Water Quality Standards

Review and Recommendations:

Arsenic, Iron and Manganese

DRAFT: August 19, 2010

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Draft Report



Last Updated: 08/19/10

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# Table of Contents

[Table of Contents 3](#_Toc269817304)

[Executive Summary 4](#_Toc269817305)

[Chapter 1 Introduction and Background 7](#_Toc269817306)

[Chapter 2. Arsenic Human Health Criteria Review and Recommendations 8](#_Toc269817307)

[**Concerns about Oregon’s Human Health Criteria for Arsenic** 8](#_Toc269817308)

[**Arsenic in Oregon** 9](#_Toc269817309)

[**Potential Health Impacts of Arsenic** 11](#_Toc269817310)

[**Current Human Health Criteria for Arsenic: State and Federal** 12](#_Toc269817311)

[**DEQ Proposed Revised Arsenic Criteria** 13](#_Toc269817312)

[**Options Considered for Revising the Arsenic Criteria** 17](#_Toc269817313)

[Chapter 3. Iron Human Health Criteria Review and Recommendations 20](#_Toc269817314)

[**Oregon’s Current Iron Criteria** 20](#_Toc269817315)

[**Federal Requirements and Recommendations** 20](#_Toc269817316)

[**Effects of Iron related to Public Water Supply** 20](#_Toc269817317)

[**Recent Actions in other States** 21](#_Toc269817318)

[**DEQ Proposed Revision** 22](#_Toc269817319)

[Chapter 4. Manganese Human Health Criteria Review and Recommendations 23](#_Toc269817320)

[**Background Information** 23](#_Toc269817321)

[**Oregon’s Current Human Health Criteria for Manganese** 23](#_Toc269817322)

[**Federal Criteria Requirements and Recommendations** 24](#_Toc269817323)

[**Recent Actions in other States** 25](#_Toc269817324)

[**DEQ Proposed Revisions to Oregon’s Manganese Human Health Criteria** 25](#_Toc269817325)

[Chapter 5. DEQ’s Proposed Arsenic Reduction Policy 31](#_Toc269817326)

[**Draft Proposed Rule Language** 31](#_Toc269817327)

[**Implementation of the Arsenic Reduction Policy** 34](#_Toc269817328)

[**Appendix A. Supplemental Information on Arsenic** 41](#_Toc269817329)

[**Appendix B. Supplemental Information on Manganese** 45](#_Toc269817330)

# Executive Summary

The Department of Environmental Quality (DEQ) is proposing to revise Oregon’s human health water quality criteria for arsenic, iron and manganese as shown in Table 1 below. The proposed criteria, the scientific basis and rationale for the proposed revisions and the process DEQ used to review these criteria are discussed in this issue paper.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Table 1. Proposed Human Health Water Quality Criteria**  **for Arsenic, Iron and Manganese (µg/l)** | | | | |
| **Pollutant** | **Water + Fish Ingestion** | | **Fish Consumption Only** | |
|  | Current Criteria | Proposed  Criteria | Current Criteria | Proposed Criteria |
| Arsenic | 0.0022 | 2.3  inorganic arsenic | 0.0175 | 2.7  inorganic arsenic |
| Iron | 300 | None | None | None |
| Manganese | 50 | None | 100 | 100  marine waters |

Notes:

1) Current criteria are from Table 20 (OAR 340-041-0033).

2) The aquatic life criterion for iron is 1000µg/l. There are no aquatic life criteria for arsenic or manganese.

**Arsenic**

DEQ derived the proposed criteria for arsenic using EPA’s calculation method. However, DEQ adapted the calculation for Oregon by using locally appropriate values rather than nation-wide default values for some variables. Specifically, the proposed Oregon criteria are based on a fish consumption rate of 175 grams per day, a cancer risk level of 1 × 10-4 for the water + fish ingestion criterion, and a cancer risk level of 1 × 10-6 for the fish consumption only criterion. Additional modifications for both arsenic human health criteria include using a bioconcentration factor (BCF) of 1 and a 10% inorganic arsenic factor. Further explanation of these variables and the criteria calculations is provided in this paper.

DEQ proposes adopting locally derived criteria rather than EPA’s nationally recommended criteria because there are natural background levels of arsenic in many Oregon waters that are much higher than the national criteria. Naturally-occurring arsenic comes from geologic sources and levels are often higher in ground water than in surface waters. DEQ’s proposed criteria for inorganic arsenic are consistent with EPA recommendations. Inorganic arsenic is the form of arsenic that is toxic to humans, however, it does not bio-accumulate in fish tissue as readily as total arsenic. While DEQ’s proposed water + fish ingestion value is higher than EPA’s recommended criteria under the Clean Water Act (CWA), it is significantly lower than the maximum contaminant level (MCL) established by EPA as protective of finished drinking water under the Safe Drinking Water Act.

DEQ concludes that the proposed criteria represent an appropriate balance of human health protection and recognition that many Oregon waters contain arsenic from natural geologic sources, commonly at levels of 1-3 µg/l. These natural levels do not represent new or added health risk to the environment. Setting criteria that would trigger widespread 303(d) listings, total maximum daily loads (TMDLs) and other CWA implementation activities would require the use of valuable public resources for administrative activities that would in most cases not result in a real reduction of arsenic levels in the water or in fish.

DEQ also proposes to include an arsenic reduction policy in the state’s water quality regulations. This rule would require permittees that discharge anthropogenic sources of arsenic within a public drinking water supply protection area to take feasible actions to minimize their arsenic discharge. This provision would apply in instances where the ambient arsenic level is below the numeric criteria in order to minimize the amount of arsenic added to surface waters.

**Iron**

DEQ is reviewing this criterion because iron is a naturally occurring earth metal that sometimes exceeds the current criterion due to natural background levels, and because the criterion is not based on levels needed to protect human health. Oregon’s current “human health” criterion for iron is 300 µg/L (0.3 mg/L). This value was EPA’s nationally recommended criterion at the time Oregon adopted the criterion. Iron is not a priority pollutant, and EPA based its recommended criterion on taste and laundry staining effects, not on human health effects.

DEQ proposes to withdraw Oregon’s human health criterion for iron for the following reasons:

* The current criterion of 300 µg/L is not based on human health effects.
* Iron criteria for the protection of human health are not necessary. The amount of iron that people can ingest without adverse effects are higher than those found in Oregon surface waters and much higher than the aquatic life criterion of 1000 µg/L.
* DEQ does not expect that discharges of iron in Oregon will impact beneficial uses, including the ability to drink water or consume fish.
* Oregon has a narrative criterion and EPA has a secondary MCL that allow DEQ or water suppliers to protect against objectionable taste and odor if a community finds there is a need to do that.

These revisions would not affect the current freshwater aquatic life criterion for iron, which is a chronic criterion of 1000 µg/L (1.0 mg/L). Aquatic life is a designated beneficial use in all surface waters of Oregon and therefore the aquatic life criterion for iron applies to all waters.

**Manganese**

DEQ agreed to review the manganese criteria because manganese is a naturally occurring earth metal in Oregon and because the “water + fish ingestion” criterion is based on taste and laundry staining effects, not on levels necessary to protect human health.

DEQ proposes to withdraw the criterion for water + fish ingestion for the following reasons:

* The criterion is not based on human health effects. EPA has not recommended a water + fish ingestion criterion for the protection of human health, nor have they recommended an MCL to protect against human health effects of manganese in drinking water. Manganese levels in Oregon surface waters are far below average daily human intake levels. There is no reason to conclude that discharges of manganese will impact beneficial uses of Oregon’s fresh waters.
* Oregon does not need a numeric manganese criterion to protect water supply based on aesthetic and organoleptic effects. The Safe Drinking Water Information System database shows only one surface water supplier with detectable levels manganese in their finish water, and the concentration was 0.8 µg/l, far below the levels where aesthetic or taste effects are objectionable (30 – 150 µg/l). DEQ has a narrative criterion for the protection of taste, odor and aesthetic affects should limits be required to protect a surface water domestic water supply source from particularly high levels of manganese from anthropogenic sources. Finally, EPA’s secondary MCL of 50µg/l established under the Safe Drinking Water Act to provide guidance to water suppliers can be used by water suppliers to prevent these non-health based effects.

In addition, DEQ proposes to withdraw the fish consumption only manganese criterion (100 µg/l) as applicable to freshwaters and leave this criterion in place for marine waters. EPA recommended the 100µg/l criterion in 1976, prior to the fish ingestion/bioconcentration factor derivation method, which was published in 1980. The EPA criterion was not based on a calculation method, but rather was recommended due to concerns about possible high bioconcentration rates among marine mollusks. Data collected since that time show that bioconcentration factors for manganese in freshwater species are low (i.e., manganese does not accumulate in freshwater aquatic species in appreciable amounts). Consequently, a freshwater fish consumption criterion for manganese is not needed.

# Chapter 1 Introduction and Background

The Oregon Department of Environmental Quality (DEQ) reviewed the science behind the human health water quality criteria for some of the naturally occurring earth metals in response to concerns expressed to the Oregon Environmental Quality Commission (EQC) at their meeting in October 2008. Arsenic, iron and manganese are the three metals that DEQ selected to review in more detail. These three earth metals are naturally occurring and are found in Oregon waters at natural background levels greater than the current human health criteria. There are water bodies listed as impaired for all three metals on the 2004/06 Clean Water Action section 303(d) list as in need of TMDLs. In addition, stakeholders point out that Oregon’s current arsenic criteria adopted under the Clean Water Act are much more stringent than the maximum contaminant level for drinking water established under the Safe Drinking Water Act.

At its October 2008 meeting, the EQC directed DEQ to revise Oregon’s human health criteria for toxic pollutants based on the recommended increased fish consumption rate of 175 grams per day; the Department is conducting a separate rulemaking process to incorporate 175 grams per day in its human health criteria for toxic pollutants. In addition, the EQC directed DEQ to “…consider the costs and benefits of the fish consumption rate and the data and scientific analysis already compiled or that is developed as part of the rulemaking proceeding.” In particular the EQC acknowledged the issue presented be certain naturally-occurring earth metals in providing this direction to DEQ. The proposed revisions to the arsenic, iron, and manganese criteria and the proposed arsenic reduction policy address these directives.

DEQ is pursuing rulemaking for these three criteria in advance of the full human health criteria rulemaking for several reasons. First, the timeframe for the larger package targets EQC adoption in mid-2011 and the revised criteria will not be effective until EPA approves the revisions. DEQ estimates that EPA’s action would not occur until late 2011 at the earliest, and possibly not until mid-2012 or later. Second, the scientific review and early stakeholder review of these proposed revisions are complete, and the proposal is ready for public comment. Third, the changes are significant for several NPDES permits that will be renewed over the next year to 18 months. Lastly, 107 stream segments, which account for 43% of the total stream segments currently listed for toxic pollutants, are listed for arsenic, iron or manganese. If the proposed revisions are adopted by the EQC in late 2010 or early 2011, they should be effective for use in the 2012 water quality assessment. This will help DEQ to target its resources and those of dischargers to address more important environmental improvements.

# Chapter 2. Arsenic Human Health Criteria Review and Recommendations

## **Concerns about Oregon’s Human Health Criteria for Arsenic**

The Oregon Department of Environmental Quality (DEQ) reviewed the science behind the human health water quality criteria for arsenic. DEQ heard the concerns expressed to the Oregon Environmental Quality Commission (EQC) at their meeting in October 2008 and the EQC’s directive to DEQ to “Develop a proposed rule and implementation methods that carefully consider the costs and benefits of the fish consumption rate and the data and scientific analysis already compiled or that is developed as part of the rulemaking proceeding.” Some of the facts leading to the concerns and direction from the EQC include the fact that arsenic is a naturally occurring earth metal found in Oregon waters at natural background levels much greater than the current human health criteria. In addition, the current human health water quality criteria for arsenic that apply in surface waters under the Clean Water Act are much lower than the Maximum Contaminant Level (MCL) developed under the Safe Drinking Water Act for finished drinking water delivered to people’s homes.

DEQ’s current arsenic criteria (see Table 3) are well below widespread natural background levels which presents several problems for the State and for cities and industries that discharge to waters of the state. First, this situation has resulted in many 303(d) listings of water bodies as impaired (currently 107 segments), and there will be many more as more data are collected, even though the arsenic levels are predominantly due to natural geologic sources. DEQ must then address the listings by developing a TMDL or providing some other explanation or plan for situations where the source of arsenic is natural and cannot be controlled. This is not a good use of public resources.

Another result of a water body being listed as “impaired” or having a background pollutant concentration above the water quality criterion is that there is no assimilative capacity or mixing available to cities and industries that discharge to the water body. Therefore, the facility must meet the water quality criterion at the “end-of-pipe,” prior to discharging into the river. DEQ expects that under the current arsenic criteria or new criteria based on changing only the fish consumption rate, many municipal wastewater treatment plants and a number of industrial facilities would not be able to meet the criteria. In some cases, a facility may need to discharge the same amount of arsenic they brought into the facility from the river via their intake water. Even if the facility adds no arsenic to its wastewater, if it concentrates the arsenic, which occurs, for example, when the water is used for non-contact cooling, the facility would not be able to meet the limitations required to discharge the water back into the river.

While DEQ’s standards contain a “natural condition” provision, EPA has stated that this type of provision should not apply to human health criteria. The criteria need to protect the uses, which are fishing, fish consumption, and domestic water supply. For aquatic life, natural conditions are reasoned to support native aquatic species which have acclimated or adapted to the natural conditions. This same reasoning does not necessarily hold true for humans at the risk levels and life span we target for human health protection. Therefore, if DEQ proposes to set human health criteria based on natural background levels, DEQ must demonstrate that those levels are protective of human health.

Another concern that has been expressed to DEQ is the fact that the current arsenic criteria and recalculated criteria based on an increased fish consumption rate are far below the maximum contaminant level (MCL). The MCL is the criterion set under the Safe Drinking Water Act to protect public drinking water supplies and applies to finished drinking water delivered to people’s homes.

For these reasons, DEQ pursued development of criteria with the objective of protecting human health along with the ability to use waters with natural levels of arsenic for domestic water supply and the costs associated with meeting the criteria. DEQ’s recommendations are presented below.

## **Arsenic in Oregon**

**Background Levels.** Based on the available data, natural background levels of arsenic in Oregon appear to be in the range of less than 1 microgram per liter (µg/l) up to 3 µg/l in many waters of the state. There are limited data available on arsenic concentrations in surface waters, partly because until recently DEQ used 5.0 µg/l as a quantitation limit. Therefore, much of the data collected by DEQ or permittees report “non-detectable” levels of arsenic. In 2008, DEQ reduced the quantitation limit for arsenic to 0.5 µg/l.

DEQ data from approximately 1979-1981 indicate that much higher levels of arsenic (greater than 5-10 µg/l) may be present in some south central and southeastern Oregon basins. More recent data also show a range of arsenic levels of less than one to greater than 10 µg/l in upper Klamath basin streams. It is not known whether these levels represent solely natural geologic sources or are elevated due to anthropogenic activity.

**Natural Sources.** There are natural geologic sources of arsenic in Oregon. The City of Portland has found arsenic levels in the Bull Run reservoir, a primary source of Portland’s drinking water that is upstream of human activity in a protected watershed, ranging from less than 1 µg/l (their minimum reporting level) up to 3 µg/l. Data from the other Oregon streams show arsenic levels in this range as well, including the Crooked River upstream of Prineville, the Little Deschutes River and some streams in the upper Klamath basin. A spring in the upper Klamath basin had an arsenic concentration of 16 µg/l (Newton Consultants Inc., for City of Klamath Falls, 2008). Samples from the upper Santiam basin were mostly below the 0.5 µg/l detection level.

A USGS (1998) report on arsenic concentrations in ground water of the Willamette Basin found concentrations ranging from < 1 to 2,000 µg/l. The report concludes:

1. Regional patterns of arsenic occurrence in the Willamette Basin indicate that the sources of arsenic in ground water are not human related. Arsenic-containing metal oxides, volcanic glass in volcanic rocks of rhyolitic to intermediate composition, and clays are likely sources.
2. High arsenic concentrations (concentrations exceeding the current MCL established by EPA) appear to be associated with particular associations of rock in some areas and with alluvial deposits in others (i.e. the Tualatin Basin). (paraphrased)
3. For alluvial ground water of the Tualatin Basin, (1) presence of competing anions and (2) occurrence of reducing conditions may be important controlling factors in arsenic adsorption/desorption reactions. Dissolution of iron oxides, with subsequent release of adsorbed and (or) co-precipitated arsenic, also may play an important role in arsenic mobility in ground water of the Tualatin Basin.

A 1998 arsenic study by the Washington Department of Ecology, that included data collection from the Columbia River, reported:

the recent data suggest that total recoverable arsenic concentrations in local rivers and streams are typically in the range of 0.2 - 1.0 µg/L, while concentrations greater than 2 to 5 µg/L may indicate contamination from anthropogenic sources. Arsenic levels in most 303(d) listed waterbodies are not clearly different from waterbodies that have no apparent sources, and some are comparable to rainwater. (Results and Recommendations from Monitoring Arsenic Levels in 303(d) Listed Rivers in Washington, WDOE, 2002)

**Human Sources.** A document titled *Toxicological Profile for Arsenic* (ATSDR, 2007) describes the various means by which humans have affected the fate and transport of arsenic in the environment, including the following:

* When ores that contain copper or lead are heated in smelters, “most of the arsenic goes up the stack and enters the air as a fine dust. Smelters may collect this dust and take out the arsenic as a compound called arsenic trioxide (As2O3).”
* Presently, about 90% of all arsenic produced is used as a preservative for wood to make it resistant to rotting and decay. The preservative is copper chromated arsenate (CCA) and the treated wood is referred to as “pressure-treated.” In 2003, U.S. manufacturers of wood preservatives containing arsenic began a voluntary transition from CCA to other wood preservatives that do not contain arsenic in wood products for certain residential uses, such as play structures, picnic tables, decks, fencing, and boardwalks. This phase out was completed on December 31, 2003; however, wood treated prior to this date could still be used and existing structures made with CCA-treated wood would not be affected. CCA-treated wood products continue to be used in industrial applications. It is not known whether, or to what extent, CCA-treated wood products may contribute to exposure of people to arsenic.
* In the past, inorganic arsenic compounds were predominantly used as pesticides, primarily on cotton fields and in orchards. Inorganic arsenic compounds can no longer be used in agriculture. However, organic arsenic compounds, namely cacodylic acid, disodium methylarsenate (DSMA), and monosodium methylarsenate (MSMA), are still used as pesticides, principally on cotton. Some organic arsenic compounds are used as additives in animal feed.
* Small quantities of elemental arsenic are added to other metals to form metal mixtures or alloys with improved properties. The greatest use of arsenic in alloys is in lead-acid batteries for automobiles.
* Another important use of arsenic compounds is in semiconductors and light-emitting diodes. (ATSDR, 2007)

**Arsenic Impaired Waters.**  The streams shown in the table below are currently 303(d) listed for exceeding the arsenic criteria for aquatic life or human health.

|  |  |  |  |
| --- | --- | --- | --- |
| Basin | River | River Miles | Year listed |
| Multi | Columbia | 0-142 | 1998 |
| Willamette | Willamette | 175 – 186 | 2002 |
| Upper Willamette | A-3 drain | --- | 2002 |
| Upper Willamette | Amazon Cr. | 0-23 | 2002 |
| Upper Willamette | Willow Cr. | 0-3 | 2002 |
| North Umpqua | N. Umpqua | 35-52 | 2002 |
| North Umpqua | Sutherlin Cr. | 0-16 | 2002 |
| North Umpqua | Unnamed Cr. | --- | 2002 |
| South Umpqua | Middle Cr. | 0-13 | 2004 |
| South Umpqua | S. Umpqua R. | 0-16 | 2002 |
| Warner Lakes | Twentymile Cr. | 0-29 | 2002 |
| Owyhee | Owyhee River | 71-200 | 2004 |
| Jordan | Jordan Cr | 0-95 | 2004 |
| Mid Col-Hood | Lenz Cr | 0-1.5 | 2004 |
| Mid Col-Hood | Neal Cr. | 0-6 | 2004 |
| Molalla-Pudding | Zollner Cr | 0-8 | 2004 |

## **Potential Health Impacts of Arsenic**

Arsenic is a known carcinogen that may cause cancer in skin or internal organs such as the liver, kidneys, lungs and bladder. Other potential health impacts from arsenic include cardiovascular, kidney, central nervous system and hyper pigmentation or keratosis effects (USEPA, 2000). Factors for how to represent these effects in the criteria equations are included in EPA’s Integrated Risk Information system (IRIS) database. The EPA recommended arsenic criteria are based on a cancer endpoint and are based on inorganic arsenic.

## **Current Human Health Criteria for Arsenic: State and Federal**

The current Oregon and EPA arsenic criteria are shown in Table 3 below.

|  |  |  |
| --- | --- | --- |
| **Table 3. Current Arsenic Criteria** | | |
|  | Water and fish ingestion (µg/L) | Fish consumption only (µg/L) |
| Currently effective Oregon criteria (Table 20) | 0.0022 | 0.0175 |
| Criteria adopted by Oregon in 2004 | 0.018\* | 0.14\* |
| Current EPA recommended criteria | 0.018\* | 0.14\* |

\* Inorganic arsenic

Oregon’s currently effective criteria (OAR 340-041-0033, Table 20) are based on EPA’s 1986 recommended criteria. These criteria were based on a fish consumption rate of 6.5 g/d. Table 20 does not specify whether the human health criteria are for inorganic arsenic or total arsenic. The toxicity data EPA used to calculate the 1986 recommended criteria were for inorganic arsenic.

EPA’s current recommended arsenic criteria for human health and the criteria adopted by the EQC in 2004 are based on a fish consumption rate of 6.5 g/d and a cancer slope factor of 1.75, and are specifically identified as criteria for inorganic arsenic. In 1992, EPA promulgated these arsenic criteria in the National Toxics Rule (USEPA, 1992). Although EPA has since changed the cancer slope factor in IRIS to 1.5 (4/10/1998) and changed their recommended fish consumption rate to 17.5 (EPA, 2000), they have not revised the nationally recommended arsenic criteria accordingly.

EPA did not promulgate human health criteria for arsenic in the California Toxics Rule (CTR) in 2000, stating that “a number of issues and uncertainties existed at the time of the CTR proposal concerning the health effects of arsenic.” Neither did EPA include arsenic criteria in its promulgation of criteria for the Great Lakes States in 1995 due to the fact that EPA was considering undertaking revisions to the arsenic criteria at that time.

Most states have human health arsenic criteria ranging from a low of the current EPA recommended criteria to a high of 50 µg/l. Almost half of the states have criteria of 10 or 50 µg/l based on the current or previous Safe Drinking Water Act maximum contaminant level (MCL). About 10 states have no “water & organism” arsenic criterion and several have no “fish consumption only” criterion. A few states have recalculated their arsenic criteria using EPA equations but altering some of the variables in those equations. The variables States have revised include the bioconcentration factor (BCF), the IRIS cancer slope factor (using the current value of 1.5), the fish consumption rate, and/or the cancer risk level (using 10-5 rather than 10-6). In addition, some states have applied an inorganic proportion to the calculation since the criterion applies to inorganic arsenic. One EPA Region (Region 6) has developed a methodology for developing alternate arsenic criteria. The factors and methods used in the Region 6 approach are discussed further below.

**How the EPA Recommended Arsenic Criteria Were Calculated.** The following two equations and accompanying table describe the variables that were used to calculate EPA’s current recommended human health criteria for arsenic.

Water + fish ingestion Criterion (µg/L) = 1000 x RF x BW

q1\*[DW + (BCF x FCR)]

Fish Consumption Only Criterion (µg/L) = 1000 x RF x BW

q1\*[BCF x FCR]

|  |  |  |  |
| --- | --- | --- | --- |
| **Table 4. Variables for calculating arsenic criteria** | | | |
| **Symbol** | **Description** | **Value Used for EPA Recommended**  **Arsenic Criteria** | **Value Used for Oregon’s Proposed**  **Arsenic Criteria** |
| RF = | risk factor (dimensionless) | 1x10-6 | fish consumption only 1x10-6  water + fish ingestion 1x10-4 |
| BW = | body weight (kg) | 70 | 70 |
| q1\* = | cancer potency factor (mg/kg/day)-1 | 1.75 | 1.5 |
| DW = | Drinking water consumption (L/day) | 2 | 2 |
| BCF = | bioconcentration factor (L/kg) | 44 | 1 |
| FCR = | fish consumption rate (**kg**/day) | 0.0065 | 0.175 |
| IF = | Inorganic proportion factor | No factor | 10% |

## **DEQ Proposed Revised Arsenic Criteria**

DEQ proposes to revise the arsenic criteria using EPA’s calculation method, but substituting the values EPA uses for some of the equation variables with values more appropriate for Oregon. The proposed criteria are shown on Table 5. DEQ concludes that the proposed criteria protect human health while recognizing that Oregon has widespread natural background levels of arsenic above EPA’s recommended criteria. The re-calculation approach used by DEQ and described here has been used by the EPA Region 6 as an interim strategy for arsenic.

DEQ’s Toxics Standards Review Rulemaking Workgroup, which is a group of stakeholders providing input to DEQ on this rulemaking, supports the recommendations below.

|  |  |  |
| --- | --- | --- |
| **Table 5. Proposed Arsenic Criteria (µg/l inorganic arsenic)** | | |
| **Approach** | **Water + fish ingestion** | **Fish consumption only** |
| OR recalculation: BCF=1, FCR=175, IF=10%,CSF=1.5, risk=1x10-6 | NA | 2.7 |
| OR recalculation: BCF=1, FCR=175, IF=10%,CSF=1.5, risk=1x10-4 | 2.3 | NA |

The Oregon specific variables, shown in Tables 4 and 5 above and discussed in more detail below, include the fish consumption rate (FCR), the bioconcentration factor (BCF), a percent inorganic arsenic factor and the risk level for the water + fish ingestion criterion only. In addition, DEQ used the current IRIS cancer slope factor of 1.5.

**Fish Consumption Rate.** DEQ’s proposed criteria were calculated using 175 g/d as the fish consumption rate (DEQ, 2008a). The current federal criteria are based on a consumption rate of 6.5 g/d. Using this higher rate is responsive to EPA’s disapproval of Oregon’s 2004 human health criteria which was based on their conclusion that criteria based on 17.5 g/d is not sufficient to protect high fish consumers in Oregon. These revisions would also be consistent with the EQC’s direction to DEQ to revise its human health criteria for toxic pollutants based on 175 g/d as well as its direction to consider the costs and benefits of the fish consumption rate and the data and scientific analyses compiled as part of the rulemaking.

In advance of EPA’s action and based on earlier concerns expressed by EPA on this issue, DEQ looked at multiple studies of fish consumption rates with the assistance of experts in toxicology and public health (the Human Health Focus Group), focusing on those studies conducted in Oregon and Washington as well as the national survey used by EPA. The rate of 175 g/d represents the 90 to 95 percentile of Oregon fish consumers as indicated by these studies (DEQ, 2008b). This value represents the total amount of fish consumed, regardless of species or origin, because it was found that different populations, depending on access and culture, will eat different species of fish. A study conducted by the Columbia River Inter-tribal Fish Commission looked at the amount of fish consumed by members of four Northwest tribes, including the Umatilla and Warm Spring Tribes in Oregon (CRITFC, 1994). According to this study, 95 percent of adult tribal members eat 176 grams or less of fish or shellfish per day. As a result, DEQ, with the support of the Confederated Tribes of the Umatilla Indian Reservation and EPA Region 10, selected 175 g/day as an appropriate value to use for the calculation of human health criteria.

**Risk Factor.** When EPA develops recommended human health criteria for carcinogens, it uses a cancer risk level of 10-6, which it characterizes as an appropriate level of risk for the general population. However, EPA also states that both 10-6 and 10-5 may be acceptable for the general population and that highly exposed populations should not exceed10-4. To date, DEQ has also used the 10-6 risk factor for water quality human health criteria and in other environmental protection programs based on human health risk, such as DEQ’s environmental clean-up program. DEQ is not re-evaluating the risk factor as a general matter.

However, for the arsenic water + fish ingestion criterion only, DEQ is recommending a criterion based on a risk factor of 10-4 DEQ is not recommending that this lower risk level be applied to the “fish consumption only” criterion. The proposed “fish consumption only” criterion would ensure that high consumers of fish (175 g/day) are protected at the cancer risk level of 10-6, with respect to potential arsenic risks due solely the consumption of fish.

DEQ’s proposed “water + fish consumption” criterion of 2.3 µg/l protects high consumers of fish who also ingest water as part of their high fish consumption pattern. It is more protective than EPA’s MCL for arsenic under the Safe Drinking Water Act, which is 10 µg/l. It is also more protective than DEQ's proposed “fish consumption only” criterion of 2.7 µg/l, which protects against fish consumption risks at a risk level of 10-6, even among high consumers. DEQ’s proposed “water + fish consumption” criterion would provide additional protection to account for exposure from drinking water at arsenic concentrations that commonly occur naturally in many streams in Oregon. The proposed criterion, set at 2.3 µg/l, affords combined protection against arsenic risks from fish consumption and arsenic risks from drinking water at a maximum allowable risk level of 10-4. DEQ concludes that in this specific circumstance, establishing the arsenic “water + fish consumption” criterion at this risk level is appropriate in light of the high natural background levels of arsenic found in Oregon waters, and notes that this risk level is within the allowable risk range for high-consuming populations, as discussed in EPA’s human health methodology.

DEQ reevaluated the arsenic criteria primarily because of the presence of naturally occurring arsenic in Oregon waters at levels that greatly exceed the current arsenic criteria. The elevated level of risk associated with drinking water containing these natural levels of arsenic has been present since people have been drinking water in Oregon; DEQ does not expect increased concentrations of arsenic in Oregon surface waters as a result this action. If DEQ did not pursue adoption of arsenic criteria as proposed, DEQ would expect that ambient concentrations of arsenic due to natural conditions would routinely exceed criteria around the state, and DEQ and other entities who implement or are regulated under the Clean Water Act will have the problems discussed in the previous section related to using resources to implement Clean Water Act programs that will not result in a real environmental gain. DEQ acknowledges that one alternative would be to remove the water supply beneficial use from those waters that naturally exceed the current drinking water criterion. However, public water supply systems use and are expected to continue to use certain surface waters as the source of their drinking water supply, since one of the common alternatives is for drinking water systems to switch to groundwater supplies which are likely to have even higher natural levels of arsenic.

DEQ concludes that using the higher risk level for the arsenic water + fish ingestion criterion in this instance is consistent with EPA guidance (EPA, 2000). DEQ used a fish consumption rate of 175 g/d to derive the proposed arsenic water + fish consumption criterion, which approximately correlates to the 95th percentile of populations within the state that eat relatively large amounts of fish. Additionally, the criterion is more stringent than the MCL established by EPA for protection of the general United States population under the Safe Drinking Water Act.

**Bioconcentration Factor**. Bioconcentration refers to the uptake and retention of a chemical by an aquatic organism from water. A bioconcentration factor (BCF) is the ratio of the concentration of a substance in tissue of an aquatic organism to its concentration in the ambient water in situations where the organism is exposed through the water only and the ratio does not change substantially over time. Past arsenic criteria recalculation efforts have explored several aspects relating to the selection and use of the BCF variable.

EPA's current BCF of 44 for arsenic is described in *Ambient Water Quality Criteria for Arsenic* (USEPA, 1980). The BCF was calculated using data from two species, the eastern oyster (BCF=350) and bluegill (BCF=4). Because it was based on only 2 species and one of those is the eastern oyster, which has a much greater BCF (350 v. 4), the BCF of 44 most likely overestimates the health risks associated with freshwaterfinfish consumption (USEPA Region 6, mid-1990s). In addition, the data sets used to establish the BCFs was relatively small (USEPA, 1980).

Additional, more recent data show lower BCFs for other species. EPA (Stephan, 1993; USEPA Region 6, mid-1990s) used the following information to support using a BCF of 1 in their draft proposed Great Lakes Initiative arsenic criteria and in an EPA Region 6 Interim Strategy for freshwater arsenic criteria:

* The 1984 criteria document for arsenic (EPA, 1985) contains BCFs for fish calculated from whole body measurements that range from 0 to 4. Results for invertebrates range from 1 to 17. Only data for the eastern oyster and bluegill were used to calculate the BCF of 44 in EPA’s 1980 criteria document.
* Spehar et al. (1980) obtained BCFs of 0 for various inorganic and organic forms of arsenic based on whole-body measurements of rainbow trout.
* DeFoe (1982) found a BCF of 3 for whole-body measurements of fathead minnow.
* Barrows et al. (1980) obtained a BCF of 4 using whole-body measurements on bluegills.

EPA notes that BCFs for muscle tissue, the portion of the fish typically eaten, should be lower than those for the whole body (Stephan, 1993). Azcue and Dixon (1994; IN USEPA, mid-1990s) conducted a study that measured arsenic in rock bass that exemplifies this. The highest concentration was found in bone and scales, followed (in decreasing concentration) by intestines and contents, muscle and liver. A BCF of 0.71 was calculated for muscle tissue whereas the BCF based on whole body concentration was 2.3, three times greater than the muscle tissue BCF.

As a result of this information, some states have adopted criteria based on BCFs that they found to be more representative of the aquatic life in their state. Idaho, Michigan and Colorado have used or are using a BCF of 1, as proposed in a draft version of the Great Lakes Initiative rule. A BCF of 1 is also used by EPA Region 6 in their interim strategy for deriving arsenic criteria. Use of a higher BCF would result in more stringent human health criteria for arsenic.

DEQ proposes using a BCF of 1, based on EPA proposals for the Great Lakes and Region 6, for the recalculation option for revising Oregon’s arsenic criteria for human health. DEQ is proposing to use a fish consumption rate of 175 g/d. Most of the fish consumption reflected by this rate will consist of the muscle tissue of finfish. The BCF data shown above for the muscle tissue of finfish are less than one. BCFs for rainbow trout, the only salmonid fish species tested, were 0. Therefore, DEQ concludes that a BCF of 1 is a reasonable and protective value to use in calculating arsenic criteria for Oregon.

**Inorganic Proportion Factor.** Arsenic is present in the environment and in fish tissue in organic and inorganic forms or “species.” Inorganic arsenic is more toxic to humans and EPA’s toxicity data for cancer and other end points are for inorganic arsenic. EPA’s recommended human health criteria only apply to the inorganic form of arsenic; however, the BCF value (44 L/kg) that EPA used in deriving the human health criteria for arsenic are based on total arsenic, not inorganic arsenic. Therefore, some states have also elected to multiply the BCF value by what might be called a “% inorganic” variable. For example, the EPA Region 6 Interim Strategy and the State of Colorado use a 30% inorganic variable, and the Maryland recalculation used 4% inorganic.

An EPA study (2002) on fish contaminants in the Columbia River found the following related to proportion of inorganic arsenic found in fish tissue: (p. 5-78)

* + Overall arithmetic average for all composite samples 6.5%
  + Average % inorganic by species ranged from 0.5% in carp to 9.2% in sturgeon.
  + Anadromous species about 1.0% on average
  + Resident species about 9% on average

The study said that these findings were consistent with the literature, which shows low percentages of inorganic arsenic levels for most saltwater fish species. A risk assessment performed as part of this EPA study assumed 10% of total arsenic was inorganic for all species. Using a higher “% inorganic” value results in more stringent human health criteria for arsenic.

DEQ is proposing to use an inorganic arsenic fraction of 10 percent based on the Columbia River fish contaminant and health risk assessment study (EPA, 2002). The criteria that would result by including this variable are shown in Table 5 (recommended criteria) above and Table 6 (options considered) below. The water + fish ingestion criterion is not very sensitive to the % inorganic fraction. Whether DEQ uses a % inorganic fraction of 1, 10 or 30 does not change the water + fish ingestion criterion. The % inorganic factor does affect the fish consumption only criterion significantly.

To incorporate the inorganic factor (IF) into the calculation, the equations are revised as shown here:

Water + fish ingestion Criterion (µg/L) = 1000 x RF x BW

q1\*[DW + (BCF x FCR x **IF**)]

Fish Consumption Only Criterion (µg/L) = 1000 x RF x BW

q1\*[BCF x FCR x **IF**]

**Toxicity Factors.** DEQ did not review the toxicity data or re-evaluate the cancer slope factor used to derive human health criteria for arsenic. DEQ relies on EPA research to provide toxicity information for our human health criteria. DEQ proposes to use the cancer slope factor in EPA’s Integrated Risk Information System (IRIS) data base as of the date of this review, which is 1.5 mg/kg/day. EPA has not updated its nationally recommended Clean Water Act criteria, which are based on a cancer slope factor of 1.75 mg/kg/day.

## **Options Considered for Revising the Arsenic Criteria**

DEQ considered three primary alternatives for deriving arsenic criteria as an alternative to EPA’s current recommended criteria:

1. Re-calculation of the federal criteria using Oregon appropriate variables,
2. Use of the MCL value for drinking water in some manner, and a
3. Natural background based approach.

Table 6 shows the possible criteria values under these three approaches.

|  |  |  |
| --- | --- | --- |
| **Table 6. Arsenic Criteria Options Considered**  **(µg/l inorganic arsenic)** | | |
| **Approach** | **Estimated**  **Water + fish ingestion** | **Estimated**  **Fish consumption only** |
| OR recalculation: BCF=1, FCR=175, % inorganic=10,CSF=1.5, risk=1x10-6 | 0.023 | 2.7 |
| OR recalculation: BCF=1, FCR=175, % inorganic=10,CSF=1.5, risk=1x10-4 | 2.3 | NA |
| Use the fish consumption only value for both criteria | 2.7 | 2.7 |
| MCL fraction: MCL × 0.25 | 2.5 | 2.5 |
| Statewide default natural background | 1-3 | 1-3 |

Notes: 1. MCL = 10 µg/l total arsenic. 2. HHC will be for inorganic arsenic.

3. The current IRIS CSF is 1.5.

**Option 1: Re-calculated Criteria using Oregon Appropriate Variables.** Option 1 is Oregon’s proposed approach, as discussed above. DEQ believes this is option provides a rationale for deriving the criteria numbers that is scientifically defensible and can be clearly explained to the public.

**Option 2: Use a Fraction of the Maximum Contaminant Level from the Safe Drinking Water Act to Derive Oregon’s Arsenic Criteria.**

The second approach DEQ considered was to use a combination of the maximum contaminant level (MCL) for drinking water and the EPA criteria calculation method to represent exposure through fish tissue. Nearly half of the states have utilized the MCL value of 10 for their arsenic criterion in place of EPA’s national criteria recommendations. DEQ believes that using a fraction of the MCL (10) as the water quality criteria is preferable over adoption of the MCL due to the additional exposure to arsenic through consumption of fish tissue.

An MCL is the maximum level of a contaminant allowed in drinking water delivered to the tap (post treatment). MCLs are enforceable standards developed by EPA under the Safe Drinking Water Act. MCLs are set as close to maximum contaminant level goals (MCLGs) as feasible using the best available treatment technology and taking cost into consideration. MCLGs are non-enforceable public health goals that describe the level of a contaminant in drinking water below which there is no known or expected risk to health and allow for a margin of safety. For all carcinogens, MCLGs are set to zero. On January 22, 2001, EPA revised its maximum contaminant level (MCL) for arsenic from 50 to 10µg/L, and established a date of January 23, 2006 for all public water supply systems to achieve compliance with the revised MCL.

One option for an MCL “hybrid” approach is to use the calculated fish consumption only criterion (2.7 µg/l) as the value for the water + fish ingestion criterion as well. The advantages of this approach include:

* it is well below the MCL of 10 µg/l,
* there is a high degree of confidence that this value protects the consumption of fish at high levels (175 g/d) without adverse health effects, and
* there is no point to having a water + fish consumption criterion that is higher, less stringent, than the fish consumption only criterion. The fish ingestion only criterion would apply wherever fishing/fish consumption is a designated use and would thus become the “driver” if the water + fish consumption criterion was less stringent.

**Option 3: Natural Background plus a Minimal Increment for Assimilative Capacity if that Value Protects Human Health.**

Under this approach, DEQ would establish a “default” statewide natural background level using the best currently available information on natural background levels of arsenic in the State. The human health criteria for arsenic would then be set at that level. This would prevent widespread identification of waters as “impaired” due to natural sources. This approach could reasonably lead to a water + fish consumption criterion of 1or 2µg/l. This criterion would protect human health as it is far below the drinking water MCL of 10 µg/l, and is also below or near the 2.7 µg/l value calculated to protect fish consumption at a consumption rate of 175 g/d and a risk level of 1×10-6.

A variation on this approach would be to add to the default natural background level, an increment for assimilative capacity, making the criterion slightly higher (for example, 1.5 to 2.5). The purpose of setting the criteria slightly above natural background would be to provide some assimilative capacity for mixing in localized areas. This would allow some discharge of arsenic at concentrations that have been increased due to evaporative cooling, for example, which can occur even if there has been no addition of mass. The discharge would be required to meet the criteria at the edge of an assigned mixing zone.

**Additional Considerations:**

The following additional considerations could be combined with the 3 primary options discussed above.

1. Apply the fish consumption only criterion where public domestic water supply is not a designated use and revise beneficial uses in a follow up rulemaking to more narrowly designate water bodies considered suitable for drinking water supply.
2. Adopt the alternate approaches on a site-specific basis by region or basin where natural background levels are above the criteria that would be set using the default calculations.

# Chapter 3. Iron Human Health Criteria Review and Recommendations

As part of the review of Oregon’s human health toxics criteria, DEQ re-evaluated the human health criterion for iron. DEQ reviewed this criterion because iron is a naturally occurring earth metal that sometimes exceeds the criterion and because the criterion is not based on levels needed to protect human health.

## **Oregon’s Current Iron Criteria**

Oregon’s current water quality criteria for iron are 300 µg/l (0.3 mg/l) for “human health,” and 1000 µg/l (1.0 mg/l) for freshwater aquatic life (chronic criterion). These were EPA’s national recommended criteria in the late 1980’s when they were adopted. DEQ has interpreted that the iron and manganese criteria are for dissolved metals rather than total recoverable.

## **Federal Requirements and Recommendations**

Iron is a “non-priority” pollutant under the CWA. Federal regulations for non-priority pollutants (40 CFR § 131.11) require that states adopt criteria based on a sound scientific rationale that covers sufficient parameters to protect designated uses. Both numeric and narrative criteria may be applied to meet these requirements (EPA, 1994).

EPA’s 1976 and 1986 *Quality Criteria for Water* (referred to as the “Red Book” and “Gold Book,” respectively) established 300 µg/l as the recommended water quality criterion for iron for protection of domestic water supplies (EPA, 1976; EPA, 1986). According to the Red Book, “the iron criterion in water is to prevent objectionable tastes or laundry staining (0.3 mg/l) [and] constitutes only a small fraction of the iron normally consumed and is of aesthetic rather than toxicological significance” (text in brackets added). EPA’s recommendation for iron in *Water Quality Criteria 1972* (EPA, 1973) specified that 0.3 mg/l soluble iron not be exceeded in public water supply sources.

EPA’s iron criterion under the Clean Water Act is the same as the secondary maximum contaminant level (MCL) established in EPA’s National Secondary Drinking Water Regulations under the Safe Drinking Water Act. Secondary MCLs are established only as guidelines to assist public water systems in managing their drinking water for aesthetic considerations, such as taste, color and odor. These contaminants are not considered to present a risk to human health at the secondary MCL (EPA, 1992b).

## **Effects of Iron related to Public Water Supply**

**Taste.** There is a range of sensitivities to the taste of iron in drinking water that can vary based on the form of iron. A 1960 study referenced by EPA’s “Red Book” (1976) indicated that the taste of iron may be detected readily at levels of 1800 µg/l in spring water and 3400 µg/l in distilled water.

**Health.** The “Red Book” also noted that the daily nutritional requirement for iron is 1000 to 2000 µg/l, but that much larger amounts of iron must be ingested due to poor absorption. Tolerable upper intake levels used for a recent revision to West Virginia’s criterion were 45,000 µg/l for adults and 40,000 µg/l for children (see below).

## **Recent Actions in other States**

As part of this review, DEQ considered information summarized here about iron criteria revisions that have been conducted in other states.

***West Virginia:*** In 2003, the State of West Virginia adopted an iron criterion of 1500 µg/l for the protection of both aquatic life and human health uses. Support for EPA approval included the following:

* EPA Region 3 had previously approved a 1500 µg/l iron criterion for Pennsylvania, citing scientific studies that demonstrate that an aquatic life criterion of 1500 µg/l for total iron is sufficiently protective of both instream and withdrawal uses of Pennsylvania’s waters.
* EPA Region 8 has approved site-specific iron criteria greater than 1000 µg/l based on scientific site-specific studies in Colorado.
* EPA’s national recommended water quality criterion for iron of 300 µg/l is based on national secondary drinking water standards, which are established only as guidelines to assist public water systems in managing their drinking water for aesthetic considerations, such as taste, color and odor.
* Tolerable Upper Intake Levels (UL) of iron for adults is 45 mg (45,000 µg) per day and for children is 40 mg (40,000 µg) per day. Maximum average intake from food and supplements is about 18 mg (18,000 µg) per day.
* Human health iron toxicity studies indicate that 1500 µg/l is protective of the majority of the population.

***Missouri:*** In 2006, the State of Missouri removed its drinking water criterion of 300 µg/l for iron. Support for EPA approval included the following:

* EPA’s recommended criterion for iron of 300 µg/l is based on aesthetic (e.g., laundry staining) and organoleptic (i.e. taste) effects and as such, was not developed to protect against toxicological effects.
* EPA reviewed data provided by the Missouri Department of Natural Resources regarding the State’s 2002 and draft 2004 lists of impaired waters. Based upon this information, EPA did not have reason to expect levels of iron to be present that would interfere with the protection of waters designated for Drinking Water Supply.
* The manner in which Missouri assigns designated uses to the state’s waters results in any water designated for Drinking Water Supply to also be designated for Warm Water Aquatic Life and Human Health-Fish Consumption. Given this method, the chronic aquatic life criterion for iron of 1000 µg/l, expressed as dissolved iron, is effective for all waters designated as Drinking Water Supplies.
* EPA also reviewed available information regarding potential human health effects from iron and analyzed this information, in combination with water quality monitoring data from waters in Missouri designated as Drinking Water Supply, in order to estimate potential exposure to iron. The results of this analysis led EPA to determine that the absence of an iron criterion for drinking water would not result in significant increased exposure to iron, and that a separate criterion for iron is not necessary to protect Missouri’s Drinking Water Supply Use.

## **DEQ Proposed Revision**

DEQ proposes to withdraw Oregon’s human health criterion for iron for the following reasons:

* The current criterion of 300 µg/l is not based on human health effects.
* Iron criteria for the protection of human health are not necessary. The levels of iron that may be consumed without adverse health effects are much higher than the levels found in Oregon surface waters and much higher than the aquatic life criterion of 1000 µg/l.
* DEQ does not expect that discharges of iron in Oregon will impact beneficial uses, including the ability to drink water or consume fish.
* Oregon has a narrative criterion that allows us to protect against objectionable taste and odor if there is a need to do so.

The proposed revision would not affect the current freshwater aquatic life criterion for iron, which is a chronic criterion of 1000 µg/L (1.0 mg/L). Aquatic life is a designated beneficial use in all surface waters of Oregon and therefore the aquatic life criterion for iron applies to all waters.

DEQ’s Toxics Standards Review Rulemaking Workgroup, a group of stakeholders providing input to DEQ on this rulemaking, supports the proposed criteria changes for iron.

# Chapter 4. Manganese Human Health Criteria Review and Recommendations

As part of the review of Oregon’s human health toxics criteria, DEQ reevaluated the human health criteria for manganese. DEQ reviewed these criteria because manganese is a naturally occurring earth metal in Oregon that sometimes exceeds the “water + fish ingestion” criterion and because that criterion is not based on levels needed to protect human health.

## **Background Information**

According to the World Health Organization (1999), manganese (Mn) is a naturally occurring element that is found in rock, soil, water and food. All humans are exposed to manganese, and it is a normal component of the human body. Food is usually the most important route of exposure for humans. (See the Appendix B for more information from the WHO document.)

Studies of manganese concentrations in soils found that they generally range from 200 to 1000 µg/g in volcanically derived soils (Alloway, 1990 in DEQ, 2008). Natural background manganese concentrations in Washington State soils average between 700 and 1500 µg/g (Juan, 1994 in DEQ. 2008). Sampling by DEQ and USGS in the Molalla-Pudding subbasin of Oregon showed dissolved manganese concentrations in groundwater ranged from less than 1 µg/l to 740 µg/l (DEQ, 2008).

Figure 1 shows surface water data for dissolved manganese from DEQ’s LASAR database. Out of over 7000 samples, less than a handful exceed 1000 µg/l and only a small portion exceed 200 µg/l dissolved manganese. DEQ’s 303d list includes 26 water bodies as exceeding the current “water + fish ingestion” criterion of 50µg/l (Table 7). Figure 2 shows seasonal dissolved manganese data from Beaverton Creek, Oregon. Manganese concentrations increased through the spring and summer, peaking in late summer/early fall and dropping for late fall and winter. This suggests that concentrations are higher relative to low base flows, which typically include a larger portion of groundwater inflow, and reduced relative to surface water runoff that occurs in response to rainfall events.

## **Oregon’s Current Human Health Criteria for Manganese**

Oregon’s currently effective CWA criteria for manganese, which apply to both fresh and marine waters, are:

* 50 µg/l manganese for “human health, water + fish ingestion,” and
* 100 µg/l manganese for “human health, fish consumption only.”

These were EPA’s nationally recommended criteria at the time Oregon adopted its manganese criteria. DEQ specified in 2004 that the manganese criteria are for dissolved concentrations.

## **Federal Criteria Requirements and Recommendations**

Manganese is not considered a “priority” pollutant by EPA. 40 CFR § 131.11 describes the federal criteria requirements applicable to non-priority pollutants. Under these requirements, states must adopt criteria based on sound scientific rationale that cover sufficient parameters to protect designated uses. Both numeric and narrative criteria may be applied to meet these requirements (EPA, 1994).

**Protection of Domestic water supply**. EPA’s 1976 and 1986 *Quality Criteria for Water* (referred to as the “Red Book” and “Gold Book,” respectively) established 50 µg/l as the recommended water quality criterion for manganese for protection of domestic water supplies. This criterion was established to protect against objectionable tastes and laundry staining. The Red Book provides that, “a criterion for domestic water supplies of 50 µg/l [for manganese] should minimize the objectionable qualities.” EPA’s recommendation for manganese in Water Quality Criteria 1972 (EPA, 1973) specified that 0.05 mg/l (50 µ/l) soluble manganese not be exceeded in public water sources based on user preference. One study found that consumer complaints about brownish staining of laundry and objectionable tastes in beverages arise when manganese exceeds 150 µg/l (Griffin, 1960 in EPA Red Book). The Red book also notes that manganese concentrations of 10 to 20 µg/l are acceptable to most consumers.

The manganese criterion of 50 µg/l for protection of domestic water supply uses that EPA recommends under the Clean Water Act is the same as the secondary maximum contaminant level (MCL) established by EPA in their National Secondary Drinking Water Regulations under the Safe Drinking Water Act. Secondary MCLs are established only as guidelines to assist public water systems in managing their drinking water for aesthetic considerations, such as taste, color and odor. These contaminants are not considered to present a risk to human health at the secondary MCL (EPA, 1992).

EPA’s recommended manganese criteria for the protection of human health in fresh waters is not based on human health effects. Manganese is a vital micro-nutrient (EPA, 1976). EPA notes that the average human intake is approximately 10 mg/day and that while very large doses of ingested manganese can cause some disease and liver damage; these are not known to occur in the United States. Additional information on human intake levels from the World Health Organization is provided in Appendix B below.

**Protection of Consumers of Marine Mollusks.** While the EPA’s Red and Gold Books provide that “manganese is not considered to be a problem in fresh waters,” they do establish a recommended human health criterion for manganese of 100 µg/l in marine waters. The following information is provided in the Red Book (1976):

* The average human intake of manganese is approximately 10 mg (10,000 µg) per day.
* Very large doses of ingested manganese can cause some disease and liver damage but these are not known to occur in the United States.
* The ambient [marine] concentration of manganese is about 2 µg/l (Fairbridge, 1966). The material is rapidly assimilated and bioconcentrated into nodules that are deposited on the sea floor. The major problem with manganese may be concentration in the edible portions of mollusks, as bioaccumulation factors as high as 12,000 have been reported (NAS, 1974). In order to protect against a possible health hazard to humans by manganese accumulation in shellfish, a criterion of 100 µg/l is recommended for marine water.

More recent bioconcentration data from EPA’s ECOTOX database shows that while marine mollusks have higher bioconcentration factors than other species, the BCFs range from 677 to 2583, with 47 of the 53 BCFs being above 1000 (see Table 8).

## **Recent Actions in other States**

In 2006, the State of Missouri removed its drinking water criterion of 50 µg/l for manganese. Support for EPA approval included the following:

* EPA’s recommended criterion for manganese of 50 µg/l is based on aesthetic (e.g., laundry staining) and organoleptic (i.e., taste) effects, and was not developed to protect against toxicological effects.
* EPA reviewed available information regarding potential human health effects from manganese and analyzed this information, in combination with water quality monitoring data from waters in Missouri, in order to estimate potential exposure to manganese. The results of this analysis led EPA to conclude that the current levels of manganese in Missouri’s waters pose no long-term risk to human health and that a numeric criterion for manganese is not necessary to ensure protection of Missouri’s Drinking Water Supply designated use. EPA concluded that the Missouri Department of Natural Resource’s remaining revised numeric metals criteria and narrative criteria protect the designated use.

## **DEQ Proposed Revisions to Oregon’s Manganese Human Health Criteria**

**Water + Fish Ingestion Criterion.** DEQ proposes to withdraw Oregon’s manganese criterion for water + fish ingestion. This criterion was not based on health effects. EPA has not recommended a water + fish ingestion criterion for the protection of human health, nor have they recommended an MCL to protect against human health effects of manganese in drinking water. Manganese levels in Oregon surface waters are far below average daily human intake levels. There is no reason to believe that discharges of manganese will impact beneficial uses of drinking water or fish consumption for Oregon’s fresh waters.

In addition, Oregon does not need a numeric manganese criterion to protect water supply based on aesthetic and organoleptic effects. Table 9 shows that only one surface water supplier detected manganese in their finish water and the concentration was 0.8 µg/l, far below the levels where aesthetic or taste effects are objectionable (30 – 150 µg/l). In addition, DEQ has a narrative criterion for the protection of taste, odor and aesthetic affects should limits be required to protect a surface water domestic water supply source from particularly high levels of manganese from anthropogenic sources. Finally, EPA has a secondary MCL of 50µg/l in place under the Safe Drinking Water Act to provide guidance to water suppliers for these non-health effects.

**Fish Consumption Only Criterion.** DEQ proposes to withdraw the 100 µg/l “fish consumption only” criterion as it applies to freshwaters, but leave the criterion in place as it applies to marine waters, specifying that it be applied as a dissolved concentration. The 100µg/l criterion was recommended by EPA in 1976, prior to the 1980 publication of its method to develop criteria based on bioconcentration. However, EPA recommended this criterion due to concerns about high bioconcentration rates among marine mollusks. A fish consumption criterion for freshwaters is not needed because BCFs for manganese in freshwater species are low.

Additional options considered for the “fish consumption only” criterion were to:

* Retain the 100ug/l criterion with 2004 clarification that it will be applied as a dissolved concentration,
* Revise the 100 µg/l manganese criterion
* Withdraw the criterion, demonstrating that it is not needed to protect the applicable designated use in Oregon.

DEQ’s Toxics Standards Review Rulemaking Workgroup, which is a group of stakeholders providing input to DEQ on this rulemaking, supported DEQ’s recommended revisions to the fish consumption only criterion at their meeting on July 13, 2009.

Figure 1. Surface water data for freshwaters of Oregon. From DEQ LASAR data base.

Note: 0.2 mg/l = 200 µg/l.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Table 7. Manganese Listings from DEQ’s 2004/06 303d Assessment, based on Table 20 Criteria | | | |  |
| Watershed (USGS 4th Field Name) | Water Body (Stream/Lake) | River Miles |  | Samples exceeding |
| COOS | Isthmus Slough | 0 to 10.6 |  | 2 of 2 |
| CROSSES SUBBASINS | Willamette River | 0 to 24.8 |  | 7 of 175 |
| CROSSES SUBBASINS | Willamette River | 119.7 to 148.8 |  | 2 of 84 |
| CROSSES SUBBASINS | Willamette River | 148.8 to 184.7 |  | 7 of 313 |
| DONNER UND BLITZEN | Bridge Creek | 0 to 3.1 |  | 4 of 4 |
| Lower Columbia | Unnamed Creek | 0 to 3.2 |  | 4 of 5 |
| LOWER OWYHEE | Overstreet Drain | 0 to 0 |  | 2 of 3 |
| LOWER WILLAMETTE | Arata Creek / Blue Lake | 0 to 0.9 |  | 7 of 25 |
| LOWER WILLAMETTE | Columbia Slough | 0 to 8.5 |  | 7 of 8 |
| LOWER WILLAMETTE | Columbia Slough | 0 to 9.8 |  | 45 of 61 |
| LOWER WILLAMETTE | South Columbia Slough | 0 to 3.2 |  | 4 of 7 |
| MCKENZIE | Blue River | 0 to 15.5 |  | 2 of 38 |
| MIDDLE COLUMBIA-HOOD | Lenz Creek | 0 to 1.5 |  | 15 of 31 |
| MIDDLE COLUMBIA-HOOD | Neal Creek | 0 to 6 |  | 0 of 13 |
| MOLALLA-PUDDING | Pudding River | 0 to 35.4 |  | 7 of 72 |
| MOLALLA-PUDDING | Zollner Creek | 0 to 7.8 |  | 2 of 2 |
| NORTH UMPQUA | Sutherlin Creek | 0 to 16 |  | 20 of 26 |
| SOUTH UMPQUA | Middle Creek | 0 to 12.8 |  | 5 of 13 |
| SOUTH UMPQUA | South Fork Middle Creek | 0 to 4.4 |  | 8 of 12 |
| TUALATIN | Beaverton Creek | 0 to 9.8 |  | 64 of 68 |
| TUALATIN | Tualatin River | 0 to 80.8 |  | 151 of275 |
| UMATILLA | Umatilla River | 0 to 32.1 |  | 11 of 50 |
| UMATILLA | Wildhorse Creek | 0 to 33.2 |  |  |
| UMPQUA | Cook Creek | 0 to 2.9 |  |  |
| UPPER WILLAMETTE | Calapooia River | 0 to 42.8 |  | 9 of 39 |
| UPPER WILLAMETTE | Long Tom River | 0 to 57.3 |  | 2 of 34 |
| UPPER WILLAMETTE | Marys River | 0 to 41.1 |  | 4 of 39 |
| YAMHILL | North Yamhill River | 0 to 32.5 |  | 3 of 63 |
| YAMHILL | Salt Creek | 0 to 32.8 |  | 2 of 2 |
| YAMHILL | Yamhill River | 0 to 11.2 |  | 3 of 67 |

Dissolved Mn ((µg/l)

Bi-MONTH

Figure 2. Seasonal Distribution of Dissolved Manganese (µg/l)

Beaverton Creek Near Orenco USGS and DEQ Data

0

50

100

150

200

250

300

350

400

450

500

550

JAN

-

FEB

MAR

-

APR

MAY

-

JUN

JUL

-

AUG

SEP

-

OCT

NOV

-

DEC

1991-2003

K-W 99%

WQ Criteria

(16)

(16)

(15)

(17)

(12)

(15)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Table 8. Summary of Manganese BCFs for Organisms in Saltwater and Freshwater | | | | | |  |
|  |  |  |  | |  |  |
| **Media** | **Species Group** | **Number of BCFs** | **Range of BCF Values** | | | **Notes** |
| **Min** | **Max** | |
| Freshwater | Crustaceans | 1 | 65 | 65 | |  |
| Freshwater | Fish | 5 | 0.2 | 220 | |  |
| Freshwater | Worms | 2 | 8.5 | 9 | |  |
| Saltwater | Crustaceans | 14 | 0 | 3.18 | |  |
| Saltwater | Fish | 23 | 10 | 9090 | | 5 of 23 BCFs were above 1000 |
| Saltwater | Invertebrates | 8 | 3 | 61 | |  |
| Saltwater | Mollusks | 53 | 677 | 2683 | | 47 of 53 BCFs were above 1000 |
| Saltwater | Worms | 17 | 2.2 | 45 | |  |
|  |  |  |  |  | |  |
|  | Values above 1000 considered high bioconcentration potential by EPA R6.  From “ECOTOX” database, EPA. <http://cfpub.epa.gov/ecotox/> | | | | | |

Table 9. Finish Water Data for Drinking Water Sources, Oregon.

This table summarizes drinking water source finish data that exceeded detection limits for manganese. Note that one sample is a surface water source and the other two are groundwater sources. Finish water is water that has undergone standard drinking water treatment.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Finish Water Data for Drinking Water Sources | | |  | **Manganese** |
|  |  |  |  | **µg/l** |
| SW | NPS OREGON CAVES NATL MON | EP FOR LAKE CREEK | 24-May-06 | 0.8 |
| GW | SUNRIVER WATER LLC | ~EP FOR WELL 12 (SERVES CROSSWATERS) | 13-Sep-06 | 93 |
| GW | CURRY CO PKS LOBSTER CREEK | EP FOR LOBSTER CREEK | 11-Sep-03 | 58 |
|  |  |  |  |  |
| From: Oregon’s Safe Drinking Water Information System (DEQ, 2009) | | | |  |

# Chapter 5. DEQ’s Proposed Arsenic Reduction Policy

DEQ proposes to adopt the following arsenic reduction policy into its water quality standards in addition to the proposed numeric criteria discussed in Chapter 2. The goal of this provision is to ensure that Oregon’s proposed numeric water + fish ingestion criterion for arsenic, which is intended to account for natural conditions, does not unintentionally allow preventable human health risk due to anthropogenic loading of arsenic from existing or new sources.

DEQ is proposing revised numeric arsenic criteria of 2.7 for the fish ingestion only criterion and 2.3 µg/l for the water and fish consumption criterion. While these proposed numeric criteria protect human health at an acceptable level given the presence of natural sources of arsenic in the state, it is the state’s policy to maintain the lowest added human health risk from anthropogenic sources of inorganic arsenic practicable, even when ambient inorganic arsenic concentrations are below the numeric criteria. This policy is targeted to dischargers that add inorganic arsenic to Oregon waters and have the potential, due to their location, to impact a public drinking water supply.

The proposed fish consumption only criterion is based on a risk level of 1×10-6 and a fish consumption rate of 175 g/day and is therefore very protective of human health. The proposed water + fish ingestion criterion, however, which applies to waters designated both for fishing and for domestic water supply use, is based on a higher risk level of 1×10-4. Because the concern is with the drinking water exposure, the approach proposed below is targeted to addressing sources that impact drinking water supplies.

## **Draft Proposed Rule Language:**

OA 340-401-0033 (4) Arsenic Reduction Policy: The inorganic arsenic criterion for the protection of human health from the combined consumption of organisms and drinking water is 2.3 micrograms per liter. While this criterion is more stringent than the federal maximum contaminant level (MCL) for arsenic in drinking water, which is 10 micrograms per liter, it nonetheless is based on a higher risk level than the Commission has used to establish other human health criteria. This higher risk level recognizes that much of the risk is due to naturally high levels of inorganic arsenic in Oregon’s waterbodies. The inorganic arsenic criterion for the consumption of organisms only is based on the same risk level as Oregon’s other human health toxics criteria. In order to maintain the lowest human health risk from inorganic arsenic in drinking water, the Commission has determined that it is appropriate to adopt the following policy to limit the human contribution to that risk.

(a) It is the policy of the Commission that the addition of inorganic arsenic from new or existing anthropogenic sources to waters of the state within a surface water drinking water protection area be reduced the maximum amount feasible. The requirements of this rule section [OAR 340-041-0033(4)] apply to sources that discharge to surface waters of the state with an ambient inorganic arsenic concentration equal to or lower than the applicable numeric inorganic arsenic criteria for the protection of human health.

(b) The following definitions apply to this section [OAR 340-041-0033(4)]:

(A) “Add inorganic arsenic” means to discharge a net mass of inorganic arsenic from a point source (the mass of inorganic arsenic discharged minus the mass of inorganic arsenic taken into the facility from a surface water source).

(B) A “surface water drinking water protection area,” for the purpose of this section, means an area delineated as such by DEQ under the source water assessment program of the federal Safe Drinking Water Act, 42 U.S.C. § 300j‑13. The areas are delineated for the purpose of protecting public or community drinking water supplies that use surface water sources. These delineations can be found at DEQ’s drinking water program website.

(C) “Potential to significantly increase inorganic arsenic concentrations in the public drinking water supply source water” means:

(i) to increase the concentration of inorganic arsenic in the receiving water for a discharge by 10 percent or more after mixing with the harmonic mean flow of the receiving water; or

(ii) as an alternative, if sufficient data are available, either the permittee or DEQ may base the determination of potential significance on a mass balance calculation to determine if the discharge will increase the concentration of inorganic arsenic in the surface water intake water of a public water system by 0.023 micrograms per liter or more.

(c) Following the effective date of this rule, applications for an individual NPDES permit or permit renewal received from industrial dischargers located in a surface water drinking water protection area and identified by DEQ as likely to add inorganic arsenic to the receiving water must include sufficient data to enable DEQ to determine whether:

(A) The discharge in fact adds inorganic arsenic; and

(B) The discharge has the potential to significantly increase inorganic arsenic concentrations in the public drinking water supply source water.

(d) Where DEQ determines that both conditions in subsection (c) of this section are true, the source must develop an inorganic arsenic reduction plan and propose all feasible measures to reduce its inorganic arsenic loading to the receiving water. The proposed plan, including proposed measures, monitoring and reporting requirements, and a schedule for those actions, will be described in the fact sheet and incorporated into the source’s NPDES permit after public comment and DEQ review and approval. In developing the plan, the source must:

(A) Identify how much it can minimize its inorganic arsenic discharge through pollution prevention measures, process changes, wastewater treatment, alternative water supply (for groundwater users) or other possible pollution prevention and/or control measures;

(B) Evaluate the costs, feasibility and environmental impacts of the potential inorganic arsenic reduction and control measures;

(C) Estimate the predicted reduction in inorganic arsenic and the reduced human health risk expected to result from the control measures;

(D) Propose specific inorganic arsenic reduction or control measures, if feasible, and an implementation schedule; and

(E) Propose monitoring and reporting requirements to document progress in plan implementation and the inorganic arsenic load reductions.

(e) In order to implement this section, DEQ will develop the following information and guidance within 120 days of the adoption of this rule and periodically update it as warranted by new information:

(A) A list of industrial sources or source categories, including industrial stormwater and sources covered by general permits, that are likely to add inorganic arsenic to surface waters of the State.

(i) For industrial sources or source categories permitted under a general permit that have been identified by DEQ as likely sources of inorganic arsenic, DEQ will evaluate options for reducing inorganic arsenic during permit renewal or evaluation of Stormwater Pollution Control Plans.

(B) Quantitation limits for monitoring inorganic arsenic concentrations.

(C) Information and guidance to assist sources in estimating, pursuant to paragraph (d) (C) of this section, the reduced human health risk expected to result from inorganic arsenic control measures based on the most current EPA risk assessment.

(f) It is the policy of the Commission that landowners engaged in agricultural or development practices on land where pesticides, fertilizers, or soil amendments containing arsenic are currently being or have previously been applied implement conservation practices to minimize the erosion and runoff of inorganic arsenic to waters of the State or to a location where such material could readily migrate into waters of the State. As a component of DEQ’s response to the Commission’s October 23, 2008 directive on toxic pollutants, DEQ, after providing an opportunity for public comment, is directed to present to the Commission a proposal for implementing this policy in an environmentally meaningful and cost-effective manner. Upon adoption by the Commission, DEQ is expected to implement the proposal as approved or modified by the Commission.

**Implementation of the Arsenic Reduction Policy**

This section describes how DEQ intends to implement the above proposed policy. Please note that nothing in this proposed arsenic reduction policy would replace or supersede technology-based permit requirements, permit limits based on numeric arsenic criteria or antidegradation requirements. All of these otherwise applicable requirements and policies would continue to apply.

DEQ recognizes that it has not specified an analytical method for inorganic arsenic or the quantitation limit (QL) that will be required for permittee monitoring. Because the proposed numeric criteria for arsenic are for the inorganic form, this information will need to be developed regardless of whether or not this reduction policy is ultimately adopted.

Point Sources – Industrial Sources:

1. Applications for new or renewed individual NPDES permits submitted to DEQ after the effective date of this rule by industrial dischargers that are required to submit arsenic data with their permit application, or are otherwise identified by DEQ as likely to add inorganic arsenic to their wastewater, **and** that discharge to a water body within a drinking water protection area delineated by DEQ for a surface water intake, shall submit with their permit application sufficient data to allow DEQ to make the determinations described in #3 below. This will include source water and effluent inorganic arsenic concentration and flow data and may also include ambient river data.
   1. A discharger that has sufficient effluent data to demonstrate that its effluent concentration of inorganic arsenic is below DEQ’s quantitation limit or below the ambient river concentration immediately upstream of the discharge may use that information to demonstrate that the discharge does not have the potential to impact the arsenic concentration in a downstream public water supply.
2. DEQ will use the data to determine:
   1. whether the discharger is adding a quantifiable load of inorganic arsenic to their wastewater (i.e. a quantifiable concentration of inorganic arsenic in the discharge is greater that the inorganic arsenic load taken in from a surface water intake source); **and**
   2. whether the added load has the potential to increase the concentration of inorganic arsenic in a downstream public drinking water supply. DEQ will determine that a discharge has the potential to increase the concentration of inorganic arsenic in a downstream drinking water supply intake if the source increases the concentration of inorganic arsenic in the river after dilution (near field/point of discharge mixing analysis) by 3% or more, unless the source can demonstrate that their arsenic contribution will not increase the arsenic concentration in the downstream water supply by more than 0.023 µg/l.
3. If the Department finds that the facility is adding inorganic arsenic and that the added load is impacting a public drinking water supply, the permittee shall develop an arsenic reduction plan, which will be incorporated into its NPDES permit subject to DEQ review and public comment. The source shall include the following in their plan:
   1. Identify how much it can minimize its arsenic discharge through pollution prevention measures, process changes, wastewater treatment, alternative water supply sources or other possible pollution prevention and/or control measures.
   2. Evaluate the costs, technical and economic feasibility and environmental impacts of the identified arsenic reduction and control measures.

Note 1: It is important to evaluate whether a potential arsenic reduction measure, such as a chemical substitution, represents an equal or worse environmental risk or other environmental impact.

Note 2: DEQ recognizes that evaluating water supply options and the environmental impacts of those is complex and there are many issues to consider other than the arsenic loading. If the source of arsenic is groundwater, there may be few if any feasible options for reduction.

* 1. Estimate the reduced arsenic load and human health risk expected to result from the control measures.
  2. Propose specific inorganic arsenic reduction or control measures, if feasible, and a schedule for implementing them.
  3. Specify monitoring and reporting requirements related to implementing the plan and the resulting effluent arsenic load reductions.

1. DEQ will identify factors that the permittee and the agency should consider in weighing the technical and economic feasibility of an inorganic arsenic reduction measure against the reduced human health risk that is expected to result and deciding which measures to implement.
2. If the timing of a permit renewal is such that the facility has not had sufficient time to collect the required data or develop an arsenic reduction plan prior to permit issuance, the permit will include the data collection and/or planning requirements and a reopener clause, which will allow DEQ to incorporate the proposed plan/measures into the permit prior to the next renewal.
3. Arsenic reduction plans and their implementation will be reviewed at each permit renewal to evaluate progress in implementation actions and inorganic arsenic reductions and determine whether and new measures are feasible and/or proposed.
4. There are existing procedures for requesting the re-consideration of a permit that can be used by persons who have grounds to believe that either the data and analysis or the reduction measures included in the permit are inadequate.

Point sources – POTWs

1. All major POTWs are required to analyze their effluent for arsenic and submit that data to DEQ as part of their permit renewal application.
2. Arsenic III (the primary inorganic from) is included on Oregon’s Priority Persistent Pollutant list developed under SB737. DEQ will rely on the water quality criteria and the “SB 737” requirements to address potential arsenic contributions from POTWs. Under “SB 737,” the 52 largest POTWs, including all major municipal dischargers, will be required to test for arsenic III in their effluent. If the effluent concentration exceeds the “plan initiation level” specified in rule, the facility will be required to develop and implement a pollutant reduction plan for arsenic.

Point Sources – Other

1. Wood treating facilities – DEQ will incorporate the following into our renewal of industrial stormwater permits for wood treating facilities:

* Review data on arsenic levels in stormwater runoff
* Determine the sources of the arsenic on the site
* Require the facility to identify measures that could be taken to reduce arsenic loading, including chemical substitution, stormwater management and erosion control practices, stormwater treatment, soil testing and remediation, chemical storage and disposal practices, and others.
* Evaluate the measures, considering: a) potential for reduction of arsenic discharge, b) cost and c) potential environmental impacts (particularly for chemical substitutions), and incorporate appropriate measures into the permit.

3. Municipal stormwater management – DEQ will incorporate the following into our municipal stormwater permitting program:

* DEQ will review data on inorganic arsenic levels in stormwater runoff and/or UIC wells to determine whether municipal stormwater is a significant source of inorganic arsenic.
* If it is determined to be a significant source, DEQ will determine whether it is possible to identify the source(s) of the arsenic and whether additional measures or best management practices could be implemented that would reduce the arsenic loading.

Nonpoint Source Options:

1. Use the agency-wide Toxics Reduction Strategy to evaluate whether any of the following actions would be: a) likely to reduce inorganic arsenic concentrations in surface water drinking water protection areas, or in waters that exceed the water quality criteria for arsenic, and b) cost effective:

* a limit on the amount of arsenic in fertilizers, pesticides and/or wood treating chemicals, or a ban on products containing arsenic if there are still such products in use;
* treated wood and/or chemical collection/take back programs,
* stormwater management in areas with large amounts of treated wood present, and/or
* enhanced erosion control practices on lands where soil inorganic arsenic levels are elevated.

2. Recommend that adequate control of runoff and erosion from urban development and agricultural lands be implemented for multiple benefits. One benefit would be to prevent arsenic and other toxic pollutants that adhere to soil particles from entering waterways. Some contaminants, such as arsenic, are no longer widely used, but may have built up in soils in certain locations from past use. In addition, such controls would also reduce nutrient (i.e. phosphorus) and sediment loading from urban and agricultural lands and therefore provide multiple benefits to fish and aquatic life and the quality of Oregon waters.

3. Construction stormwater general permit. Erosion and stormwater control practices should be employed to reduce loading of sediment and chemicals attached to sediments to the stream.

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## **Appendix A. Supplemental Information on Arsenic**

*Fate and transport in the environment*

Inorganic arsenic (As) occurs in two dominant redox states, arsenate (As(V)) and arsenite (As(III)), both highly toxic and carcinogenic (Hopenhayn 2006; Vaughan 2006). The oxidized form, arsenate, behaves chemically similarly to phosphate (P(V)) in the environment, as the two species display similar coordination chemistry and both readily bond with soil solids like iron oxides and clay particles (Stollenwerk 2003). Lab and field studies show that arsenate, like phosphate, sorbs to iron plaques that form on plant roots (Blute, Brabander et al. 2004; Liu, Zhu et al. 2006). Plants generate these plaques by pumping oxygen from the atmosphere to their roots, creating microoxic regimes in otherwise anoxic sediments (Taylor, Crowder et al. 1984).

However, a number of factors interfere with our ability to predict the mobility of As when plants are present. Arsenate, unlike phosphate, easily and commonly shifts redox states in the environment. The reduced form of As, arsenite, tends to be more mobile than arsenate and does not as strongly bond with iron oxides or natural organic matter at low and neutral pH (Stollenwerk 2003; Buschmann, Kappeler et al. 2006). In the root zone, dissolved organic carbon (DOC) exuded by plants will create high oxygen demand that result in anoxic conditions where DOC could then reduce arsenate to arsenite. Additionally, natural organic matter may compete with arsenate for sorption sites on iron oxides (Redman, Macalady et al. 2002). Both As reduction and competitive sorption may lead to greater As mobility. Conversely, both species of inorganic As sorb to natural organic matter, indicating that plants may enhance As retention up to some threshold (Buschmann, Kappeler et al. 2006).

*Potential nonpoint sources of arsenic*

Our observation of high As and Pb concentrations in the drainages down gradient of the tilled orchard is consistent with a recent regional analysis of stream sediment As and Pb concentrations that found a positive association between stream sediments that contain high As and Pb concentrations and areas inferred to have used arsenical pesticides extensively (Robinson and Ayuso, 2004). Our work extends this regional analysis by demonstrating that: (i) at least below the tilled field the As and Pb were transported to the drainage in two discrete events, with the later mobilization event occurring well after the application of the arsenical pesticides; and (ii) the masses of As and Pb apparently missing from the tilled field and present in the down gradient drainage are consistent with transport due to physical erosion associated with tilling. Most previous work investigating As mobilization due to physical erosion has focused on As contamination due to the erosion of As-rich ores (Black et al., 2004; Oyarzun et al., 2004; Savage et al., 2000). However, tilling-induced mobilization similar to postulated here has recently been documented for other strongly sorbing pesticides (Wu et al., 2004). In contrast, little horizontal redistribution of As has been observed in the untilled As-contaminated soils underlying cattle tick dip sites (Kimber et al., 2002)...

Finally, while this work only considers the effect of tilling on the mobilization of residual arsenical pesticides, our work shows that the Pb and As are bound to small and presumably highly mobile particles. It is therefore likely that other types of land disturbances will also mobilize significant amounts of Pb and As in lands where arsenical pesticides were used, particularly over longer timescales. In southern New Hampshire, for example, former orchard land is currently being rapidly developed and urbanized. Our results suggest that as this land is developed, attention should be given to the possibility of mobilizing previously immobile reservoirs of Pb and As.  *Impact of Land Disturbance on the Fate of Arsenical Pesticides*, Carl E. Renshawa,\*, Benjamin C. Bosticka, Xiahong Fenga, Christine K. Wonga, Elizabeth S. Winstona, Roxanne Karimib, Carol L. Foltb and Celia Y. Chenb.  2005.

Total Arsenic in Drinking Water Supplies in Oregon (ug/l)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | All “Surface Water” | Selected Surface Water\* | Groundwater  under direct influence of SW | Groundwater (see table below) |
| Minimum | 0.5 | 0.5 | 0.58 | 0.1 |
| Maximum | 9.0 | 5.7 | 14 | 411 |
| Average | 3.0 | 1.6 | 4.87 | 8.8 |
| # samples | 45 | 24 | 11 | 1642 |

\* Sources that use only surface water and do not include well water as part of their supply.

Note 1: This data is for finish water, which means these are the levels after the raw water has been treated.

Note 2: This data includes only sources with detectable levels of arsenic (0.5 ug/l or more). There are additional sources where arsenic was not detected. Therefore, the data above do not represent the average of arsenic levels in surface water supplies throughout Oregon, but simply represent commonly occurring levels.

From: Drinking Water data base, Oregon, May 2009 query

From Drinking Water data base, Oregon, May 2009 query.

Number of GW samples with arsenic values above previous value and

up to value shown (i.e. 0.01–0.5; 0.51-1; 1.01-2, etc.)

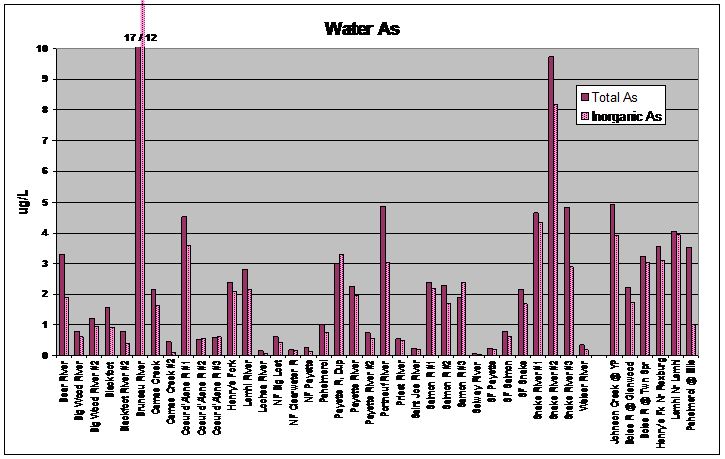


Figure 1. Data on total and inorganic arsenic from Idaho.

2008/09 total arsenic and inorganic arsenic data from 40 sites on major rivers across. They ranged from as low as 25% up to 100% inorganic arsenic; the mean was 75% inorganic.

## **Appendix B. Supplemental Information on Manganese**

World Health Organization, Geneva, 1999. Concise International Chemical Assessment Document 12: Manganese and its Compounds. <http://www.inchem.org/documents/cicads/cicads/cicad12.htm>

Manganese (Mn) is a naturally occurring element that is found in rock, soil, water, and food. Thus, all humans are exposed to manganese, and it is a normal component of the human body. Food is usually the most important route of exposure for humans. The Food and Nutrition Board of the US National Research Council establishes Estimated Safe and Adequate Daily Dietary Intake (ESADDI) levels, which generally parallel amounts of the compound usually delivered via the diet, although some individuals consume greater or smaller amounts. The ESADDI levels for manganese are 0.3-0.6 mg/day for infants up to 6 months old, 0.6-1.0 mg/day for infants 6 months to 1 year old, 1.0-1.5 mg/day for children 1-3 years old, 1.0-2.0 mg/day for children 4-10 years old, and 2.0-5.0 mg/day for people over 10 years old (NRC, 1989).

In considering development of a guidance value for oral intake of manganese, it must be noted that there is wide variability in human intake of manganese (from all sources) and that manganese is an essential nutrient for humans and animals. Daily manganese intake from food is estimated to be about 2-9 mg for adults, with an absorbed amount of about 100-450 µg/day based upon 5% gastrointestinal absorption (WHO, 1981). Some studies have reported that neurological effects may be related to ingestion of manganese in non-worker populations. However, these reports provide little information on the levels of ingested manganese that were associated with these effects. Although neurological effects might be a potential concern for people working or living at or near sites where ingestion or inhalation of high levels of manganese can occur (see section 9.2), no firm conclusion on a guidance value level for oral intake of manganese other than estimated daily intake levels is considered possible.

More recently, Kondakis et al. (1989) reported that chronic intake of drinking-water containing elevated levels of manganese (1.8-2.3 mg/litre) led to an increased prevalence of neurological signs in elderly residents (average age 67 years) of two small towns in Greece. The effects were compared with those in similarly aged residents in two other communities where manganese levels were within ambient range (0.004 and 0.0015 mg/litre). The findings suggested that above-average oral exposure to manganese might be of health concern. However, although the comparison populations were reportedly very similar to each other, differences in age, occupational exposures, or general health status could have accounted for the small differences observed. Similarly, Goldsmith et al. (1990) investigated a cluster of Parkinson's disease in southern Israel. The authors suggested that excess levels of aluminum, iron, and manganese in the drinking-water and the use of agricultural chemicals, including maneb and paraquat, in the area were common environmental factors that may have contributed to the observed cluster. However, the observed symptoms could not be conclusively attributed to manganese poisoning alone. By contrast, a recent study by Vieregge et al. (1995) on the neurological impacts of chronic oral intake of manganese in well-water found no significant differences between exposed and control populations in northern Germany. A group of 41 subjects exposed to 0.300-160 mg manganese/litre in well-water was compared with a control group of 71 subjects (matched for age, sex, nutritional habits, and drug intake) exposed to a maximum manganese concentration in well-water of 0.050 mg/litre. Neurological assessments revealed no significant difference between the two groups. Although the effects reported by Kondakis et al. (1989) and Goldsmith et al. (1990) are consistent with the known toxicological effects of manganese, the findings are inconclusive and are contradicted by the results of Vieregge et al. (1995). As a result, no firm conclusions on manganese-induced neurological effects in humans from chronic oral intake of manganese in drinking-water can be made at this time.

In considering development of a guidance value for oral intake of manganese, it must be noted that there is wide variability in human intake of manganese (from all sources) and that manganese is an essential nutrient for humans and animals. Daily manganese intake from food is estimated to be about 2-9 mg for adults, with an absorbed amount of about 100-450 µg/day based upon 5% gastrointestinal absorption (WHO, 1981). Some studies have reported that neurological effects may be related to ingestion of manganese in non-worker populations. However, these reports provide little information on the levels of ingested manganese that were associated with these effects. Although neurological effects might be a potential concern for people working or living at or near sites where ingestion or inhalation of high levels of manganese can occur (see section 9.2), no firm conclusion on a guidance value level for oral intake of manganese other than estimated daily intake levels is considered possible.

Table B-1. Manganese concentrations in selected foods. a

Type of food Range of mean concentrations

(ppm; µg/g or mg/litre)

Nuts and nut products 18.21-46.83

Grains and grain products 0.42-40.70

Legumes 2.24-6.73

Fruits 0.20-10.38

Fruit juices and drinks 0.05-11.47

Vegetables and vegetable products 0.42-6.64

Desserts 0.04-7.98

Infant foods 0.17-4.83

Meat, poultry, fish, and eggs 0.10-3.99

Mixed dishes 0.69-2.98

Condiments, fats, and sweeteners 0.04-1.45

Beverages (including tea) 0.00-2.09

Soups 0.19-0.65

Milk and milk products 0.02-0.49

a Adapted from Pennington et al. (1986).

Table 3: Summary of typical human exposure to manganese.a

Parameter Exposure medium

Water Air Food

Typical concentration 4 µg/litre 0.023 µg/m3 1.28 µg/calorie

in medium

Assumed daily 2 litres 20 m3 3000 calories

intake of medium

by 70-kg adult

Estimated average 8 µg 0.46 µgb 3800 µg

daily intake by

70-kg adult

Assumed 0.03c 1c 0.03d

absorption fraction

Approximate 0.24 µg 0.46 µg 114 µg

absorbed dose

a Adapted from US EPA (1984).

b Assumes 100% deposition in the lungs.

c No data; assumed value.

d Davidsson et al. (1988)