment Plant	Minor NPDES-DOM-Da	Sewage – less than 1 MGD	Mill Creek	5.3	Current conditions
Deer Creek Estates Water Association	Minor GEN 02	Filter backwash	Mill Creek	7.1	Current conditions
Lakewood Homeowners, Inc.	Minor NPDES-DOM-Da	Sewage – less than 1 MGD	Mill Creek	3.9	Current conditions
JLR, LLC/Bruce Pac.	Minor NPDES-IW-B05	Food/beverage processing - Large and complex. Flow greater than or equal to 1 MGD for 180 days/year or more	Pudding River	27	Current conditions
Norpac Foods	Minor NPDES-IW-N04	Food/beverage processing – Medium. Flow between 0.1 MGD and 1 MGD, or flow greater than or equal to 1 MGD for less than 180 days/year	Pudding River	1	Current conditions
Columbia Helicopters	NPDES-IW-N	Process wastewater: groundwater remediation cleanup	Pudding River	2	Current conditions

LOAD ALLOCATIONS

Surrogate Measures

The Pudding River and Zollner Creek Iron TMDL incorporates measures other than "*daily loads*" to fulfill requirements of §303(d). Allocations are in terms of percent reduction in in-stream concentrations needed to achieve the numeric criterion for protection of water and fish ingestion: 0.3 mg/L. Percent reductions apply to the Pudding River and Zollner Creek and their tributaries. The percent reduction translates load allocations into more applicable measures of performance, a percent reduction of in-stream iron concentrations.

Pudding River and Zollner Creek percent reductions have been allocated equally for all land uses – urban, agricultural, and forestry – as the Pudding River site at Aurora integrates all those land uses. All available data was used in calculating the percent reductions, not only that data that coincided with flow measurements. For that reason, the percent reductions are shown on concentration duration curves instead of load duration curves.

The percent reductions are based on one of three calculations, whichever yielded the greatest percent reduction. DEQ calculated the percent reductions required to bring the 90^{th} percentile of the iron concentrations measured at a site down to the water quality criterion of 0.3 mg/L (300 µg/L). Since the listing criterion for toxics is two samples exceeding the water quality criterion, if the 90^{th} percentile reduction did not reduce the number of exceedances to fewer than two, an additional reduction was applied to the flow interval in which the highest concentrations occurred. Figure 6 - 7 and Figure 6 - 8 illustrate the reductions necessary to bring the 90^{th} percentile of all available iron concentration measurements (combined total and dissolved results) down to the iron water quality criterion.

If the excess load calculation in the previous section (based on samples for which flow data were also available) indicated there was an excess load in a flow interval, the reduction necessary to remove that excess load was used. Finally, if neither the excess load calculation nor the 90^{th} percentile of data in the concentration duration curves indicated a necessary reduction, the reduction from adjacent flow intervals was applied. The percent reductions for the Pudding River and Zollner Creek are listed in Table 6 - 11.

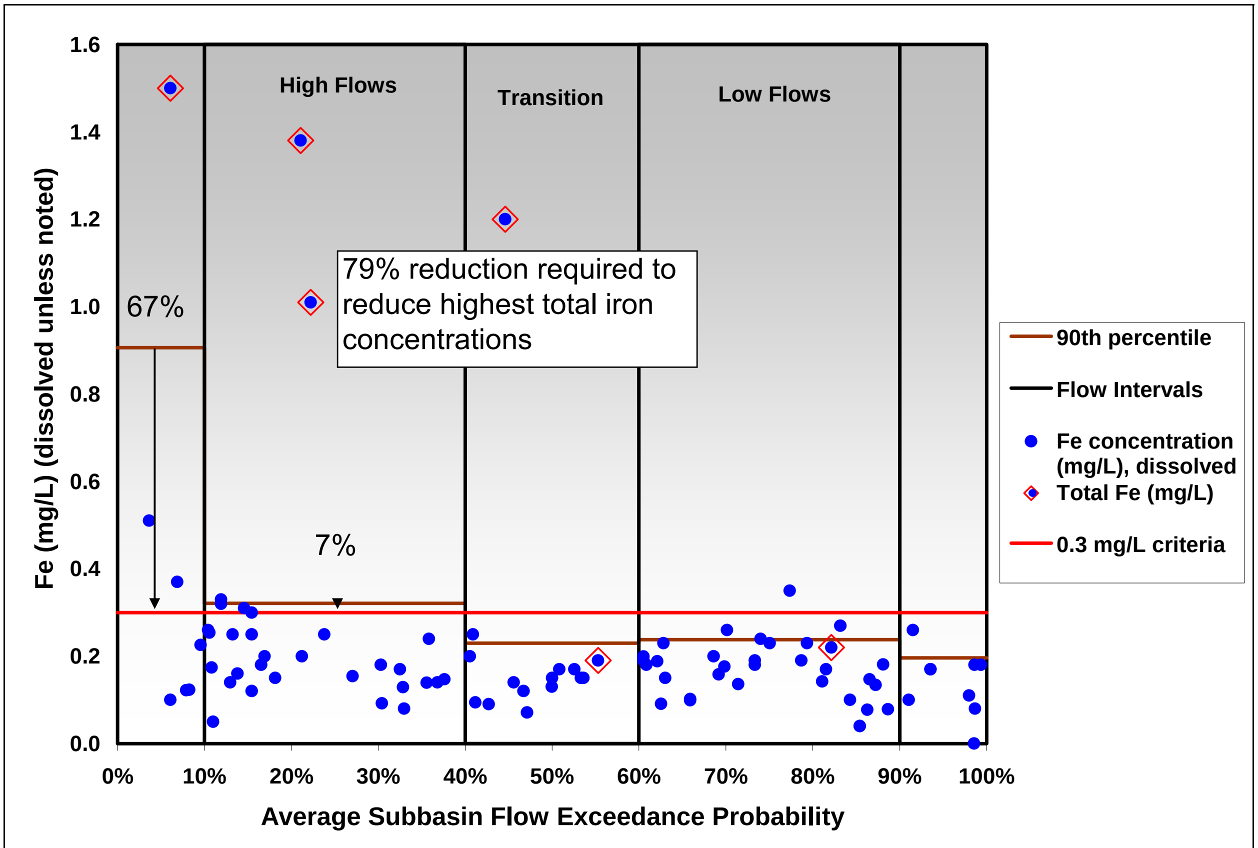

Figure 6 - 7: Pudding River measured iron concentrations and the reduction necessary to bring the 90^{th} percentile to the water quality criterion.
An additional reduction is necessary to reduce exceedances to fewer than two occurrences.

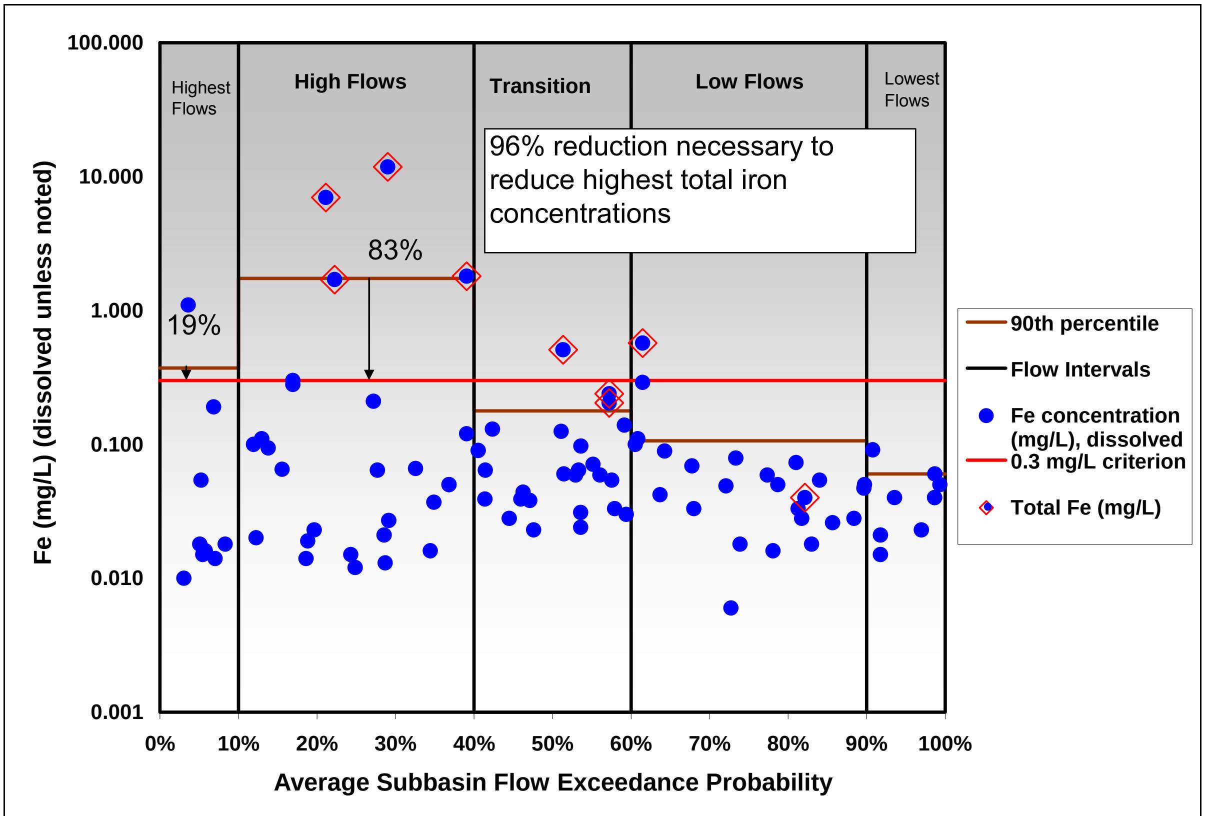

Figure 6 - 8: Zollner Creek measured iron concentrations and the reduction necessary to bring the 90th percentile to the water quality criterion.
An additional reduction is necessary to reduce exceedances to fewer than two occurrences.

Table 6 - 11: Percent reductions of iron loading required in Pudding River and Zollner Creek to meet the water quality criterion.

Stream	**Highest Flows** 0 - 10% Exceedance Probability	**High Flows** 10 - 40% Exceedance Probability	**Transitional Flows** 40 - 60% Exceedance Probability	**Low Flows** 60 – 90% Exceedance Probability	**Lowest Flows** 90 - 100% Exceedance Probability
Pudding River	79%	79%	79%	78%	54
Zollner Creek	19	96%	75	75	75

While this TMDL allocates percent reductions to achieve the iron water quality standard, a total suspended solids target can also be useful in implementing erosion control practices that will reduce sediment and iron input into streams. The TSS targets and the TSS loads in Table 6 - 12 and Table 6 - 13 are not load allocations. DEQ has provided load allocations as target TSS concentrations for the Pudding River, Zollner Creek and the Little Pudding River as part of the Pesticides TMDL, presented in Chapter 4, Table 4 - 19.

Based on an evaluation of the linear regressions presented in Figure 6 - 9 and Figure 6 - 10, DEQ determined that instream concentrations of 6 mg/L and 3 mg/L would be necessary to meet the 300 µg/L iron criterion in the Pudding River and Zollner Creek, respectively. The linear regressions are based on relatively small data sets (8 and 11 samples) and only the total iron measurements. DEQ did not find a relationship between TSS concentrations and the dissolved iron measurements from Pudding River or Zollner Creek samples. Though the data sets are small, the strong relationship between total suspended solids and total iron concentrations confirms conclusions made from the preceding analyses, that iron exceedances are likely related to excess erosion and sediment entry into surface water. Table 6 - 12 and Table 6 - 13 list target TSS loads for the Pudding River and Zollner Creek, respectively, assuming a correlation with iron concentration. These TSS loads are not load allocations, but are meant to be helpful planning targets.

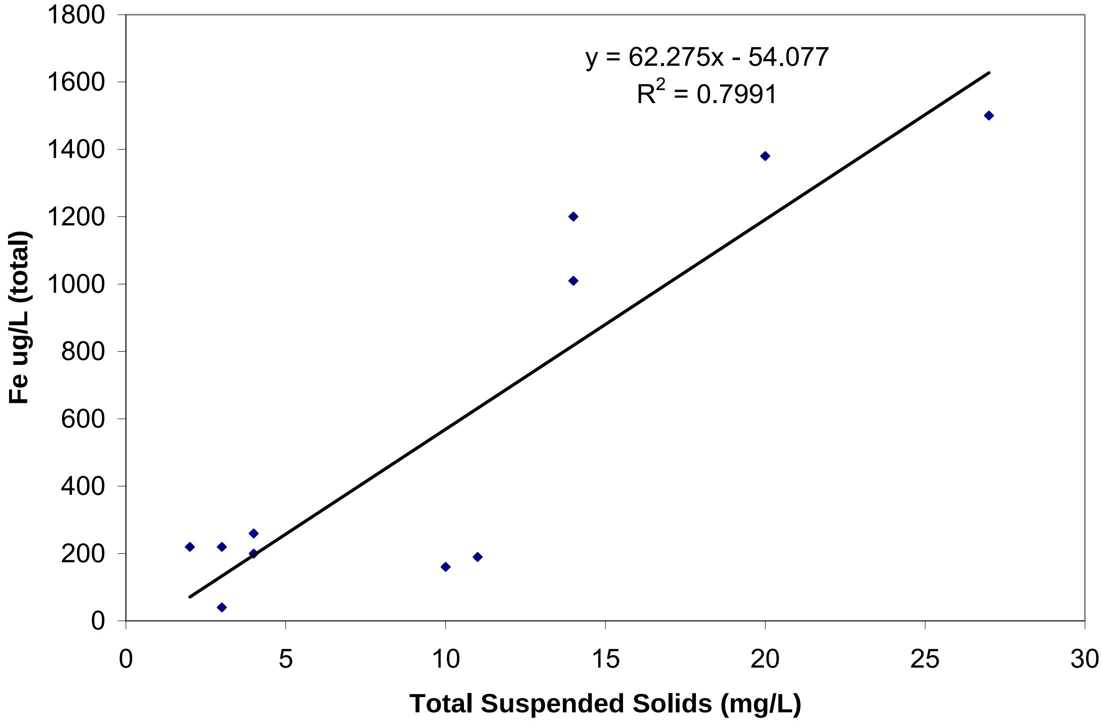

Figure 6 - 9: Linear regression of all Pudding River total iron measurements with total suspended solids measurements.

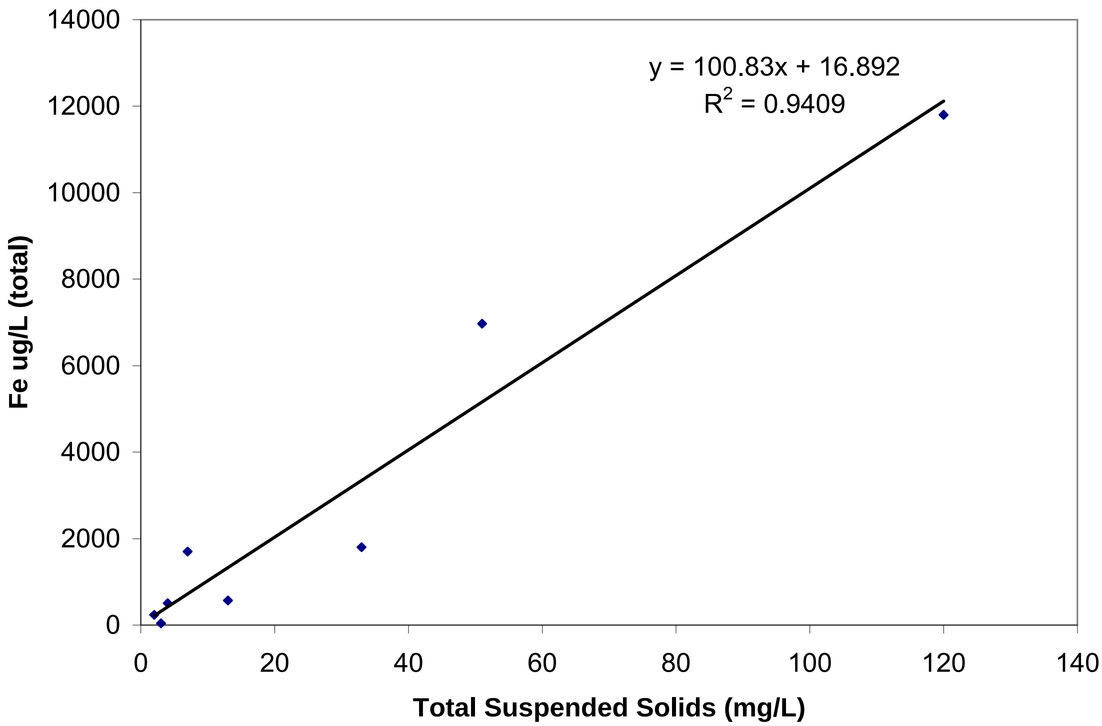

Figure 6 - 10: Linear regression of all Zollner Creek total iron measurements with total suspended solids measurements.

Table 6 - 12: Flow based TSS load to achieve iron water quality criterion in the Pudding River.

Flow (cfs)	Exceedance Probability	Load to meet target of 6 mg/L TSS (kg/day)
12	95%	176
110	75%	1,615
590	50%	8,662
1710	25%	25,105
4850	5%	71,203

Table 6 - 13: Example flow based TSS load to achieve iron water quality criterion in Zollner Creek.

Flow (cfs)	Exceedance Probability	Load to meet target of 3 mg/L TSS (kg/day)
0.17	95%	1
0.93	75%	7
4.6	50%	34
17	25%	125
108	5%	793

SEASONAL VARIATION

The load allocations, expressed as percent reductions at different stream flow levels, apply year-round and are protective at the highest iron concentrations measured. DEQ reviewed iron concentrations and their relationship to stream flow quantity and precipitation, as well as season. Seasonal analysis is presented in Appendix M.

Figures M - 4 and M – 5 in Appendix M indicate significant differences in seasonal iron concentrations at two Pudding River sites. The highest concentrations were measured in samples collected in the months of January through March. Analysis of samples collected from Zollner Creek (Figure M – 6) did not reveal as significant a seasonal difference in concentration as the Pudding River sites. Most of the iron concentrations exceeding the criterion have been measured in samples collected between the months of October and May (Figures M – 7 through M – 10). Still, the seasonal variation seems to be related to flow and precipitations levels. The percent reductions, therefore, are based on stream flows, rather than season alone.

ADDITIONAL CONSIDERATIONS

DEQ's analysis indicates that in-stream iron concentrations in the Pudding River and Zollner Creek usually reflect what are likely natural conditions. The highest measured iron concentrations likely result from anthropogenic disturbance of the riparian area that leads to erosion. The most effective strategies to reduce iron concentrations are likely to be riparian restoration and reduction of sediment entry into streams. Land managers should concentrate on these strategies as they are likely to be beneficial to achieving load allocations for other pollutants in the Molalla-Pudding Subbasin as well.

MARGIN OF SAFETY

The margin of safety applied to the iron TMDL for the Pudding River and Zollner Creek is implicit in assumptions made about the surrogate measure and percent reduction. In calculating the necessary reduction, DEQ applied the margin of safety through the conservative calculation of the 90th percentile to compare to the 0.3 mg/L criterion. The use of this "overestimation" of the median for purposes of defining percent reductions results in a slight overestimation of the needed reduction, giving an appropriate margin of safety to protect against underestimation of the median. Percent reductions are also what is necessary to reduce total iron to the water quality criterion. Data indicate that dissolved concentrations are likely to be significantly less.

RESERVE CAPACITY

DEQ allocates 10% of the iron loading capacity to reserve capacity. Future permitted sources of iron will be required to meet the water quality criteria of 0.3 mg/L or demonstrate no reasonable potential to increase iron concentrations above natural concentrations. Any additional non-point source, such as land development, could not increase the iron load more than the loading capacity.

CONCLUSIONS FROM MANGANESE ANALYSIS

A detailed analysis of measured manganese concentrations, and relationships to stream flow, precipitation, and groundwater input is presented in Appendix M. The conclusions in this section are based on the analyses in Appendix M, literature review, and results of other studies in the subbasin (summarized in the Sources and Source Categories section of this chapter).

Like the iron measured in surface water, the source of manganese in surface water is also likely derived from natural sources – i.e. soils and alluvium originating from volcanic rocks. Groundwater manganese concentrations are more than sufficient to account for the concentrations, both dissolved and total, measured in surface water.

Data analysis indicates that groundwater contribution to manganese measurements in surface water may be more significant than surface sources, such as erosion. Figures M-26, M-27, M-28, M-29, M-30 and M-31 in Appendix M show that the means of groundwater dissolved and total manganese concentrations tend to exceed or be statistically similar (at an 80% confidence level) to the means of both Pudding River and Zollner Creek dissolved and total manganese concentrations. Measured manganese concentrations in the Pudding River and Zollner Creek are relatively consistent over time and along the stream (Figure M-17). Exceedances of the water quality criterion do not relate to precipitation events, but are observed across seasons and flow conditions. Although the ratio between total and dissolved manganese does vary with precipitation (based on only three samples), rather than the total concentration increasing with precipitation, the dissolved fraction decreases.

The manganese concentrations measured in the Pudding River and Zollner Creek are higher than sub-basinwide concentrations (Table M-3) and concentrations at the site DEQ considered representative of predominantly forestry land use (Butte Creek at Butte Creek Road). Since the estimated percent groundwater baseflow to these streams is similar to that for the Pudding River (Lee and Risley, 2002), one explanation may be higher dissolved oxygen measured in these tributaries and the Molalla River than in the Pudding River and Zollner Creek, particularly in the summer months. Manganese is readily oxidized and precipitated from solution (Kalff, 2002, p. 288). More of the relatively high concentrations in groundwater may remain in solution to a greater extent in the Pudding River and Zollner Creek than in the more oxygenated tributaries.

Like the seasonality of iron concentrations, seasonality of manganese concentrations is slightly more pronounced at river mile 21 on the Pudding River than further down stream (river mile 8) (Figures M-19 and M-20). Unlike the iron seasonality, the highest dissolved concentrations were measured in the summer and fall months.

Manganese loading and concentrations in the Pudding River tend to exceed the water quality criteria more under lower stream flow conditions (Figures M-22 and M-23) . In Zollner Creek exceedances occur across all flow and precipitation conditions (Figures M-24 and M-25). Exceedances are more frequent during summer months than winter months.

These analyses indicate that anthropogenic activities that would increase erosion and sediment loading to streams do not appear to be contributing significantly to manganese loading. Most measurements made in the Pudding River and Zollner Creek do exceed the manganese water quality criteria, but the data suggest manganese moves into surface water from groundwater to a greater extent than from surface sources.

DEQ's analysis indicates that manganese concentrations in surface water do not increase to unnatural concentrations in response to anthropogenic activities. The data do not show increased manganese concentrations correlating with higher stream flows or precipitation. At this time the DEQ concludes that a TMDL for manganese is not necessary and recommends delisting.

CONCLUSIONS FROM ARSENIC ANALYSIS

An analysis of measured arsenic concentrations is presented in Appendix M. Few detectable concentrations were available, but the limited analyses in Appendix M are the basis for the conclusions in this section.

Exceedances of water quality criteria for arsenic, iron and manganese are common throughout the Molalla-Pudding Sub-Basin. It appears that arsenic, iron and manganese are mobilized in groundwater due to their natural presence within local volcanic and associated sedimentary rocks. Surface water concentrations of arsenic and manganese appear to be a reflection of the natural geochemical environment and regional groundwater hydrology within the Molalla-Pudding Sub-Basin. While surface water concentrations are high relative to water quality criteria, they are similar to national averages and most likely reflect natural background conditions.

DEQ's analysis indicates that arsenic concentrations in surface water do not increase to unnatural concentrations in response to anthropogenic activities. The data do not show increased arsenic and manganese concentrations correlating with higher stream flows or precipitation. At this time DEQ concludes that a TMDL for arsenic is not necessary and recommends delisting.

REFERENCES

Alloway, B.J. 1990. Ed. Heavy Metals in Soils. Blackie Academic & Professional Publishing, Glasgow, UK, 339p.

Aroner, E.R.. 1997. WQHydro – Water Quality/Hydrology Graphics/Analysis System – Environmental Data Analysis Technical Appendix. WQHydro Consulting, Portland, Oregon, 223 pp.

Anderson, L.C. and Bruland, K.W. 1991. Biogeochemistry of Arsenic in Natural Waters: The Importance of Methylated Species. *Environmental Science and Technology*, Vol. 25, No. 3, pp. 420-427.

Baldwin, L. and McCreary, H. 1998. Study of State Soil Arsenic Regulations. Association for the Environmental Health of Soils, Amherst, MA.

Chang, A., Page, A., Krage N. 2004. Role of Fertilizer and Micronutrient Applications on Arsenic, Cadmium, and Lead Accumulation in California Cropland Soils. Department of Environmental Sciences, University of California, Riverside, California.

Drever, J. 1988. The Geochemistry of Natural Waters. Prentice Hall, Englewood Cliffs, New Jersey.

Edwards, M. 1994. Chemistry of arsenic removal during coagulation and Fe-Mn oxidation. *Journal of the American Water Works Association*, 86 (9): pp. 64-78.

Environmental Protection Agency. 1986. *Quality Criteria for Water*, EPA 440/5-86-001.

Ferguson, J.F. and Gavis, J. 1972. A review of the arsenic cycle in natural waters. *Water Research*, Vol. 6, pp 1259-1274.

Gilbert, R. 1987. Statistical Methods for Environmental Pollution Monitoring. VanNostrand Reinhold Company, New York.

Hampton, E. 1972. Geology and Ground Water of the Molalla-Salem Slope Area, Northern Willamette Valley, Oregon. U.S. Geological Survey, Water-Supply Paper 1997.

Hinkle, S.R. and Polette, D.J. 1999. Arsenic in Ground Water of the Willamette Basin, Oregon. Water Resources Investigations Report 98-4205, 28p.

Juan, C.S. 1994. Natural Background Soil Metals Concentrations in Washington State. Washington Department of Ecology Publication No. 94-115.

Johnson, A. and Golding, S. 2002. Results and Recommendations from Monitoring Arsenic Levels in 303(d) listed rivers in Washington. Washington State Department of Ecology Publication number 02-03-045.

Kalff, J. 2002. Limnology. Prentice-Hall, Inc. Upper Saddle River, NJ.

Klein, C. and Hurlbut, C. 1985. Manual of Mineralogy. John Wiley & Sons, Inc., New York.

Korte, N. 1991. Naturally Occurring Arsenic in Groundwaters of the Midwestern United States. *Environmental Geology and Water Science*, Vol. 18, No. 2, pp. 137-141.

Lee, K. and Risley, J. 2002. Estimates of Ground-Water Recharge, Base Flow, and Stream Reach Gains and Losses in the Willamette River Basin, Oregon. U.S. Geological Survey Water-Resources Investigations Report 01-4215.

Tetra Tech 1992. *Willamette River Basin Water Quality Study, Component 2: Review and Summary of Toxic Pollutants in the Willamette River and Major Tributaries*, Draft Report #TC 8983-02, Prepared for the Oregon Department of Environmental Quality.

Walker, G. W. and MacLeod, N. 1991. Geologic Map of Oregon, U.S. Geological Survey, scale 1:5000,000.

Webb, J.L. 1966. Enzyme and Metabolic Inhibitors, Vol. III, Chapter 6. Academic Press, New York.

Welch, A.H., Lico, M.S., and Hughes, J.L. 1988. Arsenic in Ground Water of the Western United States. Ground Water, 26 (3): pp. 333-347.

Hart, J., Fletcher, R., Landgren, C., Horneck, D., Webster, S., Bondi, M. 2004. Christmas Tree Nutrient Management Guide for Western Oregon and Washington. Oregon State University Extension Publications EM 8856-E.