



# Memorandum on Arsenic

**To:** Integrated Report Work Group

**Date:** Feb. 20, 2018

**From:** Integrated Report Improvement Team

**Subject:** Arsenic assessment methodology recommendations

## 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.

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, since 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 they used a study from the Idaho Department of Environmental Quality which calculated a median percent inorganic arsenic fraction from total arsenic sample results equal to 76%. In order to evaluate available data for the 2012 Integrated Report, DEQ multiplied total arsenic data results by 76% to approximate the inorganic arsenic fraction and evaluated that amount against the most stringent applicable criterion.

## Issue:

In order to develop an Oregon specific relationship for arsenic, DEQ simultaneously began sampling both total recoverable and total inorganic arsenic in 2012. Since its inception, DEQ has run inorganic arsenic samples for approximately 460 samples through June 2017. Of those 460 samples, 349 had measurable inorganic arsenic levels above method quantitation limits. Ninety-one of the 349 samples had inorganic arsenic levels greater than the human health criterion of 2.1 µg/L.

Number of Inorganic arsenic samples	Number of quantifiable inorganic arsenic samples	Number of samples > 2.1 µg/L.	% samples above criterion
460	349	91	26%

For those samples that will be assessed as only total recoverable arsenic, 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.

When the entire dataset is plotted, a strong linear relationship between total and inorganic arsenic is evident ( $R^2= 0.98$ ) (Figure 1a), however there is increased scatter in the relationship within the range of 2.0 to 5.0  $\mu\text{g/L}$  (Figure 1b) where the translator is likely to have the greatest impact. Root Mean Squared Error (RMSE) was calculated for the two regression lines to determine the curve fit of the two regression equations predicting total inorganic arsenic from total recoverable arsenic. Interpretation of the RMSE values demonstrates that the smaller the RMSE, the closer the total inorganic arsenic prediction is to actual measured values. The RMSE for the regression equation illustrating total recoverable arsenic values greater than 2.1  $\mu\text{g/L}$  is  $\pm 2.02 \mu\text{g/L}$  while the RMSE for the total recoverable arsenic range of 2.0 to 5.0  $\mu\text{g/L}$  is 0.37  $\mu\text{g/L}$ .

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 greater than the 2.1  $\mu\text{g/L}$  criterion was used, the translator would be equivalent to 0.92. Alternatively, if the total recoverable data range from two to five  $\mu\text{g/L}$  were used, the translator would correspond to a value of 0.79.

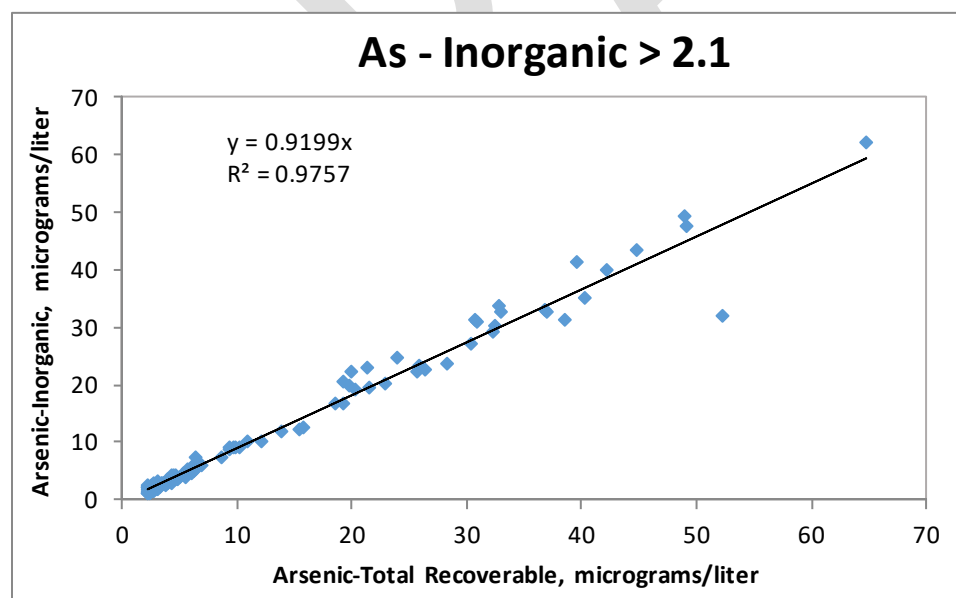


Figure 1a. RMSE = 2.04 (Total recoverable arsenic > 2.1  $\mu\text{g/L}$ )

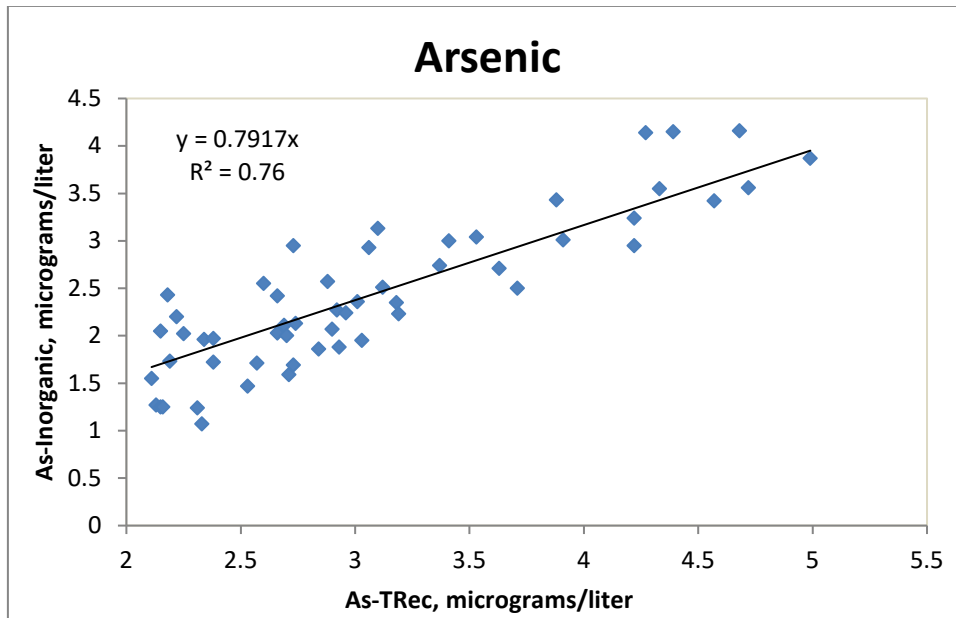


Figure 1b. RMSE=0.38 (Total recoverable arsenic between 2.0 and 5.0 µg/L)

### 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 when only total recoverable data were available based on the slopes of the total recoverable to total inorganic arsenic relationship.

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 each alternative (Table 1).

### Analysis:

A preliminary analysis on possible translators was performed on existing data to identify the number of false positives and false negatives that were generated (Table 1).

Table 1. Type I and Type II error rates for translators

	No. of Exceedances	No. of false positives	No. of false negatives
Existing Methodology (0.76)	88	4	<b>7</b>
Alternative translator (0.79)	96	8	3
Alternative translator (0.92)	104	<b>15</b>	2
<b>Actual</b>	<b>91</b>	--	--

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). Based on the data analyzed, it appears that use of the 0.92 translator produces the highest number of false positive errors, but also the lowest number of false negatives. The number of false negatives is greatest, however, when the current 0.76 translator methodology is employed. Use of the 0.79 value, which is based on total recoverable data within the range of two to five µg/L appears to limit the number of false negatives while still minimizing the number of false positives.

There are 460 paired samples of total recoverable and inorganic arsenic in DEQ's dataset. All of the samples that have total recoverable arsenic concentrations above 3 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 above 3 µg/L, we can be relatively certain that the waterbody would not be attaining 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. Consequently, the range of total arsenic values that falls between 2 µg/L and 3 µg/L is primarily of concern for identifying if inorganic arsenic would lead to a different finding of impairment than total recoverable arsenic. For the Oregon dataset, all of the false positive and false negative exceedances fall within the total arsenic range between 2 and 3 µg/L (45 samples or ~ 13% of quantified samples). The 45 samples represent 22 distinct water bodies. Of those twenty-two waterbodies, nine of the waterbodies have at least one measured inorganic arsenic sample that exceeds the 2.1 µg/L criterion.

## Conclusion

Based on the analysis conducted above, it appears that assessment of total recoverable arsenic data using the existing translator of 0.76, currently results in a slight bias toward failing to identify impairment, while the alternative translator of 0.79 based on the slope of the regression line for total recoverable arsenic between 2.0 and 5.0 µg/L reverses the bias toward falsely listing a water body as impaired. In the absence of measured

total inorganic arsenic data, it is DEQ's recommendation that a 0.79 translator should be used to predict total inorganic arsenic values from total recoverable arsenic. For total recoverable arsenic data, if the predicted inorganic arsenic results are greater than 2.1 µg/L calculated as a geometric mean, then the waterbody will be placed in Category 5. For datasets that contain both measured and predicted inorganic arsenic values, if predicted inorganic arsenic exceeds the 2.1 µg/L criterion, while measured values attain the criterion, then the water body will be placed in Category 3B until measured inorganic arsenic data can be collected.

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