White Paper

Integrated Report Improvements

Arsenic

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Environmental
Quality

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DEQ is a leader in restoring, maintaining and enhancing the quality of Oregon's air, land and water.

Introduction/Background

Human health water quality criteria for arsenic were revised and approved by EPA in October 2011. The revised criteria in OAR 340-041-0033 Table 40 are based on total inorganic arsenic (CAS No. 7440-38-2) rather than total recoverable arsenic. Total inorganic arsenic is a measurement of the concentration of the more toxic bioavailable forms of arsenic, the sum of As(III) + As(V). Total recoverable arsenic measures both inorganic arsenic and organic complexes of arsenic, which are less bioavailable. The human health criterion for arsenic is 2.1 µg/L of inorganic arsenic for freshwater and 1.0 µg/L for marine water.

Much of the available data for arsenic used in previous Integrated Report assessments were expressed as either total recoverable or total dissolved arsenic. For the 2012 Integrated Report (IR), DEQ did not have sufficient data or information for Oregon waters to estimate how much of the total arsenic concentration was in the inorganic form. DEQ used a study from the Idaho Department of Environmental Quality which calculated the median proportion of inorganic arsenic to total arsenic in samples as 76%. In order to evaluate available data for the 2012 Integrated Report, DEQ assumed that the Idaho value was applicable to Oregon's waters and multiplied total arsenic data results by 0.76 to estimate the inorganic arsenic fraction expected to be present and evaluated that concentration against the most stringent applicable criterion. Since 2012, the DEQ laboratory analyzed rountine samples for organic and inorganic arsenic in order to calculate an Oregon specific translator. This paper presents the results of that analysis and presents a new translator for the 2018 IR.

Arsenic and the Integrated Report

The Clean Water Act section 303(d) requires states to identify waters not meeting water quality criteria. The 303(d) list of impaired waters is one component of the IRrequirements. Beginning in 1998, DEQ began to include waters on the 303(d) list of impaired waters for exceedances of the arsenic criteria. There are currently 38 Category 5 listings on the 2012 303(d) list. Once a water body is on the list, DEQ is required to develop a Total Maximum Daily Load (TMDL) for that water body.

Development of an Oregon specific translator

For this analysis, DEQ ran inorganic arsenic samples for approximately 930 samples (freshwater and estuarine) through December 2015. Of those 930 samples, 345 had paired measurable total

recoverable and inorganic arsenic levels above method quantitation limits. Of the 345 paired quantifiable results, 298 were freshwater samples and 47 were estuarine (Table 1).

Table 1. Number of Oregon specific paired quantifiable arsenic samples

Paired quantifiable inorganic arsenic samples (2012 - 2015)		
Estuarine	**Number of samples> 1.0 ug/L (saltwater criterion)**	**% quantified samples above criterion**
47	12	26%
Freshwater	**Number of samples> 2.1ug/L (freshwater criterion)**	**% quantified samples above criterion**
298	90	30%

For the 2018 IR, where only total recoverable arsenic data are submitted, DEQ set out to determine an Oregon-specific quantifiable relationship between total recoverable arsenic and inorganic arsenic. Data analyses indicate that the range of percent inorganic (% Inorganic) to total arsenic is quite variable (19% to >100%) and varies with geology, base flow and groundwater hydrology. Regional geographic differences in the inorganic fraction were not statistically significant, but differences between estuarine and freshwater were ($p < 0.001$).

Since the chemistry of estuarine and freshwater can vary significantly, and the difference in inorganic arsenic fractions is statistically significant, translators were developed separately for freshwater and estuarine waters.

When the entire freshwater dataset is plotted, a strong linear relationship between total and inorganic arsenic is evident (R^2= 0.98) (Figure 1). However, there are more samples and less variability in the range of 2.0 to 5.0 µg/L (Figure 2). Total arsenic levels above 5.0 µg/L, ensure the inorganic arsenic criteria is almost always exceeded. Therefore greater accuracy is desired in the critical range of 2.0 – 5.0 µg/L where the translator is likely to have the greatest impact.

When the regressions were run through the origin (zero total recoverable arsenic = zero total inorganic arsenic), the slope of the lines can be used to generate an Oregon-specific translator. If the entire total recoverable data range was used, the translator would be equivalent to 0.92. Alternatively, if the total recoverable data range from 2.0 to 5.0 µg/L were used, the range of data where the translator has the greatest impact, the translator would correspond to a value of 0.80.

Root Mean Squared Error (RMSE) was calculated for each regression to determine the magnitude of estimation error for predicting total inorganic arsenic concentration from total recoverable arsenic. RMSE is calculated as the standard deviation of the residuals (prediction errors). Residuals are a measure of how far the actual data points fall from the prediction of the regression line. A smaller RMSE values demonstrates less average prediction error, and more accuracy, for the regresson relationship.

The RMSE for inorganic arsenic estimates for the full range is +/- 1.88 µg/L (Figure 1) while the RMSE for the reduced critical range of 2.0 to 5.0 µg/L is 0.36 µg/L (Figure 2). The relationsip for the smaller critical range is a better predictor of actual inorganic arsenic values

below 5.0 µg/L. The RMSE for the full range of the estuarine dataset using a 0.58 translator was 0.14 µg/L, which indicates that it is a good predictor of estuarine inorganic arsenic values over the entire range (Figure 3).

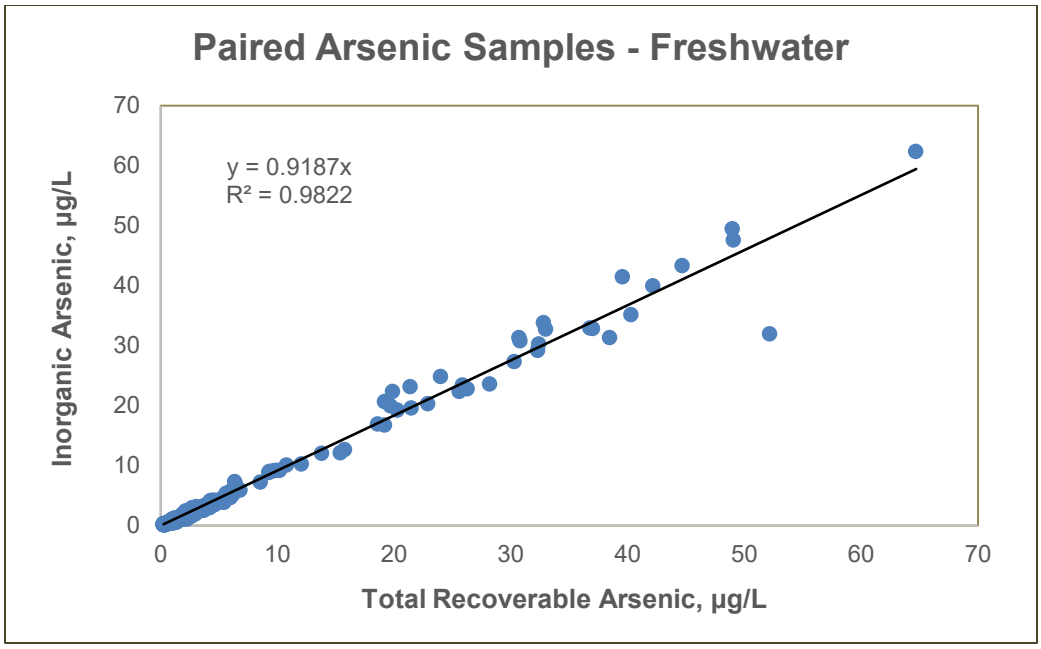

Figure 1. RMSE = 1.88

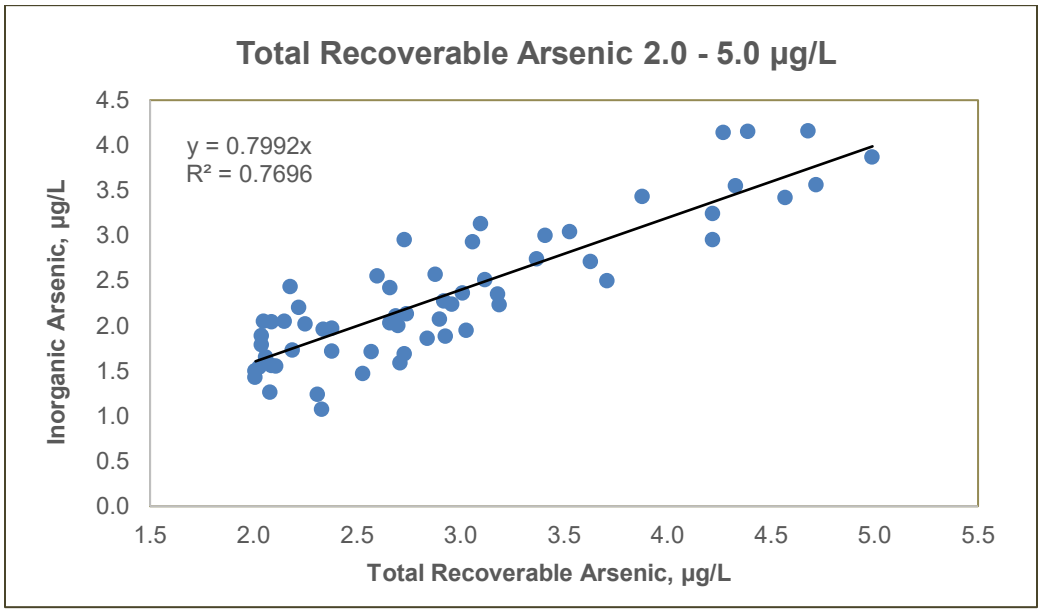

Figure 2. RMSE=0.36

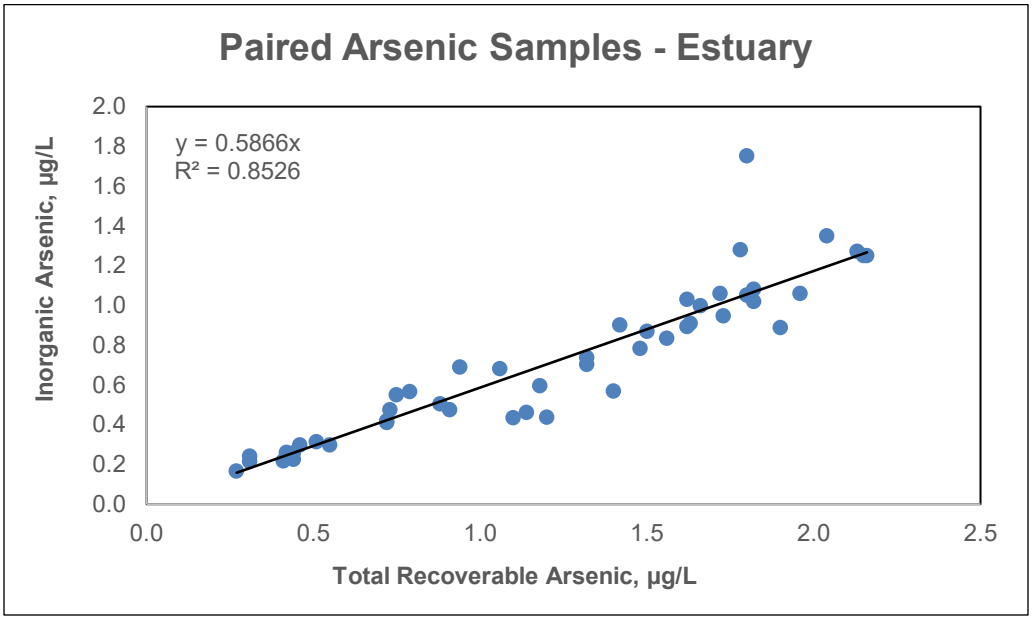

Figure 3. RMSE=0.14

Translator Alternatives

In addition to the current translator, DEQ looked at two alternatives for calculating the total inorganic fraction of arsenic for Oregon-specific data.

Similar to the procedure that was followed for the 2012 Integrated Report, where total inorganic arsenic data was not provided for assessment, an inorganic translator would be applied as a percentage of total recoverable arsenic based on Oregon-specific data. Use of a translator may have the potential to create both Type I (false positives) and Type II (false negatives) errors, therefore it is important to assess the impact of adopting each alternative (Table 2).

Analysis

A preliminary analysis of possible arsenic translators was performed on existing data to identify the number of false positive and false negative exceedances that may be generated (Table 2). The false positives and false negatives refer to the number of errors for estimated sample concentrations above or below the criteria, not 303(d) listings.

Table 2. Type-I and Type-II error rates for translators

	No. of false positive predictions	Type-I error rate	No. of false negative predictions	Type-II error rate
Existing Methodology (0.76)	4	7%	**7**	12%
Freshwater Translator Option #1 (0.80)	8	13%	3	5%
Freshwater Translator Option #2 (0.92)	**15**	25%	2	3%
Estuarine Translator (0.58)	2	17%	2	17%

There are 60 paired samples of total recoverable and inorganic arsenic in DEQ's dataset in the critical range of 2 to 5 µg/L total recoverable arsenic. All of the samples that have total recoverable arsenic concentrations above 5 µg/L also have inorganic arsenic concentrations that exceed the inorganic arsenic criteria of 2.1 µg/L. That is, when total recoverable arsenic is greater than 5 µg/L, we can be relatively certain that the waterbody would also not attain the inorganic arsenic criterion. Conversely, when total recoverable arsenic concentrations are below 2 µg/L, it is not possible for inorganic arsenic to exceed the criterion.

The assessment challenge is to determine, with limited amounts of sample data, whether or not an assessment unit should be listed as impaired. A robust assessment method would minimize false positive (Type-I) and false negative (Type-II errors) (Table 2). Use of the 0.92 translator produced the highest number of false positive errors (25%), but also the lowest number of false negatives (3%). The number of false negatives is greatest when the "Idaho" translator of 0.76 was employed (12%). Use of the 0.80 value, which is based on total recoverable data within the range of 2.0 to 5.0 µg/L limits the number of false negatives while also minimizing the number of false positives. The estuarine translator of 0.58 balanced Type-I and Type-II errors with an equal probability of 17% of making a false impairment prediction.

Regardless of the translator that is chosen, the use of a geometric mean decreases the effect of the false positive predictions (Table 3). Under the 2012 listing methodology, where any two exceedances of the criteria was used to assign a Category 5 listing, each of these water bodies would have been listed based on the predicted inorganic arsenic concentration. Under DEQ's revised approach, the water bodies would not be proposed for listing since their geometric means are less than the 2.1 µg/L inorganic arsenic criteria if the inorganic arsenic translator predictions were in fact, false positives.

Table 3. Example datasets for calculation of a geometric mean. As inorganic arsenic (µg/L).

Example 1	Example 2	Example 3
2.8	2.03	2.00
3.2	1.71	**2.93**
2.6	**2.95**	1.96
1.8	1.24	**2.57**
2.0	1.95	1.27
1.6	**2.27**	
1.4	1.50	
1.5	1.54	
1.9	2.02	
1.8	2.07	
Geomean: 1.99	Geomean: 1.88	Geomean: 2.06

Conclusion

Based on the analysis conducted above, it appears that using a translator of 0.80 for total arsenic samples < 5.0 ug/L is the most accurate for assessing total arsenic data against inorganic arsenic criteria. In the absence of measured total inorganic arsenic data, it is DEQ's recommendation that a 0.80 translator for freshwater and a 0.58 translator for estuarine water should be used to predict total inorganic arsenic values from total recoverable arsenic concentrations.

For total recoverable arsenic data, if the predicted inorganic arsenic results are greater than 2.1 µg/L in freshwater and 1.0 µg/L in estuarine water, calculated as a geometric mean, then the water body will be placed in Category 5. For datasets that contain both measured and predicted inorganic arsenic values, if predicted inorganic arsenic exceeds the appropriate numeric criterion, while measured values attain the criterion, then the water body will be placed in Category 3B - Exceedances until measured inorganic arsenic data can be collected.

Alternative formats

Documents can be provided upon request in an alternate format for individuals with disabilities or in a language other than English for people with limited English skills. To request a document in another format or language, call DEQ in Portland at 503-229-5696, or toll-free in Oregon at 1-800-452-4011, ext. 5696; or email deqinfo@deq.state.or.us.