

Assessing Results Below the Limit of Quantitation (LOQ)

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Assessing Results Below the LOQ

- Reporting Limit - the concentration or quantity below which data are not reported. Analytical results below the reporting limit are expressed as “less than” the reporting limit.
- Ambient Water Reporting Limit (AWRL) – the highest concentration or quantity of a target variable that can be used as a reporting limit by the laboratory unless laboratory capabilities prohibit attaining an AWRL.
- Limit of Quantitation (LOQ) – the lowest concentration or quantity of a target variable (e.g., target analyte) that can be reported with a specified degree of confidence.
 - The laboratory LOQ for each analyte must be equal to or less than the AWRL as a matter of routine practice

Assessing Results Below the LOQ

The ambient water reporting limit (AWRL) and the limit of quantitation (LOQ) for each analyte of interest is specified Table A7 of the *Surface Water Quality Monitoring Program, Water Quality Standards Program, and Water Quality Assessment Program Quality Assurance Project Plan (QAPP)*

Table A7.2 Measurement Performance Specifications

CAS	Parameter	Units	Matrix	Method	Parameter Code	<u>AWRL</u>	<u>Limit of Quant. (LOQ)</u>	Precision (RPD of LCS/LCSD)	Bias %Rec of LCS	LOQ Check Smpl % Rec	Lab
Metals in Water Parameters											
Routine Metals, Dissolved											
7429-90-5	Aluminum, dis.	µg/L	water	EPA 200.7	01106	200	100	20	80-120	70-130	TCEQ
7440-38-2	Arsenic, dis.	µg/L	water	EPA 200.8	01000	5	2.5	20	80-120	70-130	TCEQ
7440-43-9	Cadmium, dis.	µg/L	water	EPA 200.8	01025	0.1 where hardness<50 mg/L 0.3 where hardness≥50 mg/L	0.1	20	80-120	70-130	TCEQ
7440-70-2	Calcium, dis.	mg/L	water	EPA 200.7	00915	NA	0.4	20	80-120	70-130	TCEQ
7440-47-3	Chromium, dis.	µg/L	water	EPA 200.7	01030	10	4	20	80-120	70-130	TCEQ
7440-50-8	Copper, dis.	µg/L	water	EPA 200.8	01040	1.0 where hardness<50 mg/L 3.0 where hardenss≥50 mg/L	0.4	20	80-120	70-130	TCEQ



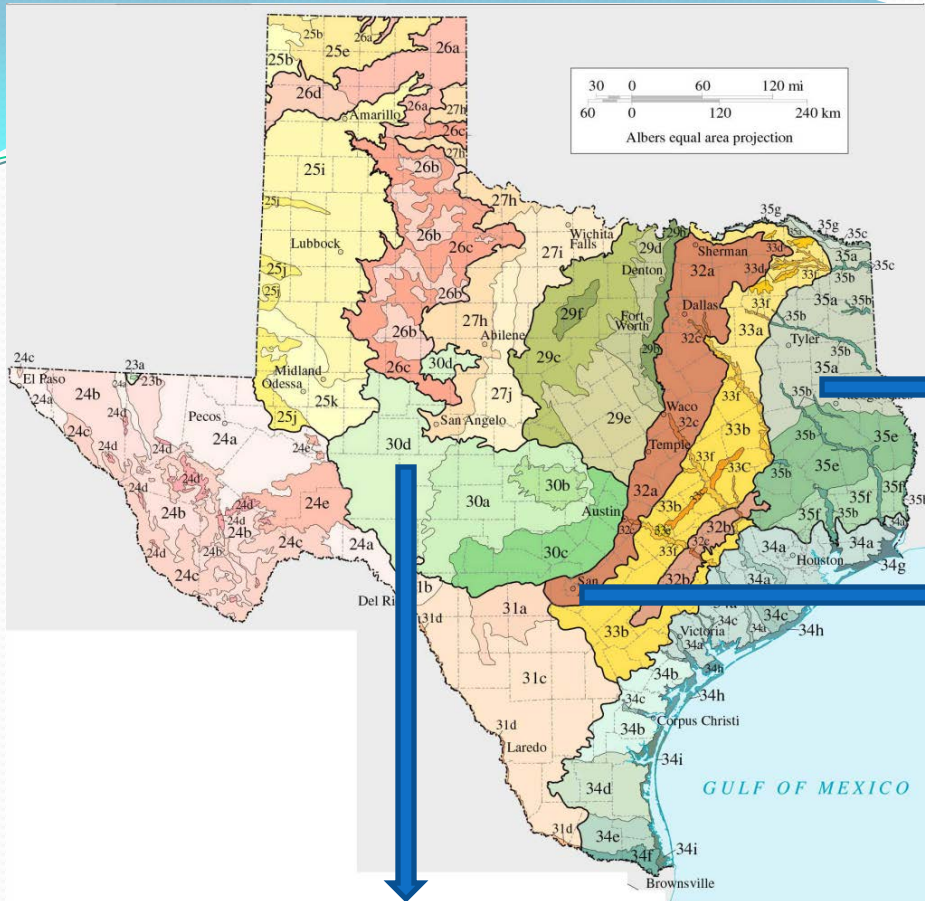
Assessing Results Below the LOQ: Why Include in Assessment?

2010 Guidance for Assessing and Reporting Surface Water Quality in Texas: “This (include sample values below the LOQ in assessment) is done to include as many individual data points in the analysis as possible and to indicate the level of monitoring effort.”

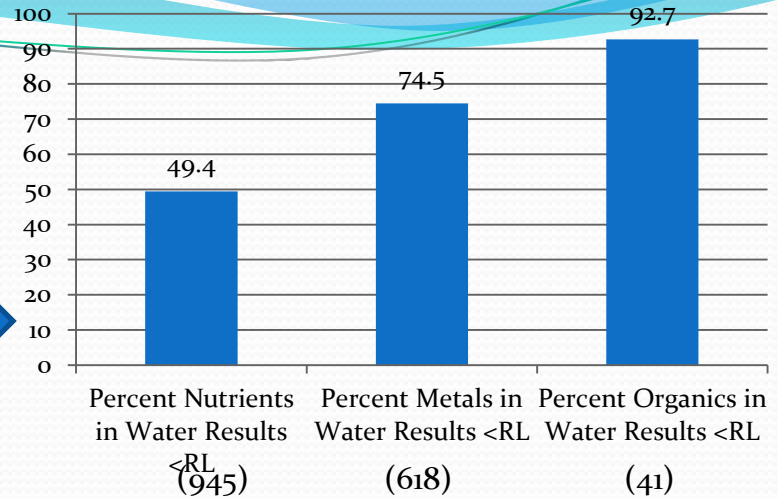
- Section 26.0135 in the Texas Water Code states:
 - To ensure clean water, the commission (TCEQ) shall establish the strategic and comprehensive monitoring of water quality and the periodic assessment of water quality in each watershed and river basin of the state.
 - The assessment must include a review of ... nutrient loading, toxic materials, and biological health of aquatic life.

Assessing Results Below the LOQ: Why Include in Assessment?

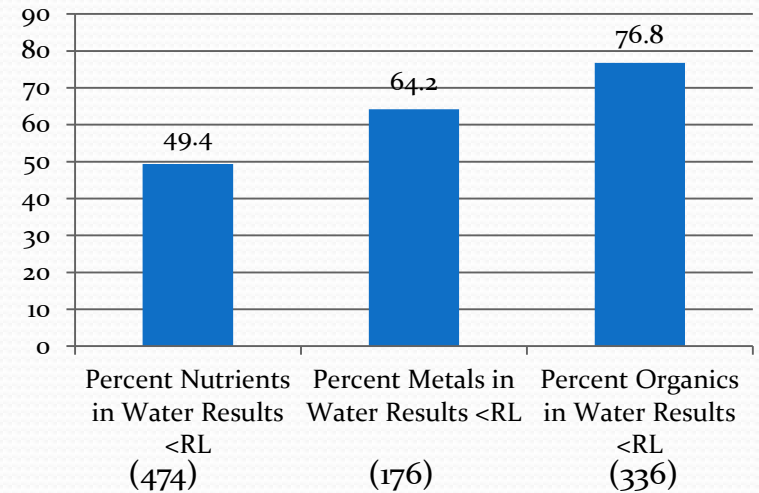
- Significant level of effort to collect samples;
- Results Below the Reporting Limit Contain Important Information
 - Evidence that “actual” concentration is between Zero and the Reporting Limit;
 - When the reporting limit is lower than the criterion, a result of < provides assurance that the actual concentration is below that specified in TSWQS to support and protect desired uses;
- Often, monitoring conducted in water bodies of special public interest at request of public, directly related to analytes for which a result of less than the reporting limit is common.
 - In other words, the **public is interested in knowing the concentration is below a certain level of concern.**



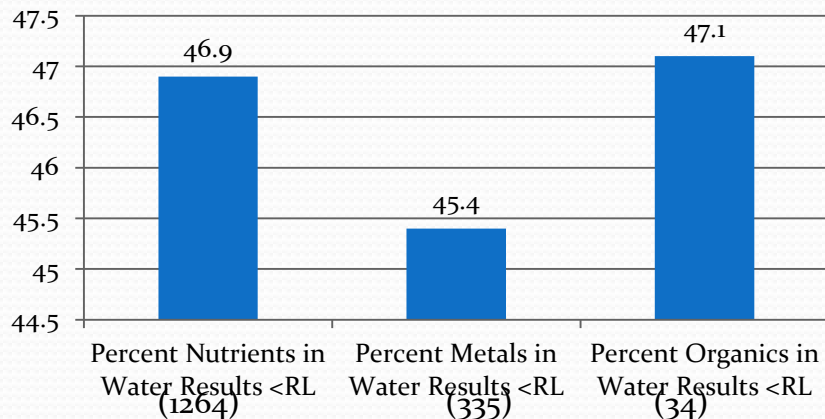
South Central Plains (35)



Texas Blackland Prairies (32)



Edwards Plateau (30)



How Common Is It?: Comparison of the occurrence of surface water sample results below the LOQ for nutrients, metals, and organics in three ecoregions (1995 - 2010).

Assessing Results Below the LOQ

Three primary elements of approach to evaluating sample values below the Limit of Quantitation:


- Evaluate individual sample values;
- Evaluate proportion of total samples below LOQ;
- Ensure the criterion and LOQ are exceeded more than one time before identifying impairment.

Assessing Results Below the LOQ

- Helsel D.R., and R.M. Hirsch, 1997. Statistical Methods in Water Resources

Identify three classes of methods for estimating summary statistics of data which include sample values below the LOQ:


- **Simple Substitution Methods** – Substitute a single value such as one-half the LOQ for each less-than value;
- **Distributional Methods**– Use characteristics of an assumed distribution to estimate summary statistics;
- **Robust Methods** – Combine observed data above the LOQ with below-LOQ values extrapolated assuming a distributional shape, in order to compute estimates of summary statistics.



Assessing Results Below the LOQ: Individual Sample Values - Simple Substitution

2010 Guidance for Assessing and Reporting Surface Water Quality in Texas:


- There is no generalized way to determine the true value for an individual result in the range between zero and the reporting limit.
- For assessments requiring either averages, or evaluation of the rate of exceedance, half of an analytical reporting limit or half the criteria (whichever is lower), may be used (**substituted for <LOQ**) in calculations.



Assessing Results Below the LOQ: Evaluating Support of Aquatic Life Use Based on Toxic Substance Acute Criteria - Evaluation of Number of Samples above the Criterion

2010 Guidance for Assessing and Reporting Surface Water Quality in Texas:

- For evaluation of acute toxicity, individual measurements of 12 metals and 29 organic substances are compared against acute criteria established in the TSWQS to determine the rate (percent of samples) of exceedance of the criterion.
- The acute criteria have additional statistical safeguards and safety factors incorporated into them.



Assessing Results Below the LOQ: Evaluating Support of Aquatic Life Use Based on Toxic Substance Acute Criteria - Evaluation of Number of Samples above the Criterion

- Acceptable Type I Error rate* for conventional samples is 20%. Acceptable Type I error rate for Acute Toxic Substances is 40%.
 - Three exceedances required out of ten samples for identification of impairment with conventional parameters.]
 - Two exceedances required out of ten samples for identification of impairment based on acute toxic substances.

Thus, a water body will **not be listed based on a data set with several to many sample results below the LOQ, and only one sample result above the criterion.**

* Type I Error: Identifying a water body as not supporting when that water body is actually fully supporting.

Assessing Results Below the LOQ: LOQ Less than Criterion

AU	Station	Method	Sample Date	Parameter	Gltt Symbol	Value (µg/L)	Value Assessed	Statistic Direction	Crit.	Exceed (Y/N)
8888_01	99999	Acute Toxic Substances in Water	8/17/07	Lead in Water		0.11	0.11	>	12.3701	N
8888_01	99999	Acute Toxic Substances in Water	12/6/07	Lead in Water	<	0.05	0.025	>	2.1933	N
8888_01	99999	Acute Toxic Substances in Water	1/30/08	Lead in Water	<	0.05	0.025	>	9.3549	N
8888_01	99999	Acute Toxic Substances in Water	5/9/08	Lead in Water		0.07	0.07	>	2.3692	N
8888_01	99999	Acute Toxic Substances in Water	6/6/08	Lead in Water	<	0.05	0.025	>	9.3549	N

For acute toxics in water, the number of exceedances out of the total number of samples is evaluated to determine support of aquatic life use.


Assessment Outcome: Zero values greater than the criterion, out of five samples
 Limited Data, No Concern

Assessing Results Below the LOQ: LOQ Greater than Criterion; Evaluating the number of exceedances of the criterion

AU	Station	Method	Sample Date	Parameter	Gtlt Symbol	Value (µg/L)	Value Assessed	Statistic Direction	Crit.	Exceed (Y/N)
8888_01	99999	Acute Toxic Substances in Water	12/5/02	Organic Substance in Water	<	0.2	0.0445	>	0.0891	N
8888_01	99999	Acute Toxic Substances in Water	9/11/02	Organic Substance in Water		0.3	0.3	>	0.0891	Y
8888_01	99999	Acute Toxic Substances in Water	8/25/02	Organic Substance in Water	<	0.2	0.0445	>	0.0891	N
8888_01	99999	Acute Toxic Substances in Water	7/15/02	Organic Substance in Water		0.4	0.4	>	0.0891	Y
8888_01	99999	Acute Toxic Substances in Water	5/15/02	Organic Substance in Water		0.4	0.4	>	0.0891	Y

Assessment Outcome: Three values greater than the criterion, out of five samples, two sample results below LOQ.

Limited Data, Not Supporting Aquatic Life Use based on Acute Toxics in Water analysis.



Assessing Results Below the LOQ: Evaluating Support of Aquatic Life Use Based on Toxic Substance Chronic Criteria: Evaluation of the Number of Samples above the Criterion

2010 Guidance for Assessing and Reporting Surface Water Quality in Texas:

- Should the average be exceeded over the period of record, the data set is subsequently evaluated to **ensure the criterion is also exceeded more than one time**.
- If the average exceeds, and this is the result of only an occasional high value, the assessor will use judgment in the evaluation of the data set and a concern rather than impairment, is identified.

Assessing Results Below the LOQ: LOQ Greater than Criterion; Evaluating the average

AU	Station	Method	Sample Date	Parameter	Gtlt Symbol	Value (µg/L)	Value Assessed	Statistic Direction	Crit.	Exceed (Y/N)
8888_01	99999	Chronic Toxic Substances in Water	9/4/02	Dissolved metal in water	<	1.0	0.5	>	1.5	N
8888_01	99999	Chronic Toxic Substances in Water	6/5/02	Dissolved metal in water		1.2	1.2	>	1.5	N
8888_01	99999	Chronic Toxic Substances in Water	3/18/02	Dissolved metal in water	<	4.0	0.75	>	1.5	N
8888_01	99999	Chronic Toxic Substances in Water	3/6/02	Dissolved metal in water		1.2	1.2	>	1.5	N
8888_01	99999	Chronic Toxic Substances in Water	12/17/02	Dissolved metal in water	<	5	0.75	>	1.5	N

Chronic Toxic Criterion Assessment - Average of data is compared to the criterion to determine support:

$$\frac{0.5 + 1.2 + 0.75 + 1.2 + 0.75}{5} = 0.88 \quad \text{Assessment Result: Limited Data, No Concern}$$

Assessing Results Below the LOQ: Proportion of total samples below LOQ;

2010 Guidance for Assessing and Reporting Surface Water Quality in Texas:

- When most of the reported values for a parameter are less than the LOQ, and the LOQ is significantly greater than the criterion (note that a margin of safety of about two for aquatic life and five to ten is incorporated into criteria), the samples are not used for calculation of averages or percent exceedances.
 - A status of Not Assessed may be identified, rather than fully supporting or no concern.
 - The assessor will use judgment when identifying parameters as fully supporting or delisting when the dataset includes nondetects.

Assessing Results Below the LOQ: Summary of Current Methods in 2010 Guidance for Assessing and Reporting Surface Water Quality in Texas

- For criteria that are expressed as single samples or averages which ever of the following measurements is smaller is used (**substituted for <LOQ**) in calculating the average—half of the reporting limit or half of the criterion.
- Should the average be exceeded over the period of record, the data set is subsequently evaluated to **ensure the criterion is also exceeded more than one time**.
- When most of the reported values for a parameter are less than the LOQ, and the LOQ is significantly greater than the criterion (note that a margin of safety of about two for aquatic life and five to ten is incorporated into criteria), the samples are not used for calculation of averages or percent exceedances.

For Future Assessments Considering Alternative Methods for Dealing with Results Below the Reporting Limit: Estimating Summary Statistics (e.g. Mean, Standard Deviation, Median, etc.)

- Distributional Methods – Use the characteristics of an assumed distribution to estimate summary statistics.
 - Maximum Likelihood (MLE)
 - Probability Plotting Procedures
- Robust Methods – Combine observed data above the reporting limit with below-limit values extrapolated assuming a distributional shape, in order to compute estimates of summary statistics.
 - Distribution fit to the data above the reporting limit by either MLE or probability plot procedures, but fitted distribution is used only to extrapolate a collection of values below the reporting limit. Extrapolated values used collectively, along with values above the reporting limit to estimate summary statistics.