STORMWATER MONITORING COALITION LABORATORY GUIDANCE DOCUMENT
Second Edition

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and
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Southern California Coastal Water Research Project

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(Second Edition)

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September 2007

Technical Report 521

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INTRODUCTION

A continuing goal of the southern California Stormwater Monitoring Coalition (SMC) is to compile monitoring data from separate programs to make region-wide assessments. This task has been difficult, thus far, because the various monitoring programs have differing project goals and objectives, differing mandates from regulatory agencies, differing sampling designs, and differing laboratory analytical methods. The goal of this document is to provide the basis for ensuring comparability among stormwater chemical analytical laboratories. The comparability issues that revolve around goals, objectives, and study designs were addressed through a related, but separate document (Bernstein and Schiff, 2003).

There are at least three reasons why laboratory analytical data are not comparable including differences in target analytes, reporting levels (detection limits), and laboratory methods. In 2003, a laboratory intercalibration study sponsored by the SMC established common reporting levels, target analytes, and iterative round robin exercises that surmounted many of these obstacles (Gossett, Renfrew, and Schiff, 2003). However, there are new laboratories, or new staff within existing laboratories, which have not been evaluated and periodic intercalibrations are a necessity. In an effort to improve and update laboratory performance, a new intercalibration study was conducted with 14 laboratories that conduct stormwater analysis in California (Table 1). Like the previous exercise, this study was aimed at developing a consensus-based approach for achieving minimal levels of comparability among typically disparate laboratories. The success of the 2003 exercise and this subsequent study was primarily due to three factors including communication and commitment among laboratory personnel, setting performance-based criteria for establishing standards of success, and round robin testing using locally derived reference materials.

Objectives and Goals of this Document

The objective of this guidance manual is to update and present the performance-based guidelines established during the SMC interlaboratory studies of 2003 and 2007. This document sets the minimum standards of sensitivity, precision, and accuracy across laboratories so that individual data sets can be combined with estimated levels of confidence for making regional assessments of stormwater quality. The philosophy of performance-based guidelines is key to achieving this comparability. Although every laboratory involved in the stormwater intercalibration study was certified by the State of California Environmental Laboratory Accreditation Program (ELAP), inventories of existing methods demonstrated that most analytes are not analyzed in exactly the same manner. This will continue as new laboratories, or new equipment at existing laboratories continues to proliferate. Rather than mandate specific methods that are inflexible and discourages existing laboratories from achieving faster, more sensitive, and more cost-effective methods, this document merely sets minimum levels of comparability so that data sets can be combined no matter what technology currently exists. These procedures are also outlined herein.

This guidance manual is a living document. It should be revisited each time an intercalibration exercise is conducted and can be expanded to include additional constituents, additional laboratories, or to refine the recommended performance-based sensitivity, accuracy, and precision requirements as new information becomes available.

This document and laboratory intercalibration study is not a certification program. The guidelines set by this document merely express the desired needs of the stormwater agencies throughout the southern California region. Therefore, these stormwater agencies can use these guidelines in establishing specifications for work assignments or requests for proposals to conduct stormwater analyses. Alternatively, or in combination, stormwater regulatory agencies may use these specifications in the development of regulatory expectations for laboratory performance by monitoring agencies.

Table 1. Participating Laboratories in the 2007 SMC Intercalibration Study (listed alphabetically).

Laboratory Name	Contact
Advanced Technology Labs	Bing Roura
Associated Labs	Jim McCall
California Department of Fish and Game	Patricia Bucknell
CalScience Environmental Labs	Larry Lem
Capco Analytical Services	Dan Farah
City of Los Angeles- EMD	Mahesh Pujari
CRG Marine Labs	Rich Gossett
FGL Environmental	David Terz
Los Angeles County- ACWM	Wai Leung
MWH Labs	Andrew Eaton
Soil Control Labs	Mike Galloway
Truesdail Labs	Norm Hester
UC Santa Barbara MSI	George Paradis
Weck Labs	Alan Ching

GUIDANCE INFORMATION

This document consists of four elements. First is a list of target analytes and minimum levels of sensitivity (reporting levels). Second are minimum levels of accuracy and precision. Third are recommended protocols for method specific comparability. Fourth are participation requirements for intercalibration studies and the laboratory evaluation criteria and results.

Analytes and Reporting Levels

Target Analytes

A core group of target analytes was specified for comparability (Table 2). This list includes total suspended solids (TSS), total organic carbon (TOC), nutrients, and trace metals. This list was based on three criteria. First, these analytes are consistently measured by existing monitoring programs throughout the region. Second, these constituents are routinely detected in stormwater samples. Third, although standard methods exist, there is sufficient disparity in protocols among laboratories that consistency guidance is warranted.

The list of target analytes is not meant to be an exhaustive list of all constituents that could or should be measured in individual programs. For example, there are no pesticides, herbicides, or polynuclear hydrocarbons on the list of target analytes. Any or all of these target analytes may be the focus of individual monitoring programs. At this point in time, however, there has not been an intercalibration study conducted for these constituents to make performance-based recommendations for stormwater laboratories.

While the list of target analytes focuses on total trace metals, they can be applied to dissolved trace metals. Since the analytical methodology is similar among both total and dissolved metals, the performance-based guidelines may be applied to both. Bear in mind that for dissolved trace metals, the preparation step of filtration is a major source of potential contamination and was not evaluated in this study.

Reporting Levels

Targeted reporting levels (RLs) are provided in Table 2. This guidance was based on the philosophy that analyses should be sufficient to assess if samples are below water quality thresholds of concern. In this instance, the water quality thresholds of concern are established in the California Toxics Rule (CTR). Further, reporting levels should be technologically achievable, but far enough below water quality thresholds that exceedences cannot be attributable to methodological uncertainty. Therefore, the philosophical approach for setting RLs was to select guidelines that were one-half of the lowest water quality threshold concentration. In the case of the CTR, there are thresholds for both marine and fresh waters. For a participating laboratory to achieve these reporting levels, it should include a calibration standard at or below this level (e.g. the reporting level is a quantitation level and not an MDL).

Table 2. Target analytes and Reporting Levels for the Stormwater Monitoring Coalition Monitoring Program.

Analyte	Units	SMC Target Reporting Level	California Toxics Rule Limit (Freshwater)	California Toxics Rule Limit (Seawater)
General Constituents				
TSS	mg/L	5	-	-
Nitrate+Nitrite as N	mg/L	0.2	-	-
Ammonia as N	mg/L	0.1	-	-
Total Phosphorus as P	mg/L	0.1	-	-
Total Kjeldahl Nitrogen	mg/L	0.2	-	-
Total Organic Carbon	mg/L	1	-	-
			-	-
Total Metals				
Arsenic	µg/L	2	150	36
Cadmium	µg/L	1	2.2	9.3
Chromium (total)	µg/L	5	11	50
Copper	µg/L	2	9	3.1
Nickel	µg/L	4	52	8.2
Lead	µg/L	1	2.5	8.1
Selenium	µg/L	2	5	71
Silver	µg/L	1	3.4	1.9
Zinc	µg/L	10	120	81

Accuracy and Precision

Analysis of spiked samples or reference materials provides a mechanism for assessing within laboratory accuracy. Reproducibility among replicate sample analyses provides a determination of within laboratory precision. General guidance provided by ELAP and the US EPA (40 CFR Part 136) are recommended for assessing within laboratory accuracy and precision by analyzing two replicate sample matrix spikes per batch of 20 or less samples. Matrix spike concentrations of approximately 10 times the lab reporting level are recommended for most meaningful spike recovery measurements. As general guidance, matrix spike concentrations should be in the same general range as relevant regulatory limits to truly represent accuracy and precision at these concentrations. It is also recommended that a set of laboratory replicate samples are analyzed with each batch of samples to indicate precision using actual sample matrices, which is typically larger due to natural variation of sample homogeneity. The relative percent difference (RPD) between replicate spikes for the parameters listed in Table 2 should be less than 20%. Accuracy limits for MS and MSD are provided in Table 3. These accuracy limits mimic ELAP and US EPA guidelines. Accuracy limits for Certified Reference Materials are provided by the supplier.

Additional QAQC requirements in the methods referenced by each laboratory should conform to the requirements listed within that method by Standard Methods or the US EPA

(i.e. Blank Spikes). Project specific QAQC requirements may also be listed in the Quality Assurance Project Plan (QAPP). Since spiked samples can be complicated by matrix interferences, this can confound assessments of accuracy. Therefore, the analysis of Certified Materials, when available, is also a recommended (but not required) option for the monitoring agency.

Intercalibration studies evaluate the accuracy and precision of analysis among laboratories. For this document, interlaboratory precision guidelines were developed by analyzing each of three matrices by fourteen different laboratories (Table 1) throughout southern California. These matrices included a specially prepared performance evaluation (PE) sample, an urban runoff sample, and a rural runoff sample.

Table 3. Laboratory accuracy and precision guidelines for concentrations greater than 10x the RL for ongoing analysis of stormwater samples.

Target Analyte	Precision (RPD of Duplicate Samples)	Accuracy (Percent Recovery of MS or MSD [a])
General Constituents		
TSS	0 - 20	[b]
Ammonia-N	0 – 20	80 – 120
Nitrate-N+Nitrite-N	0 – 20	80 - 120
Total Kjeldahl Nitrogen	0 – 20	70 – 130
Total Phosphorus as P	0 – 20	70 – 130
Total Organic Carbon	0 – 20	80 – 120
Trace Metals		
Arsenic	0 – 20	80 – 120
Cadmium	0 – 20	80 – 120
Chromium	0 – 20	80 – 120
Copper	0 – 20	80 – 120
Lead	0 – 20	80 – 120
Nickel	0 – 20	80 – 120
Selenium	0 – 20	80 – 120
Silver	0 – 20	80 – 120
Zinc	0 – 20	80 – 120

[a-]   For certified reference materials, use supplier recommendations
[b-]   defined by supplier

For each of the 3 matrices, the grand mean and standard deviation were calculated using the pooled results from all fourteen laboratories (Table 4). A Grubb's test was used to identify outliers that were removed along with the "not detected" values from the data set prior to calculating the grand means and standard deviations. It should be noted that not all laboratories analyzed every target analyte so that the number of results varied by parameter. Upper and lower "Warning" limits were based on two standard deviations within the grand mean and upper and lower "Control" limits were based on three standard deviations within the grand mean.

Table 4. Grand mean, warning limits, and control limits of each matrix from the combined results of all fourteen laboratories participating in the intercalibration. Warning limits and control limits are indicated as maximum difference from the mean (e.g., TSS for LU control limits are 106 to 138 ppm).

Target Analyte	Units	ERA[a] Mean	ERA[a] Warning Limit (+2 SD)	ERA[a] Control Limit (+3 SD)	LU[b] Mean	LU[b] Warning Limit (+2 SD)	LU[b] Control Limit (+3 SD)	LR[c] Mean	LR[c] Warning Limit (+2 SD)	LR[c] Control Limit (+3 SD)
General Constituents										
TSS	mg/L	-	-	-	122	11	16	337	83	124
Ammonia-N	mg/L	0.551	0.51	0.76	1.33	0.45	0.66	0.341	0.166	0.249
Nitrate-N+Nitrite-N	mg/L	1.88	0.19	0.29	0.675	0.109	0.162	0.755	0.144	0.216
Total Kjeldahl Nitrogen	mg/L	0.796	0.554	0.834	2.95	0.89	1.33	3.64	2.13	3.19
Total Phosphorus as P	mg/L	0.746	0.171	0.258	0.288	0.220	0.330	0.388	0.338	0.507
Total Organic Carbon	mg/L	-	-	-	26.5	6.4	9.5	6.63	3.77	5.64
Trace Metals										
Arsenic	µg/L	7.05	1.59	2.38	3.13	0.81	1.22	2.58	1.14	1.70
Cadmium	µg/L	2.96	0.33	0.49	0.306	0.074	0.111	0.466	0.112	0.168
Chromium	µg/L	30.2	3.4	5.2	5.51	2.08	3.12	13.2	4.2	6.4
Copper	µg/L	12.7	2.3	3.5	116	25	37	19.3	8.8	13.2
Lead	µg/L	7.10	0.71	1.06	8.74	1.30	1.96	8.87	2.53	3.77
Nickel	µg/L	32.1	4.0	6.03	13.1	2.0	2.94	5.08	1.15	1.72
Selenium	µg/L	17.7	4.3	6.6	1.88	0.89	1.33	1.44	0.81	1.21
Silver	µg/L	6.74	1.18	1.77	0.106	0.041	0.063	0.069	0.060	0.09
Zinc	µg/L	79.1	21.7	32.6	153	28	42	468	106	159

[a] certified reference material
[b] simulated rainfall runoff from an urban catchment
[c] simulated rainfall runoff from a rural catchment
- no limit

Using the same data set as the grand means and standard deviations, the overall relative standard deviation (RSD) for each matrix was calculated and is presented in Table 5. Precision among laboratories is expected to be less than 30% for those analytes that are present at concentrations at least 10 times the MDL. The RSD for Ammonia and TKN was greater than 30% for the ERA sample but within 30% for the LU and LR samples. Total P RSD was greater than 30% for the LU and LR samples, but the concentration was below 10 times the MDL. The same was true for Silver in the LR sample.

Table 5. Relative standard deviation results for each matrix for the combined results from all fourteen laboratories.

		Relative Standard Deviation		
Target Analyte	**Units**	**ERA[a]**	**LU[b]**	**LR[c]**
General Constituents				
TSS	%	-	5	12
Ammonia-N	%	46	17	24
Nitrate-N+Nitrite-N	%	5	8	10
Total Kjeldahl Nitrogen	%	35	15	29
Total Phosphorus as P	%	11	38	43
Total Organic Carbon	%	-	12	28
Trace Metals				
Arsenic	%	11	13	22
Cadmium	%	6	12	12
Chromium	%	6	19	16
Copper	%	9	11	23
Lead	%	5	7	14
Nickel	%	6	7	11
Selenium	%	12	24	28
Silver	%	9	20	44
Zinc	%	14	9	11

[a] certified reference material
[b] simulated rainfall runoff from an urban catchment
[c] simulated rainfall runoff from a rural catchment
- no limit

Standardization

Although this document is founded on performance-based guidelines enabling flexibility within each laboratory to achieve consistency, the laboratory intercalibration studies have identified four protocols whereby recommended standardization can dramatically increase comparability. This standardization includes sub-sampling, Total Phosphorus digestion, TKN digestion, and trace metal digestion techniques.

Sub-Sampling Techniques

Sub-sampling techniques are an important component of both within and among laboratory variability. This was especially true for particle-laden samples, such as those from more rural catchments with unlined channels. Particle-bound constituents have the potential to be dramatically biased if sub-sampling techniques selectively target or avoid particles within samples. To this end, standardized laboratory techniques for sub-sampling were developed for splitting large volume stormwater samples collected in the field into smaller bottles for distribution to the laboratory and for subsequent sampling of smaller aliquots in the laboratory at the time of analysis.

Sub-sampling of large-volume composite containers

In order to ensure that sample containers destined for an analytical laboratory all contain water that is similar and representative of the original composite sample, it is important to maintain a well-mixed composite sample during sub-sampling and to prevent stratification and the settling out of heavier particles. This is accomplished by the use of a large-capacity stirrer and a 2 to 3-inch, pre-cleaned, Teflon-coated stir bar; larger stir bars can be used for larger volume containers. Adjustment of stirring speed is important. Speeds that are too fast will create a large vortex within the composite bottle that can actually concentrate heavier particles and should be avoided. Speed should be based on a visual assessment of the most even mixing throughout the composite bottle.

Sub-sampling from the homogenized composite bottle is accomplished using a peristaltic pump and pre-cleaned (inside and outside) sub-sampling hose. Filling sample containers by pumping from the composite bottle is best performed by two people. One person is responsible for filling individual sample containers and one person is responsible for constantly moving the intake tubing up and down in the water column of the composite sample. Based on experimental evidence, this up and down movement of the intake is a procedure that helps obtain a more representative sub-sample. This is because there can still be some stratification of heavier particles in the composite sample despite the mixing created by the stirrer. The up and down movement of the intake tubing should be limited to approximately 80-90 percent of the depth of the water column and should never touch the bottom of the composite bottle.

Sub-sampling of sample containers for analysis

The goal of sub-sampling bottles in the laboratory for analysis is similar to field sampling techniques, to maintain a homogeneous particle distribution. Analysis of particle-

associated constituents will be biased if non-representative particle suspensions are used for analysis. In order to maintain homogeneous particle distributions, we recommend the use of sub-sampling techniques described by the US Geological Survey (Charles J. Patton, USGS National Water Quality Laboratory, Denver, CO). Appropriately, a similar technique to large composite container sub-sampling is used. Briefly, a "+" shaped magnetic stirring bar is placed into the sample container and the sample is stirred while a sub-sample is aspirated and dispensed into the processing container.

Total Kjeldahl Nitrogen

Total Kjeldahl Nitrogen (TKN) analysis was affected by the digestion technique during the laboratory intercalibration exercise. This was due to the influence caused by particle content and size distribution. Therefore, minimum standardization of the digestion procedure for stormwater samples is recommended. Either micro or macro Kjeldahl digestions are acceptable. However, the length of time of digestion should be set at a minimum of 1 hour at 380ºC, until copious fumes are generated and the digestion solution turns yellow, and then for an additional 30 minutes (to ensure adequate recovery) prior to analysis.

Total Phosphorus

Total Phosphorus analysis was also affected by the digestion technique during the laboratory intercalibration exercise. Therefore, we are recommending standardization of the digestion procedure to the use of an acid persulfate digestion.

Trace Metals

Trace metal analysis was also affected by the digestion technique during the laboratory intercalibration exercise. This is because trace metal concentration may be influenced by particle content and size distribution. Therefore, minimum standardization of trace metal digestion is recommended for stormwater samples. Trace metals should be digested using a nitric/hydrochloric acid digestion at 95ºC for 2-4 hours until the sample has evaporated from 50mL down to 10mL.

Dissolved metals analysis should be performed on filtered samples and does not require digestion if the turbidity is <1. Sample spiking for the Matrix Spike should be done after filtering. Filtration is a common source of contamination and when measuring dissolved metals. All other criteria for trace metals in this guidance document are applicable to both total and dissolved metals.

Participation Requirements

Proficiency Testing

Laboratories performing analyses for SMC Stormwater Monitoring Programs should pass a SMC performance evaluation (PE) sample and participate successfully in SMC intercalibration exercises. The PE and intercalibration exercises are strongly recommended to be performed on an annual basis. This frequency is recommended

because: 1) new laboratories may wish to participate; 2) existing laboratories need to evaluate new personnel; and 3) new and existing laboratories with new equipment or altered laboratory techniques need to be evaluated. Intercalibrations should occur within the first six months of the calendar year to ensure evaluations prior to the following wet season that typically begins on October 15th.

SMC PE samples should be spiked between 1 and 10 times the established reporting limit (Table 2) for the analytes of concern for minimum proficiency. All sample results should meet the criteria provided by the commercial supplier of the sample to evaluate accuracy. PE samples are to be coordinated through the SMC, or their representatives on a Chemistry subcommittee, and can be purchased from private companies such as Environmental Resource Associates, Inc. (ERA), Wibby Environmental, APG, or other NELAC approved proficiency testing sample providers.

Intercalibration studies require laboratories to analyze one PE sample and three replicates of two runoff samples, one from an urban area and one from a rural catchment. Each intercalibration study should be performed with one or more iterations to evaluate consistency and allow for laboratory corrective actions if deficient analysis resulted from the first iteration.

New Laboratories

New laboratories that have not participated in previous intercalibration exercises may still be able to analyze stormwater samples during the present wet season. These labs, however, will need to provide resources to purchase a PE sample with the same requirements used in the intercalibration study in Section 3.1 (i.e. samples will be spiked at 1 to 10 times the established reporting limits in Table 2). These samples should be delivered to the new laboratory blind and as whole volume samples. All new laboratories are required to participate in the next intercalibration exercise to remain qualified for the SMC program.

Laboratory Intercalibration Exercise Evaluation Criteria

Laboratories participating in the intercalibration exercise will be evaluated to determine if their results are within acceptable accuracy and precision insuring comparability of data between the different SMC stormwater monitoring programs. For the present study, a scoring system was used to assign a numeric value and letter grade to each laboratory indicating the quality of their performance in the exercise. A grade of "C" or better is recommended for a laboratory to be eligible to perform analyses for SMC programs.

Scoring System and Results

Based on the combined results from all fourteen laboratories participating in the exercise, a Grubb's test was performed to identify outlier data points. After removal of the outlier data, the "not detected" results were removed and the grand mean and standard deviation were calculated for each analyte. Upper and lower warning and control limits were based on 2 and 3 times the standard deviation, respectively (see table 4). The results, upper and

lower warning, and upper and lower control limits are presented in graph form in Appendix I.

A scoring system was established to rate each laboratory's performance. Each replicate analysis by a laboratory was given 3 points if the result for that sample-analyte combination was within the warning limit and 2 points if the result was within the control limit (Figure 1). Zero points were given if the result was outside the control limit. For example, if a laboratory got all three replicate results within 2 SD, then they received 9 points for that analyte. If two results were within 2SD and one was within 3SD, then the laboratory was given 3+3+2 or 8 points out of 9. The Relative Standard Deviation (RSD) was also calculated for each parameter and 1 point was given for each analyte/matrix with an RSD of < 20%. The total points awarded to each laboratory were combined for the General Constituents (TSS, Ammonia-N, Nitrate-N + Nitrite-N, TKN, TOC, and Total P) and then divided by the total possible points, then multiplied by 100 for the final score. Trace metals were all combined as a separate score using the same criteria.

Laboratories that did not analyze a particular analyte were not given a score for that parameter so that they were not penalized. The omitted analyte is listed in the scoring results summary so that SMC programs managers have the option of using another laboratory for that specific analysis. A letter grade was assigned based on 90-100% being an "A", 80-89% being a "B", 70-79% being a "C", and below 70% being an "F".

The results from the 2007 laboratory intercalibration exercise are presented in Table 6a and b. Since this is a public document and participation in this exercise is intended to be kept anonymous, the laboratories are listed by randomly assigned number. SMC member agencies will be given the key to the laboratory names upon request.
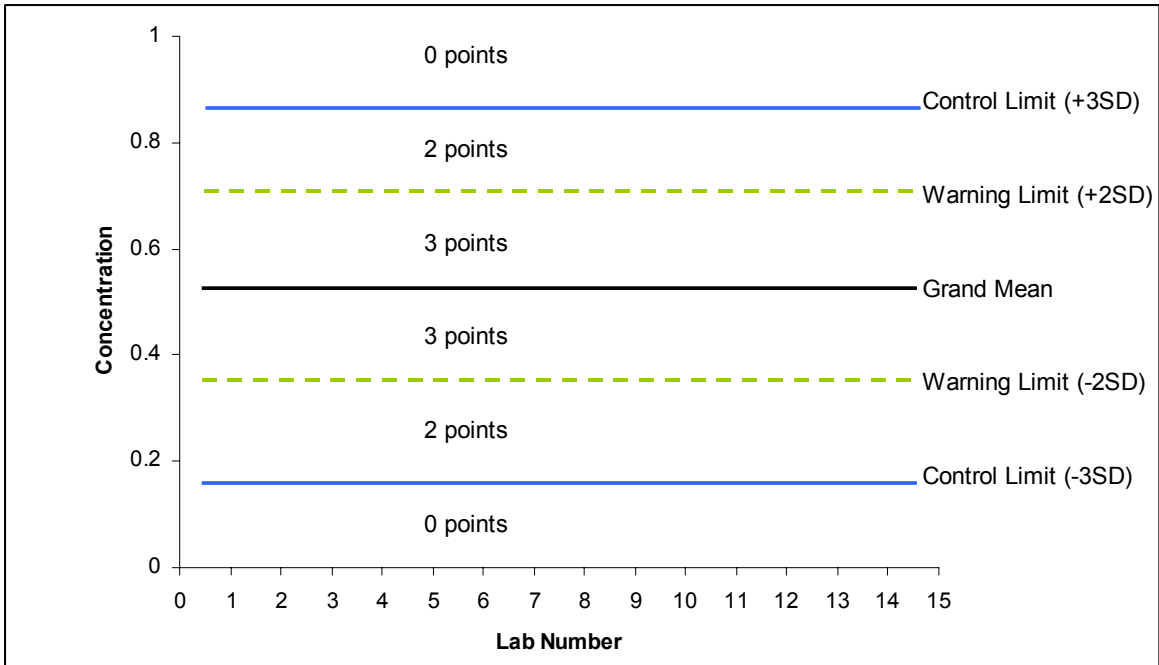
Figure 1. Example of scoring system for SMC intercalibration studies without any specific data shown.

Table 6a. Scoring results for General Constituents in the 2007 Laboratory Intercalibration Exercise.

Laboratory Number	Analytical Result Score	RSD Score	Percent Success	Letter Grade
1	93 out of 120	11 out of 12	79 %	C
2	120 out of 120	12 out of 12	100%	A
3 (did not analyze TKN or TOC)	79 out of 81	8 out of 8	98 %	A
4	116 out of 120	12 out of 12	97%	A
5	118 out of 120	12 out of 12	98%	A
6	98 out of 120	11 out of 12	83%	B
7	120 out of 120	12 out of 12	100%	A
8 (did not analyze TOC)	110 out of 120	11 out of 12	92%	A
9	112 out of 120	11 out of 12	93%	A
10 (did not analyze Nitrate-N + Nitrite-N or TOC)	11 out of 11	0 out 8	58%	F
11 (did not analyze TOC)	91 out of 102	9 out of 10	89%	B
12	117 out of 120	12 out of 12	98%	A
13 (did not analyze TSS, TKN, TOC, or Total P)	42 out of 42	4 out of 4	100%	A
14 (did not analyze TKN or TOC)	79 out of 81	8 out of 8	98%	A

Table 6b. Scoring results for Trace Metals in the 2007 Laboratory Intercalibration Exercise.

Laboratory Number	Analytical Result Score	RSD Score	Percent Success	Letter Grade
1	186 out of 189	18 out of 18	99%	A
2	180 out of 189	18 out of 18	96%	A
3	185 out of 189	18 out of 18	98%	A
4	186 out of 189	18 out of 18	99%	A
5	179 out of 189	18 out of 18	95%	A
6	189 out of 189	18 out of 18	100%	A
7	187 out of 189	16 out of 18	98%	A
8	not analyzed	-	-	-
9	189 out of 189	17 out of 18	100%	A
10	26 out of 189	16 out of 18	20%	F
11	187 out of 189	78 out of 18	99%	A
12	189 out of 189	18 out of 18	100%	A
13	not analyzed	-	-	-
14	178 out of 189	18 out of 18	95%	A

DEFINITIONS

Batch – An analytical batch consists of 20 or fewer client samples.

Method Blank (MB) – Analyte free water that is carried through the entire analytical process. The method blank is used to evaluate contamination contributed from the method. Analyte detections in the method blank must be less than 10x the analyte result for a client sample to be considered usable without flagging.

Duplicate – A client sample analyzed in duplicate. Duplicate RPD should be summarized in the report.

Blank Spike/Blank Spike Duplicate – A blank spike (laboratory control sample) is a certified standard reference material that is spiked into a reagent blank. It is carried through all steps of sample preparation to demonstrate method performance inclusive of sample preparation steps. The blank spike should be spiked near the mid point of the calibration curve.

Matrix Spike/Matrix Spike Duplicate – A matrix spike is a regular sample that is split into three sub-samples. Two of the replicates are spiked with analyte solution at the same concentration and are defined as the matrix spike and matrix spike duplicate (MS/MSD). The MS/MSD samples are carried through the sample preparation and analysis procedure with each batch of 20 or less samples. The MS/MSD results provide information regarding laboratory precision, sample matrix effects, and method efficiency.

RPD- Relative Percent Differnce is calculated using the following formula:
$$RPD=(Results1-Result2)/(Result1+Result2)/2*100$$

RSD- Relative Standard Deviation is calculated using the following formula:
$$RSD=(Standard\ Deviation)/(Mean)*100$$

REFERENCES

Bernstein, B. and K. Schiff. 2003. Model Stormwater Monitoring Program for Urban Runoff Programs.

Gossett, R., Renfrew, D., and K. Schiff. 2003. Stormwater Monitoring Coalition Laboratory Guidance Document.

APPENDIX A

ERA SAMPLE: Ammonia-N (Lab 6 and Lab 11 were ND)
(True Value= 0.698mg/L)
(Mean= 0.626 mg/L)
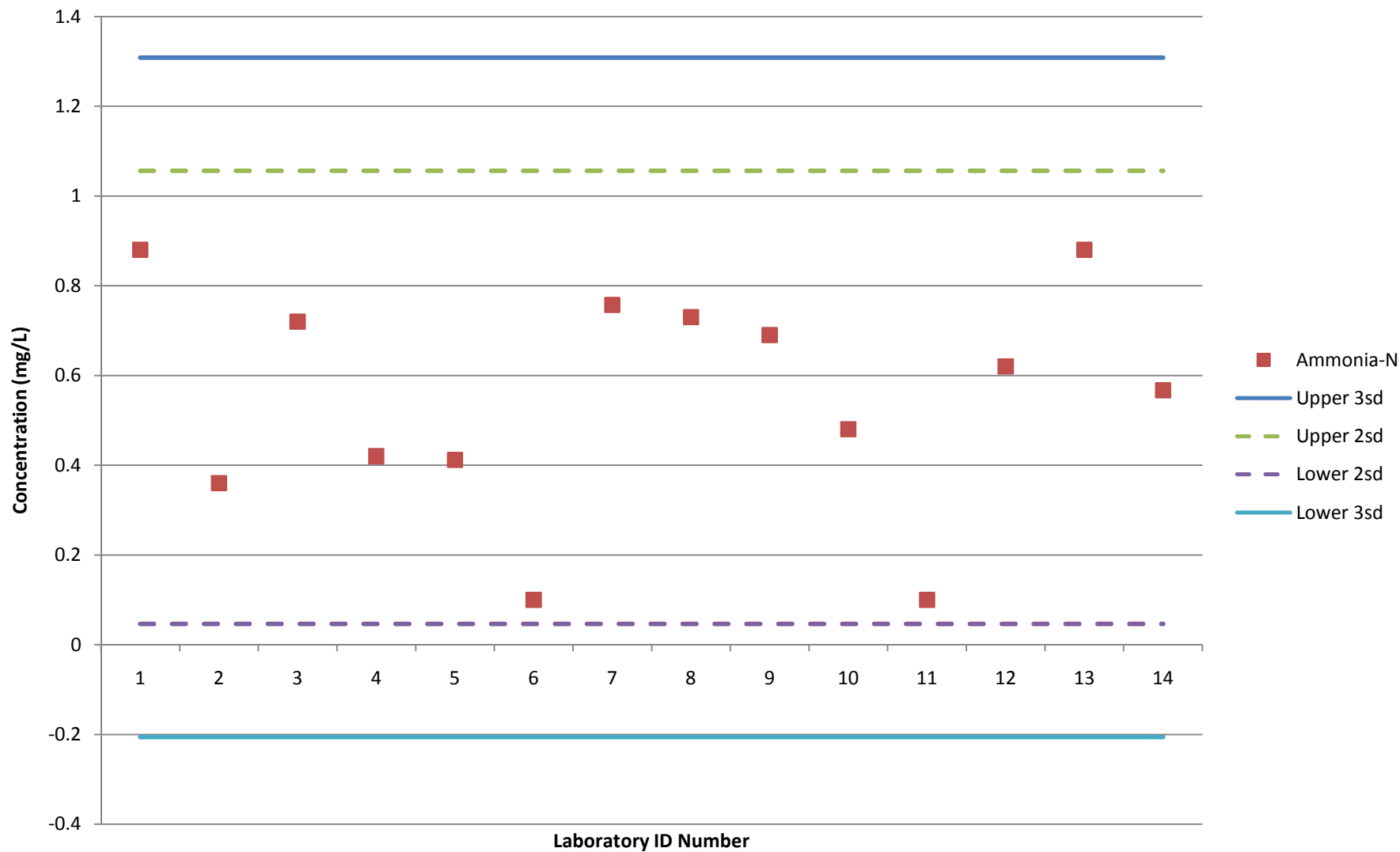
ERA SAMPLE: Nitrate+Nitrite-N (w/o Lab 11 Data)
(True Value= 1.99 mg/L)
(Mean= 1.88 mg/L)
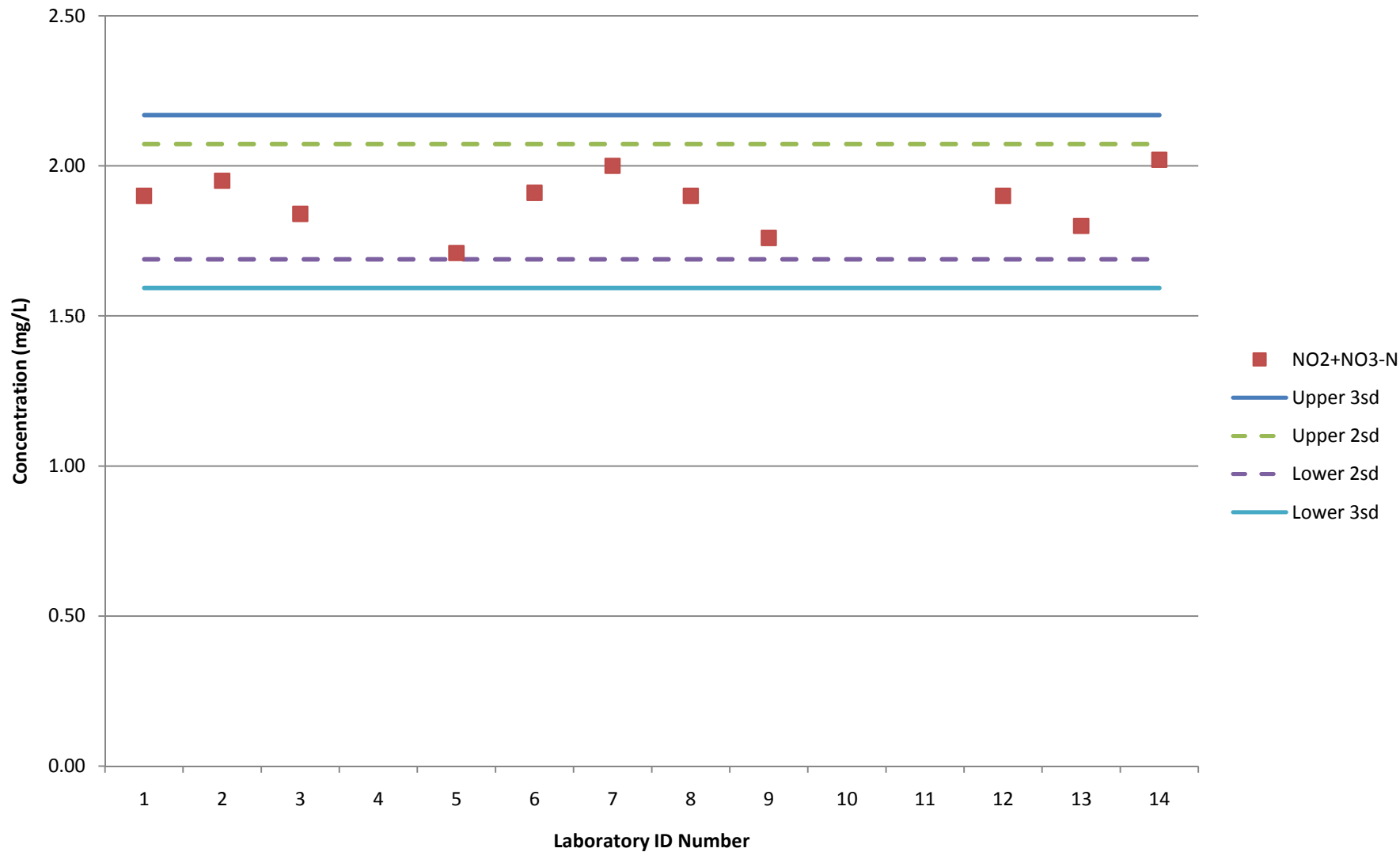
ERA SAMPLE: TKN (Lab 11 was ND)
(True Value= 0.698 mg/L)
(Mean= 0.776 mg/L)
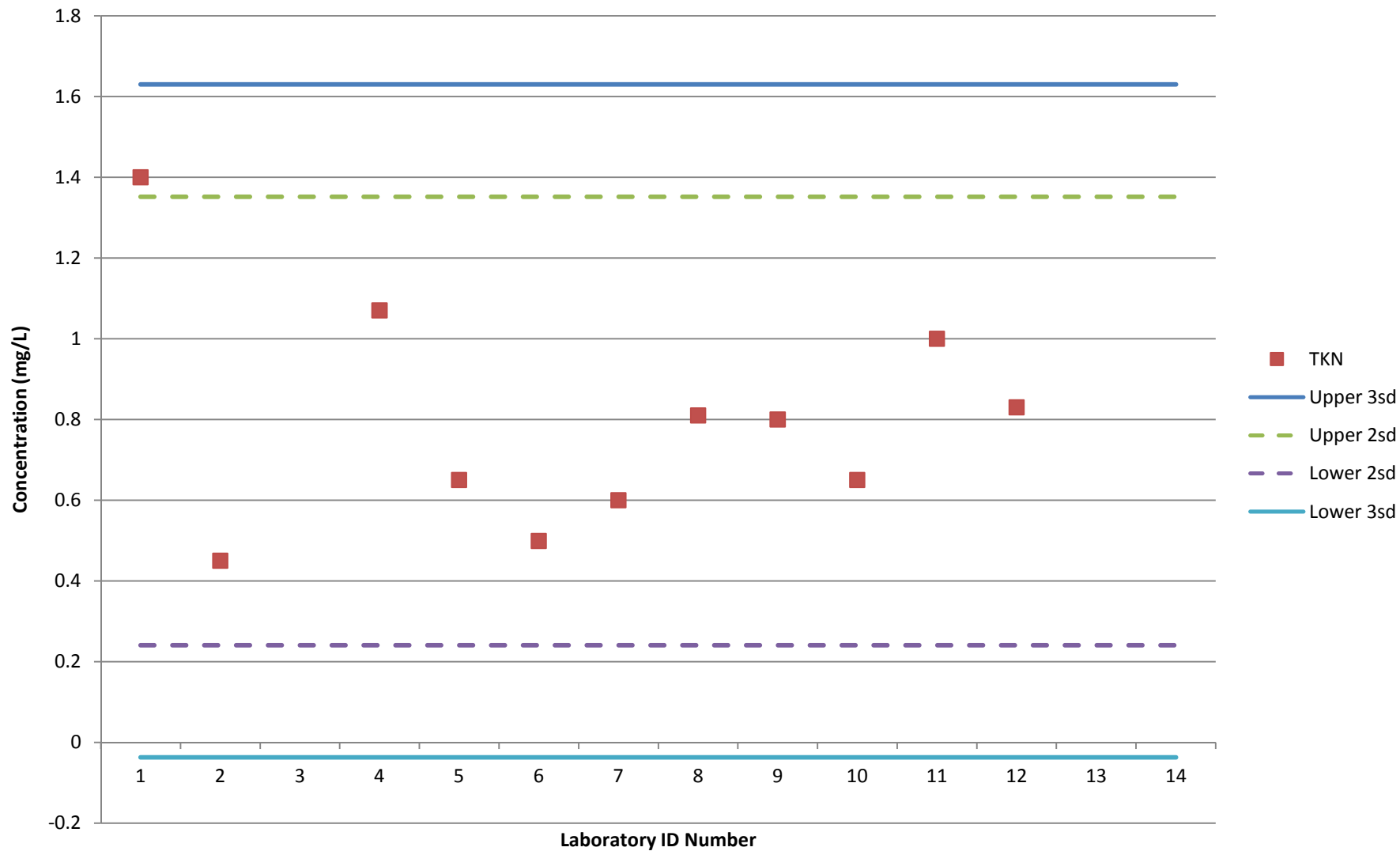
ERA SAMPLE: Total Phosphorus (w/o Lab 12 Data)
(True Value= 0.747 mg/L)
(Mean= 0.746 mg/L)
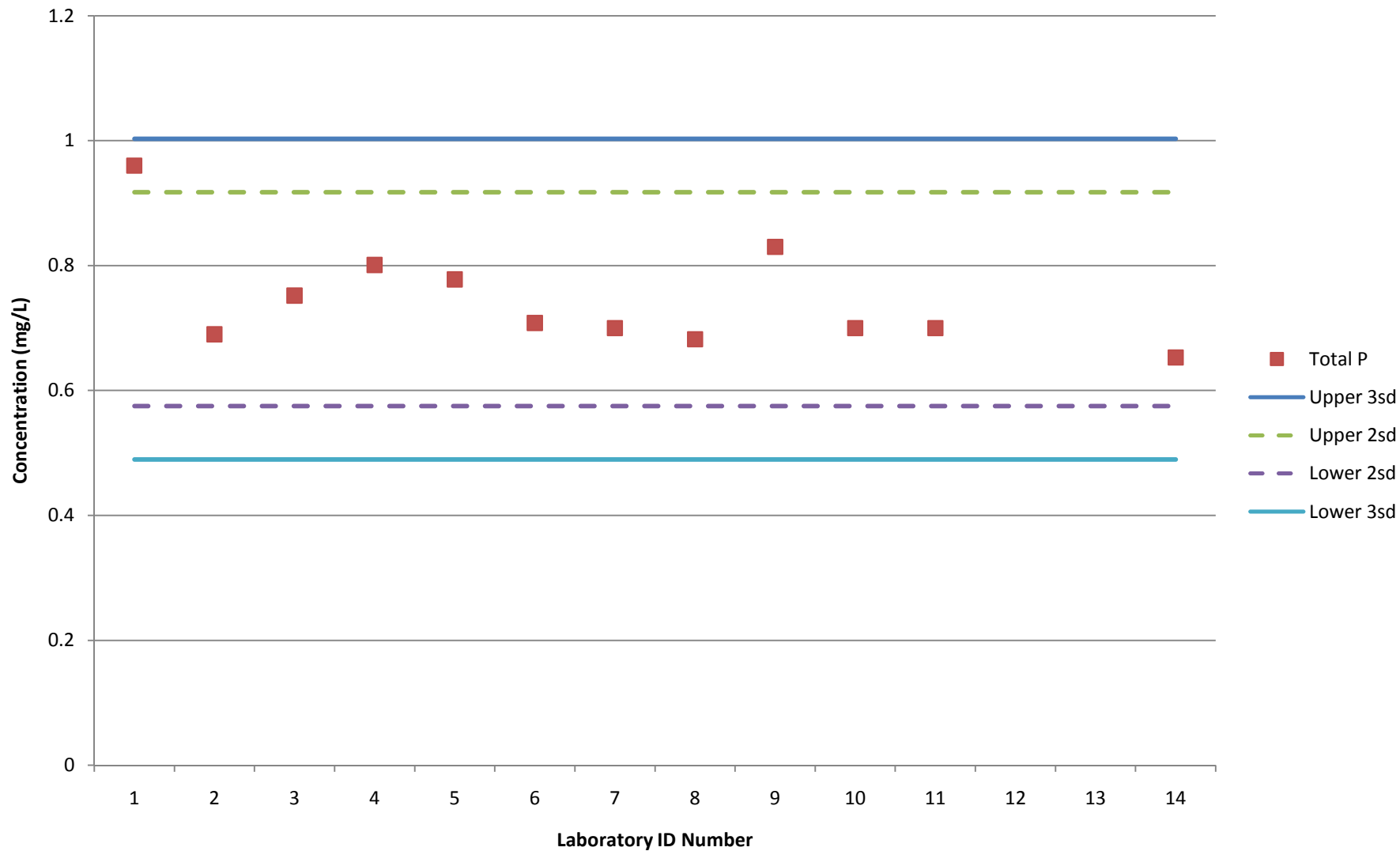
ERA SAMPLE: Arsenic (Lab 10 was ND)
(True Value= 7.16 µg/L)
(Mean= 7.05 µg/L)
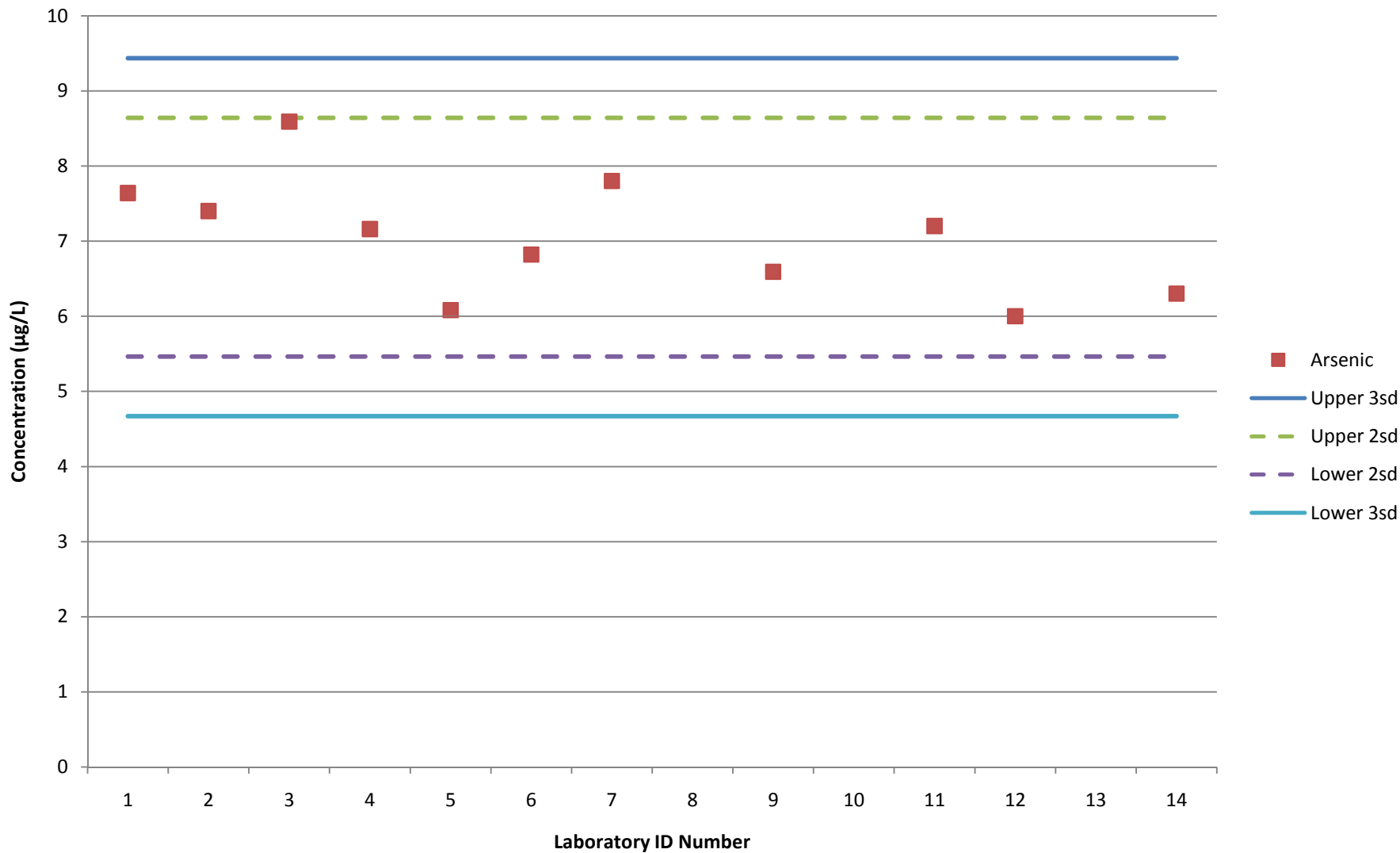
ERA SAMPLE: Cadmium (Lab 10 was ND)
(True Value= 3.11 µg/L)
(Mean= 2.96 µg/L)
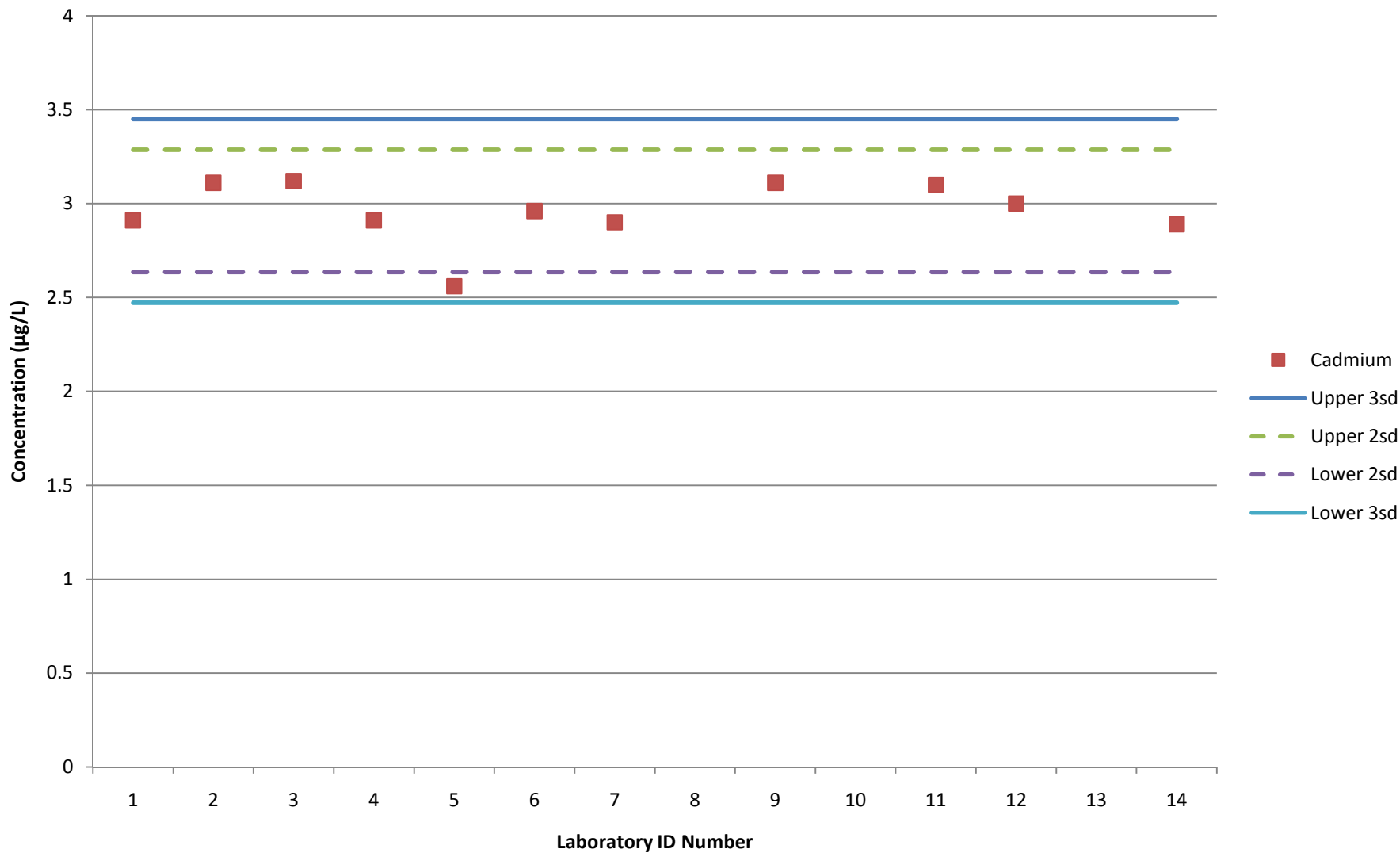
ERA SAMPLE: Chromium (w/o Lab 10 Data)
(True Value= 30.7 µg/L)
(Mean= 30.2 µg/L)
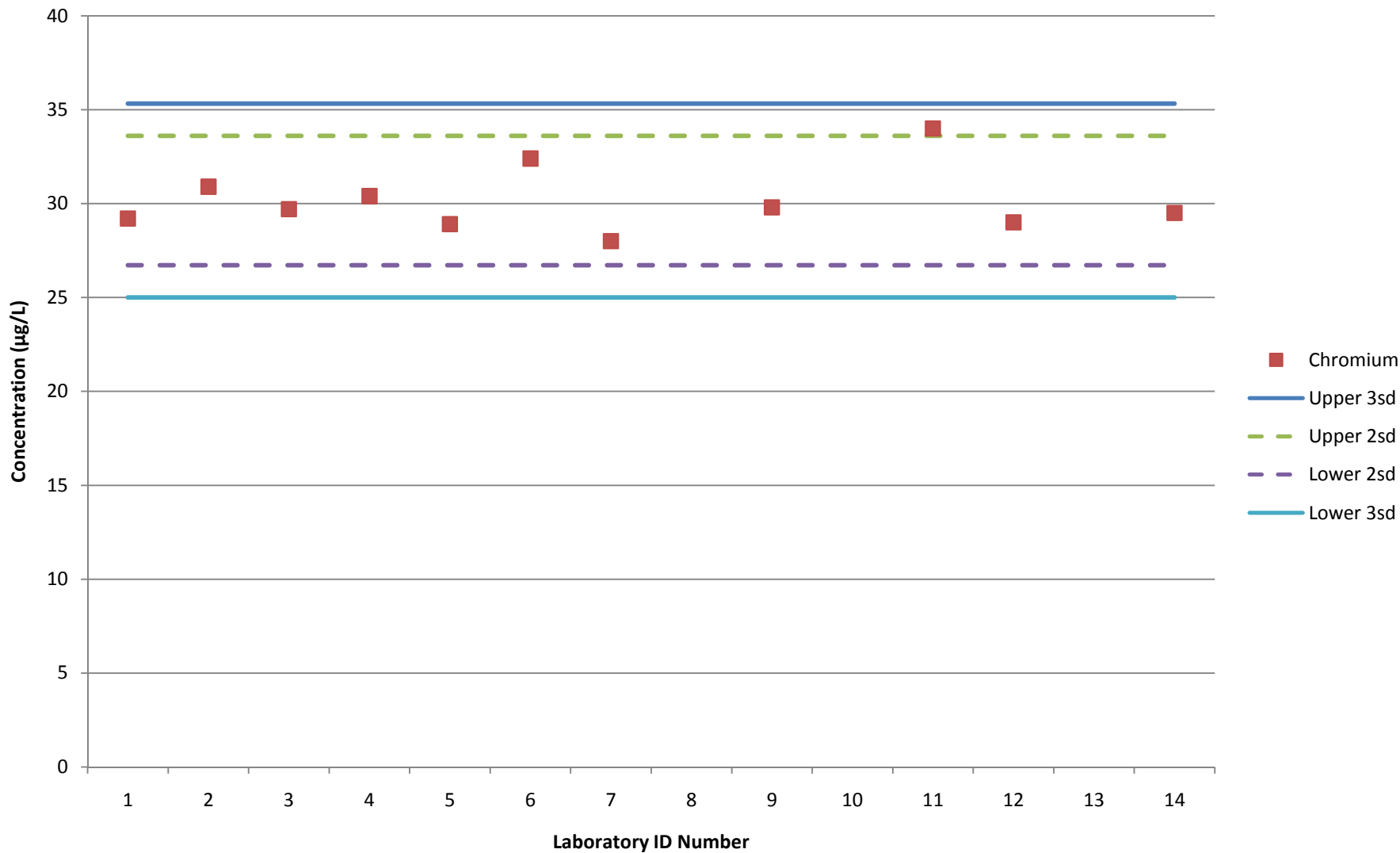
ERA SAMPLE: Copper (w/o Lab 10 Data)
(True Value= 10.3 µg/L)
(Mean= 12.7 µg/L)
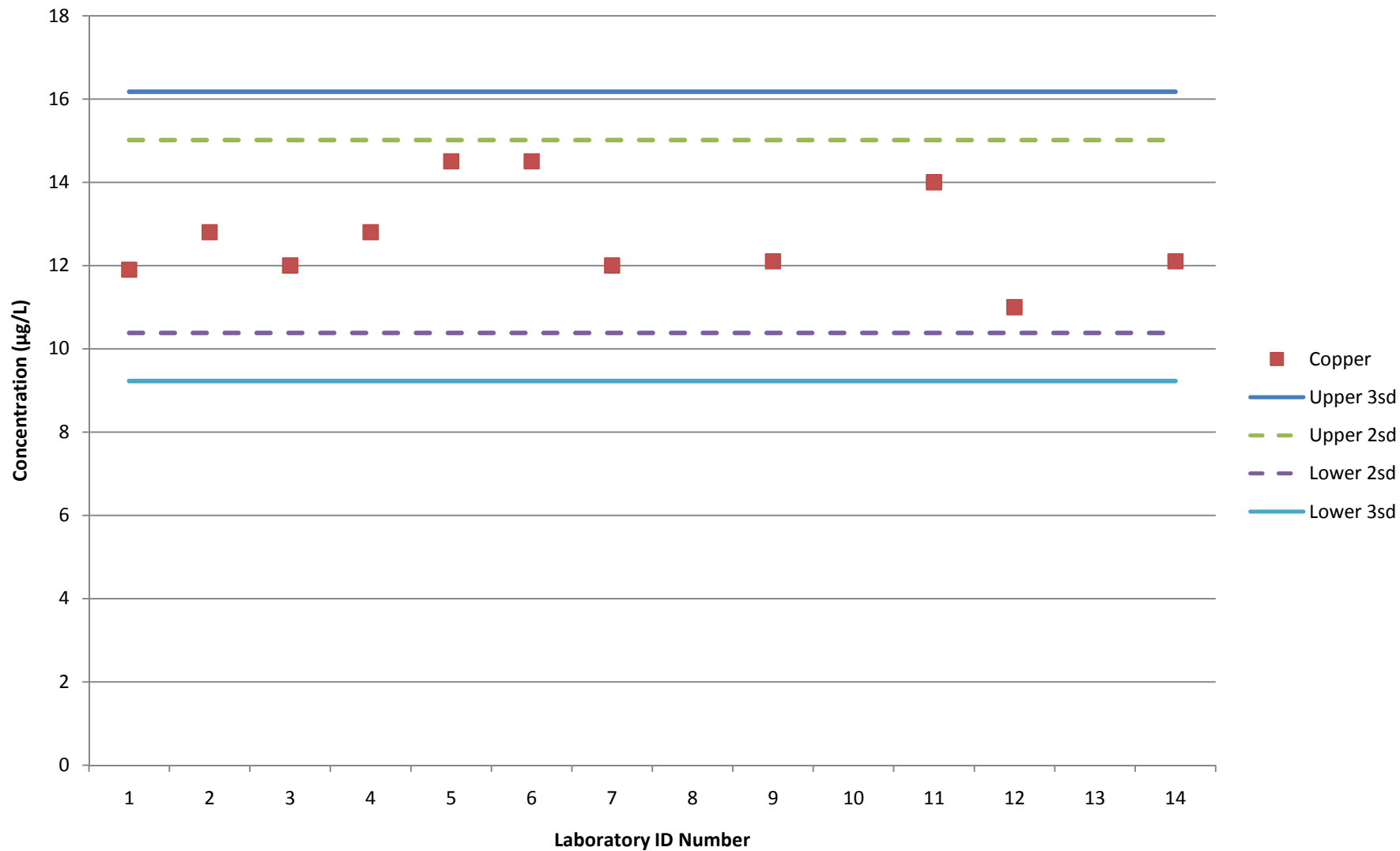
ERA SAMPLE: Lead (Lab 10 was ND)
(True Value= 7.24 µg/L)
(Mean= 7.10 µg/L)
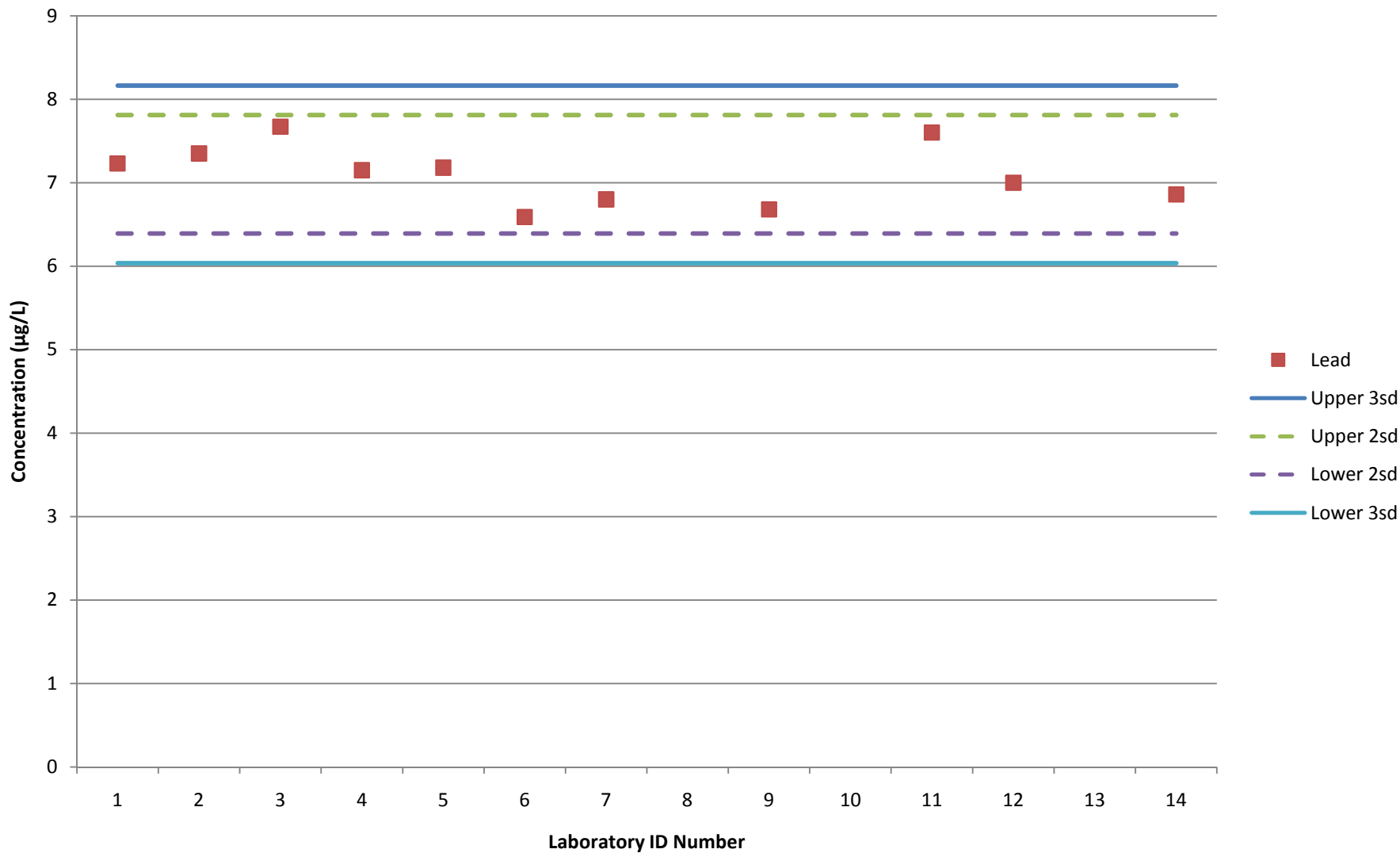
ERA SAMPLE: Nickel (w/o Lab 10 Data)
(True Value= 33 µg/L)
(Mean= 32.1 µg/L)
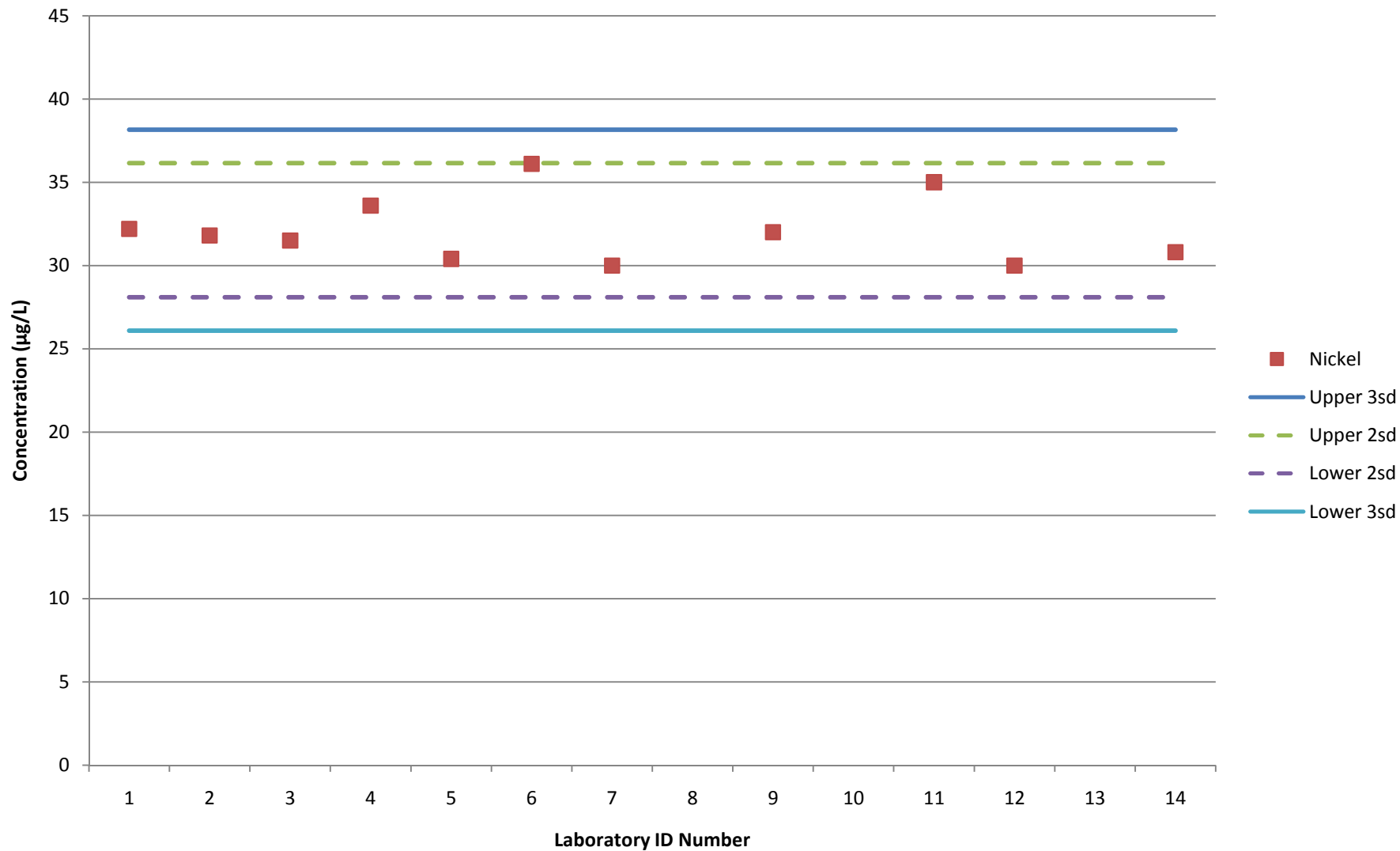
ERA SAMPLE: Selenium (w/o Lab 10 Data)
(True Value= 18.4 µg/L)
(Mean= 17.7 µg/L)
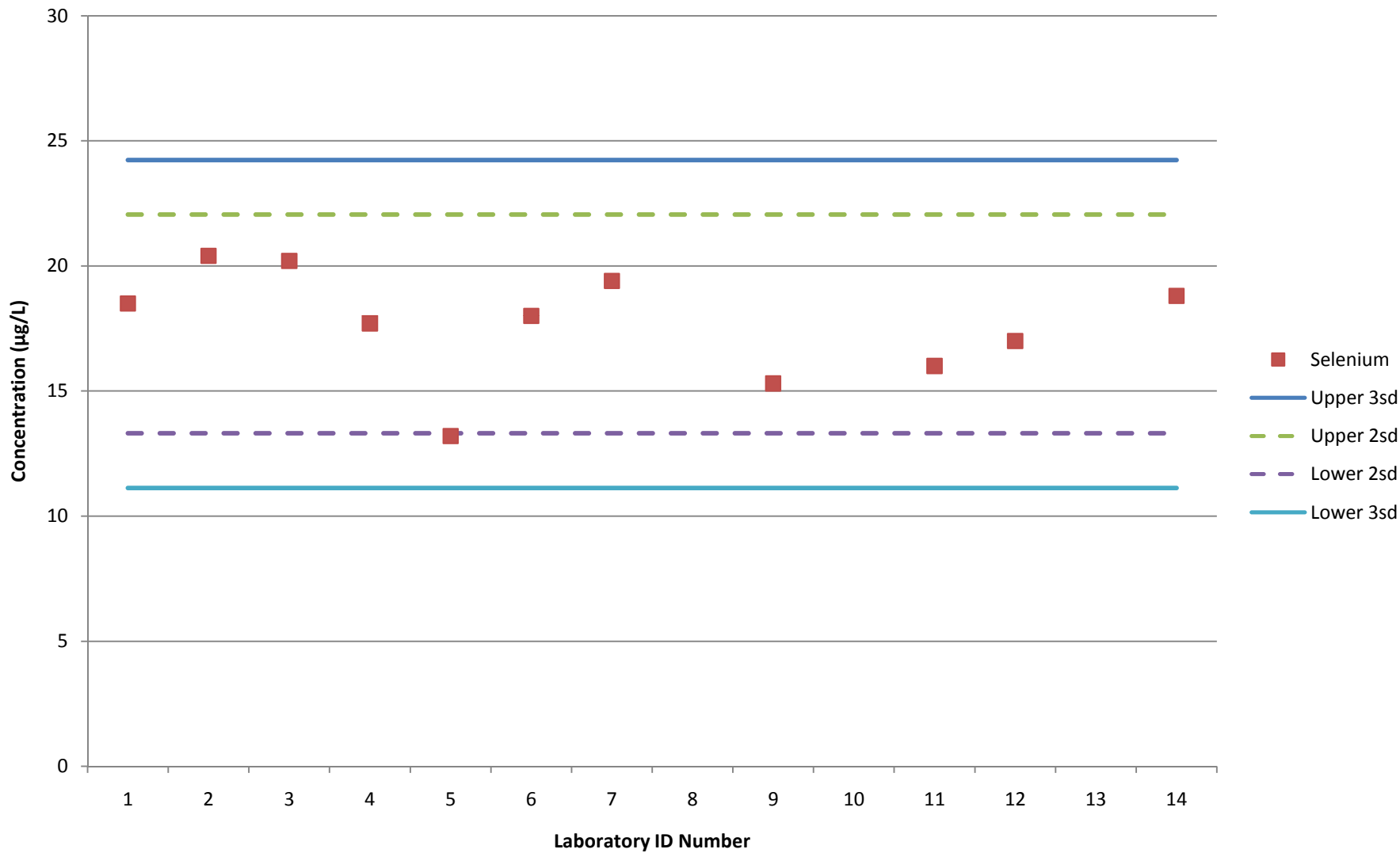
ERA SAMPLE: Silver (w/o Lab 3 or Lab10 Data)
(True Value= 7.16 µg/L)
(Mean= 6.74 µg/L)
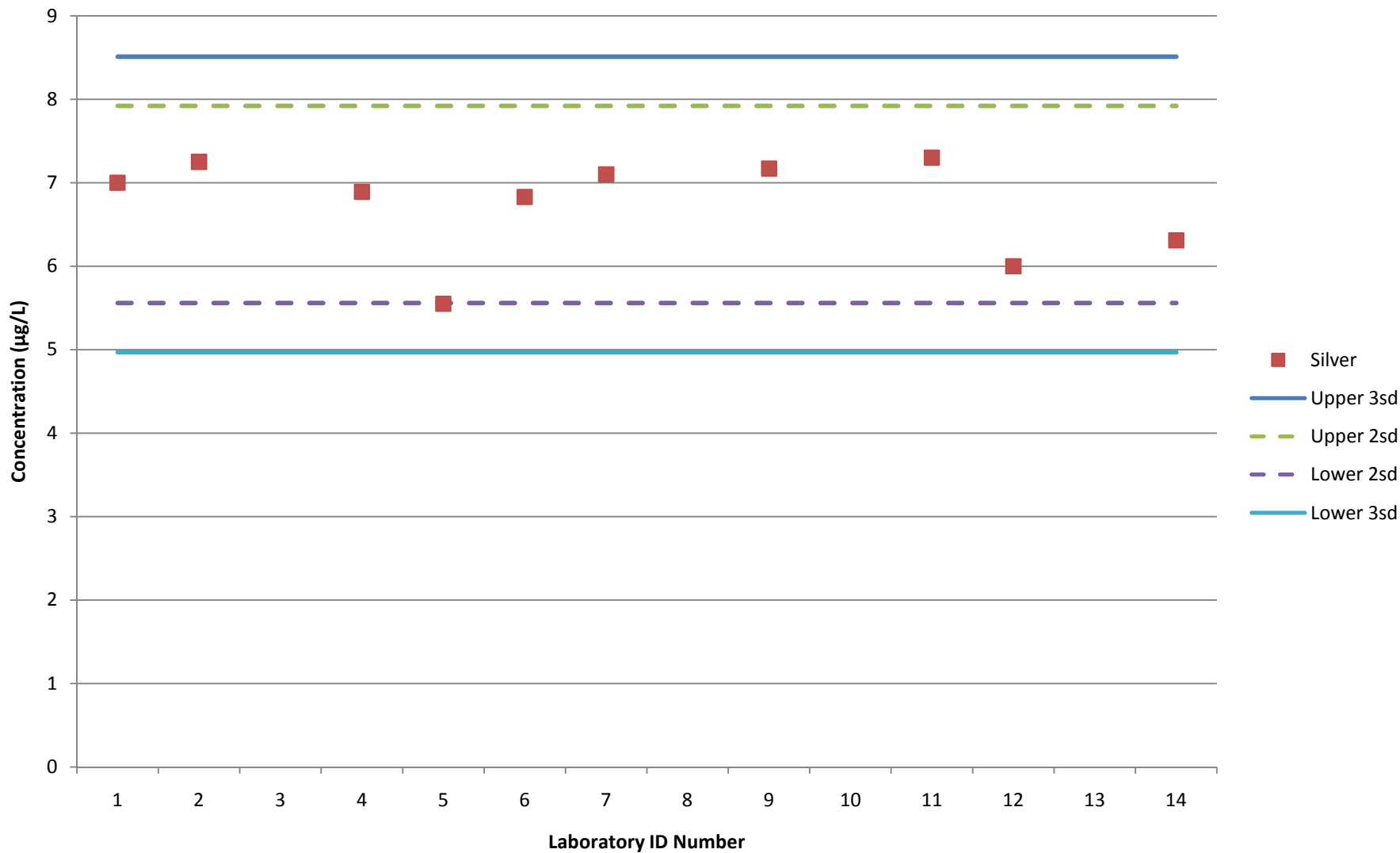
ERA SAMPLE: Zinc (w/o Lab 10 Data)
(True Value= 75.4 µg/L)
(Mean= 79.0 µg/L)
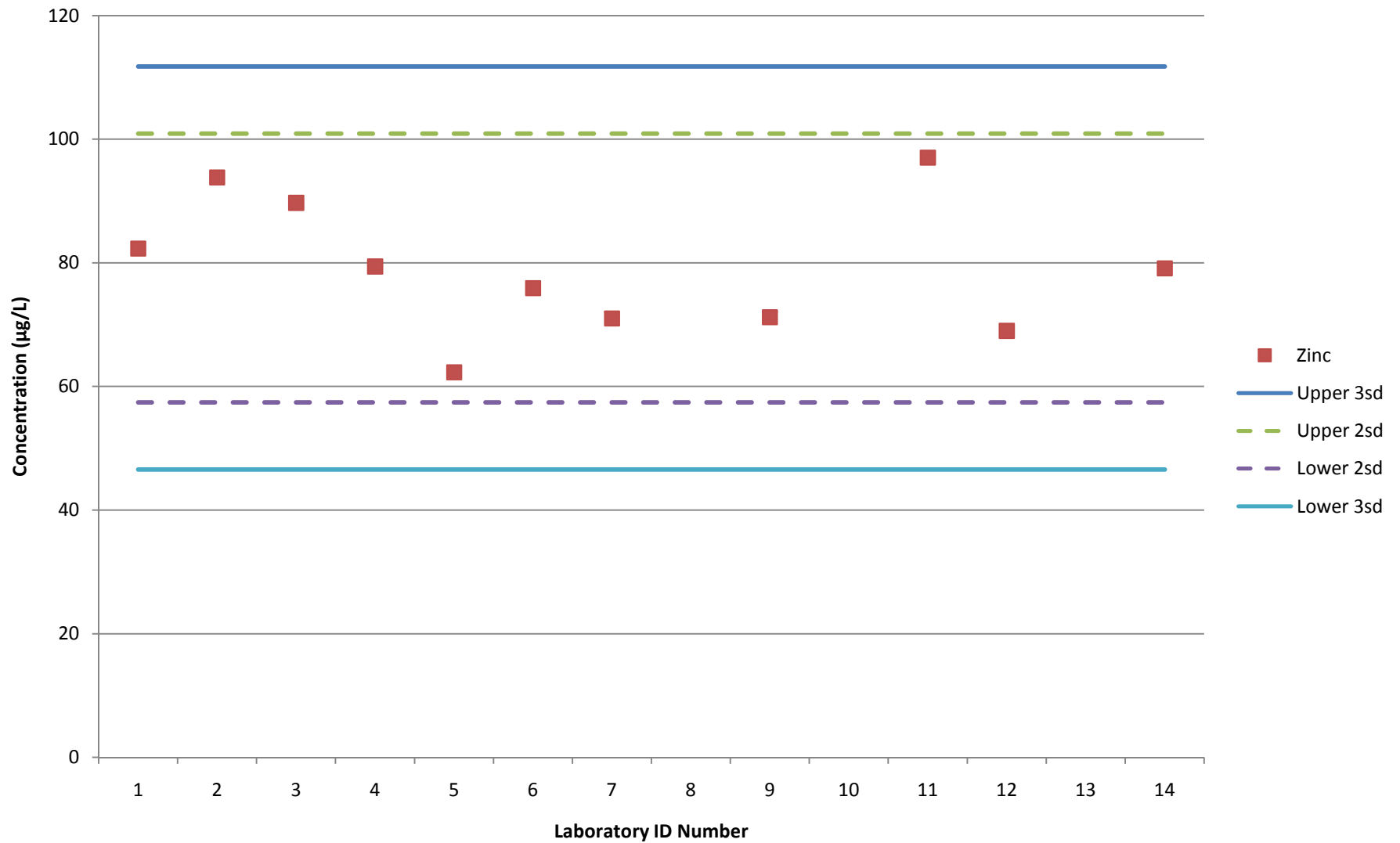
LU1: TSS (mean= 337 mg/L)
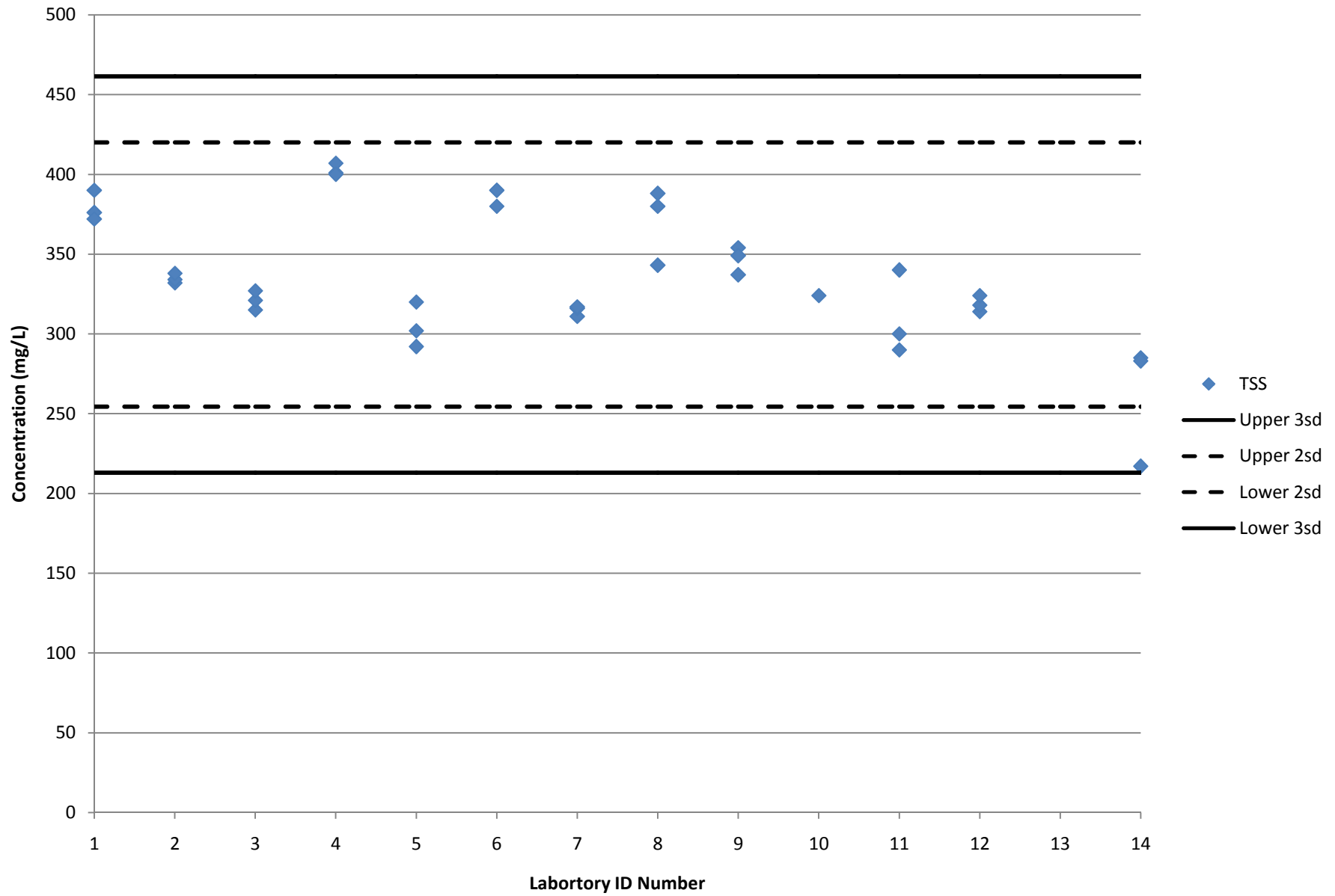
LU1: Ammonia-N (mean= 0.341 mg/L)
(w/o Lab 1 Data, Lab 6 was ND)
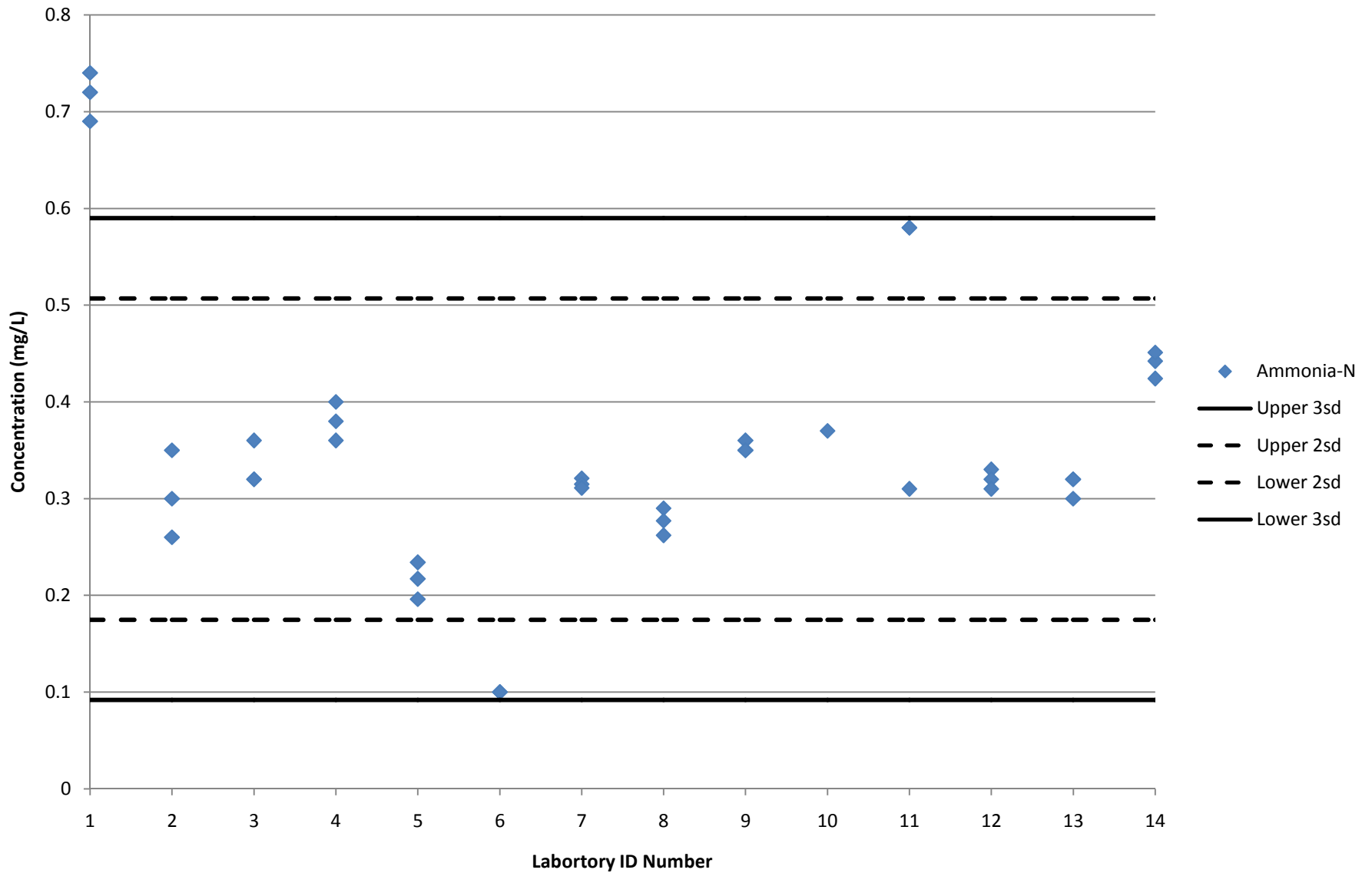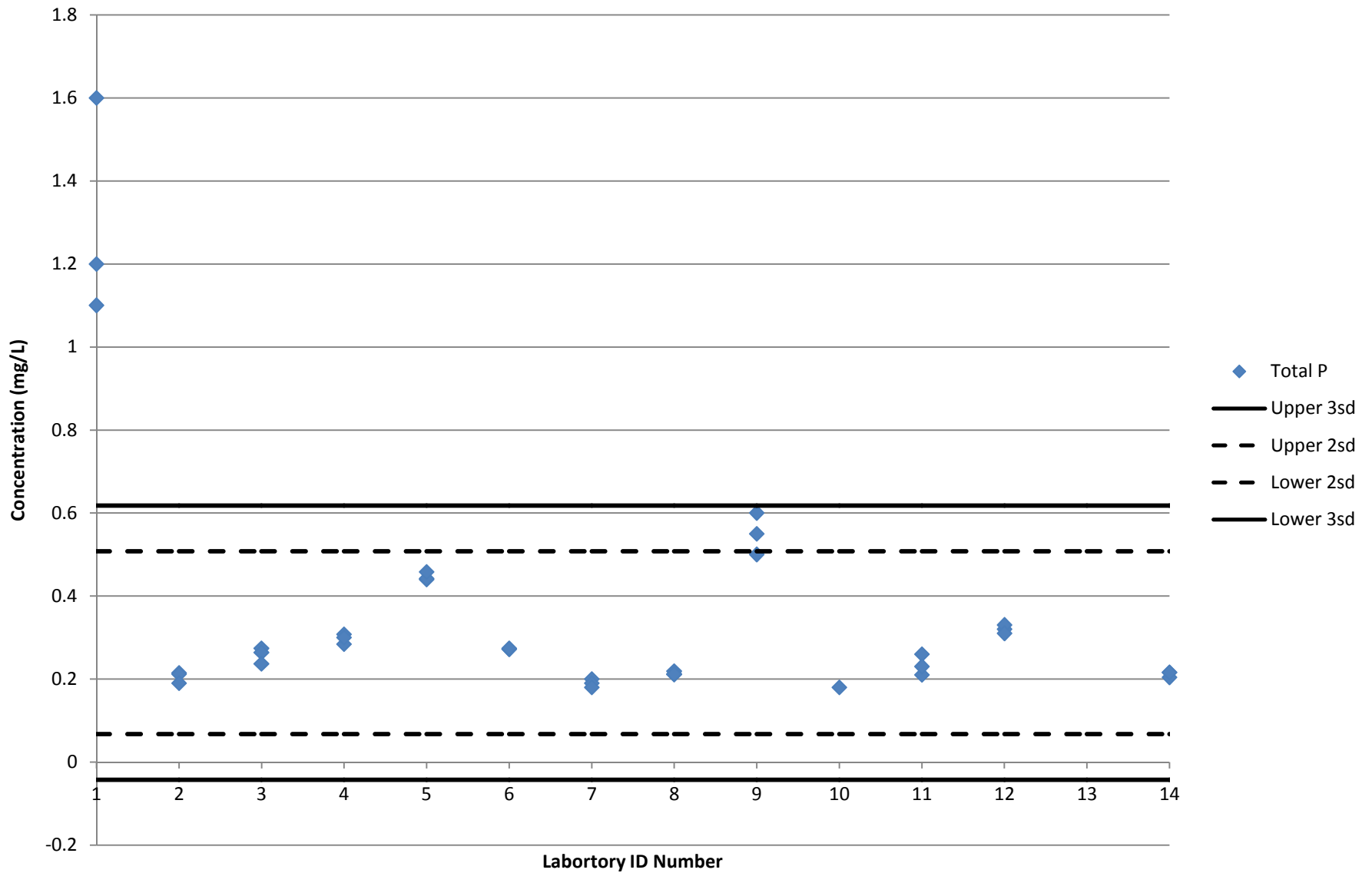
LU1: Nitrate+Nitrite-N (mean= 0.755 mg/L)
(w/o Lab 9 Data)
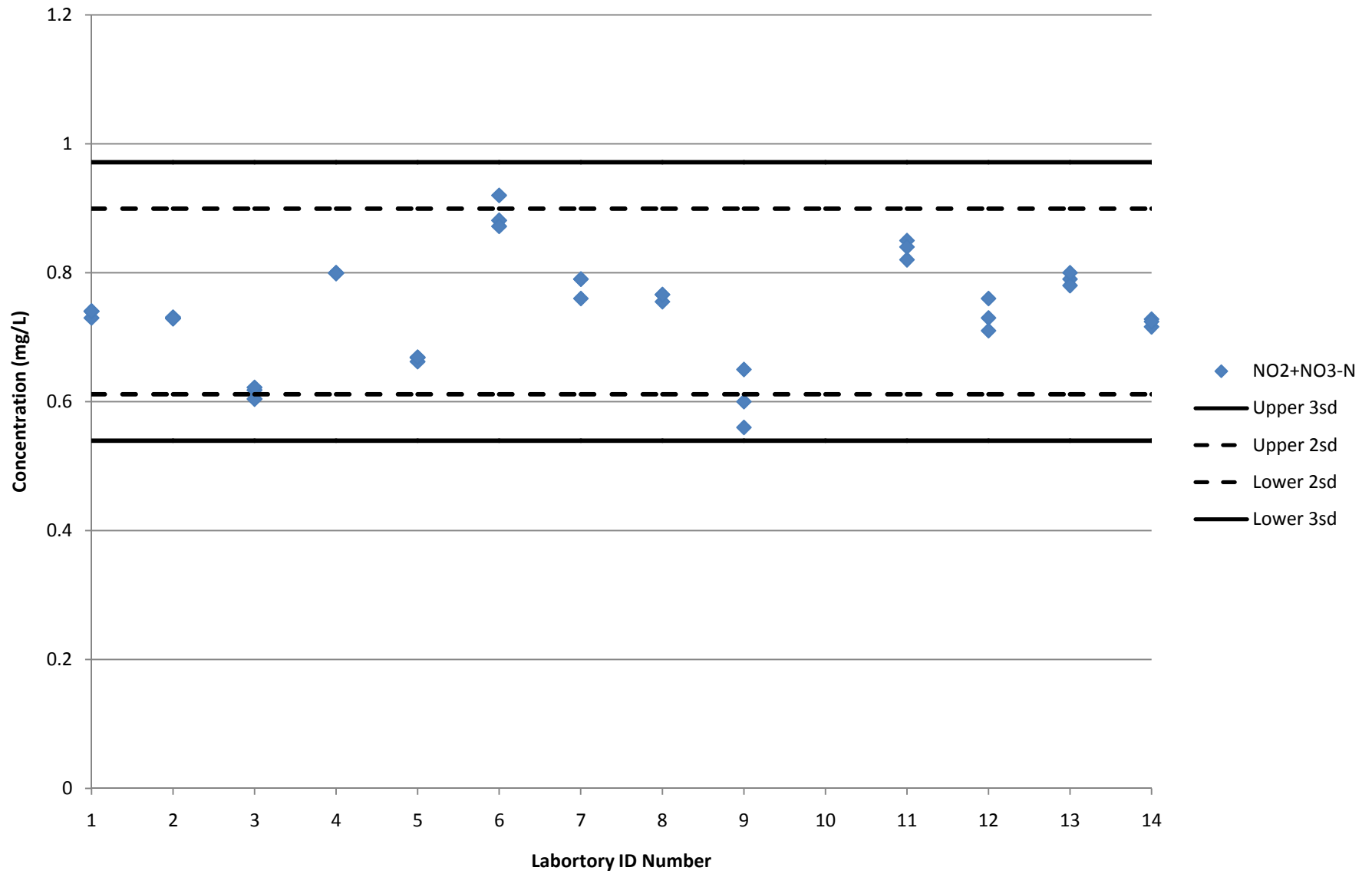
LU1: TKN (mean= 3.64 mg/L)
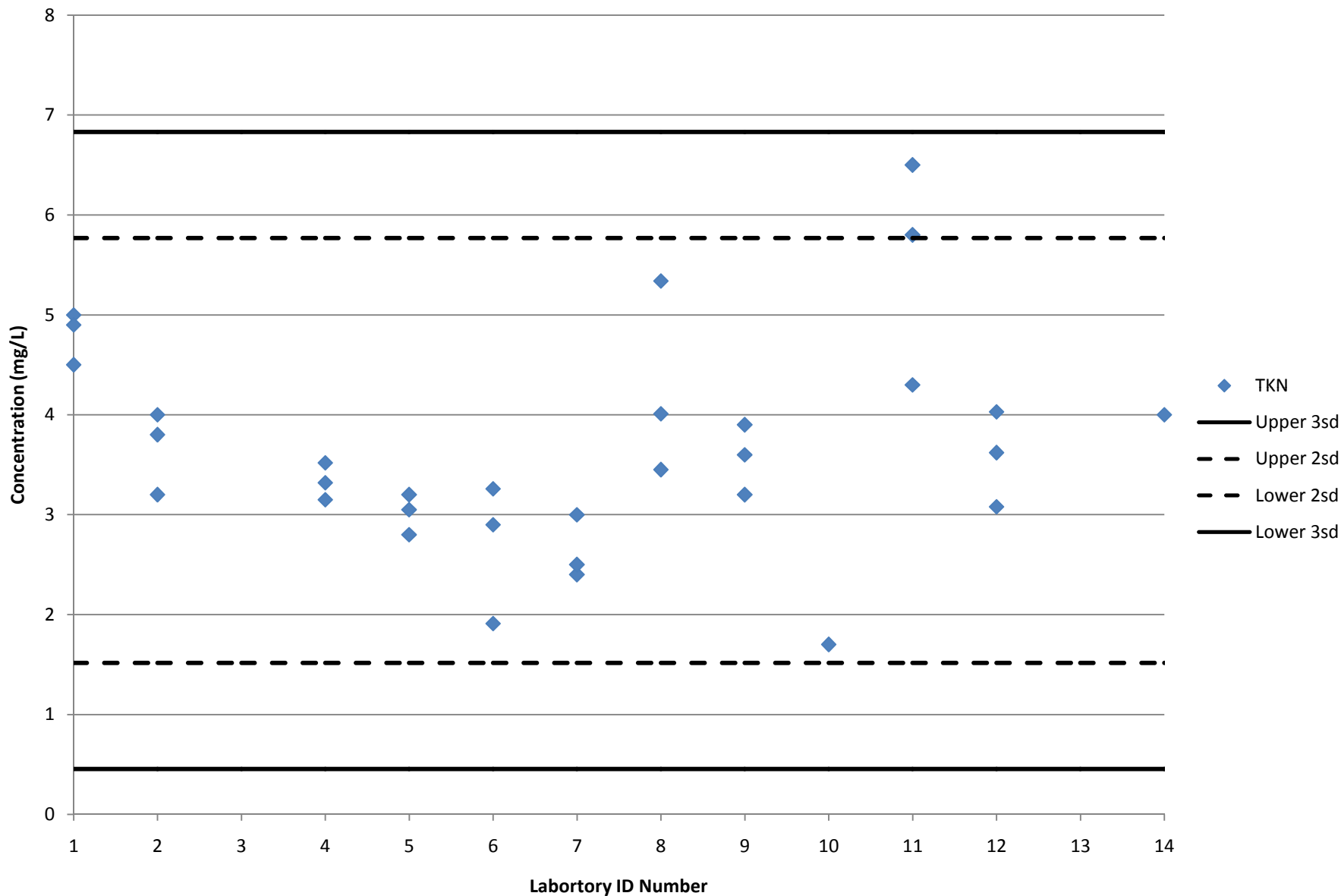
LU1: TOC (mean= 6.63 mg/L)
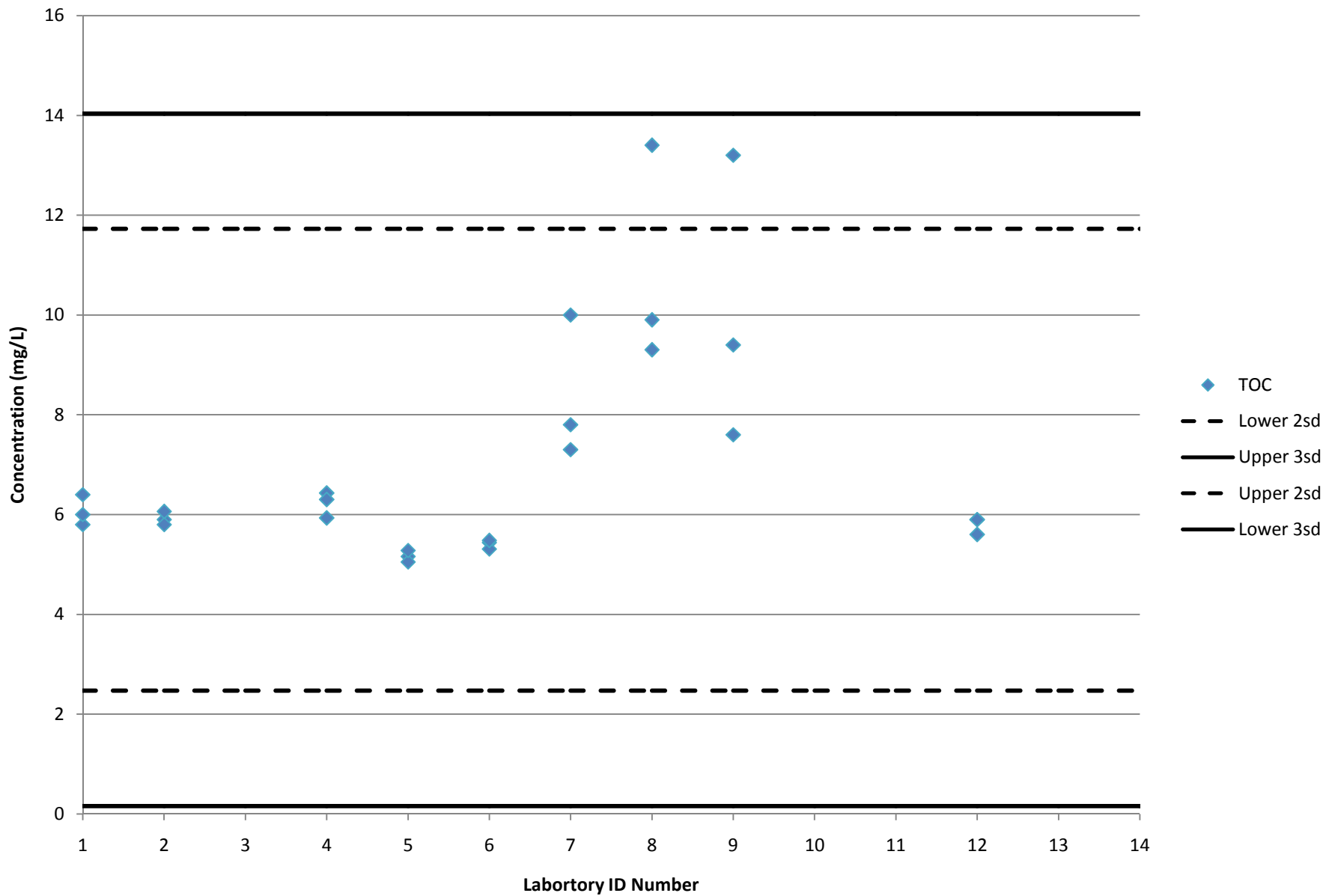
LU1: Total Phosphorus (mean= 0.388 mg/L)
(w/o Lab 1 Data)

Legend:
- Total P
- Upper 3sd
- Upper 2sd
- Lower 2sd
- Lower 3sd

X-axis: Labortory ID Number
Y-axis: Concentration (mg/L)
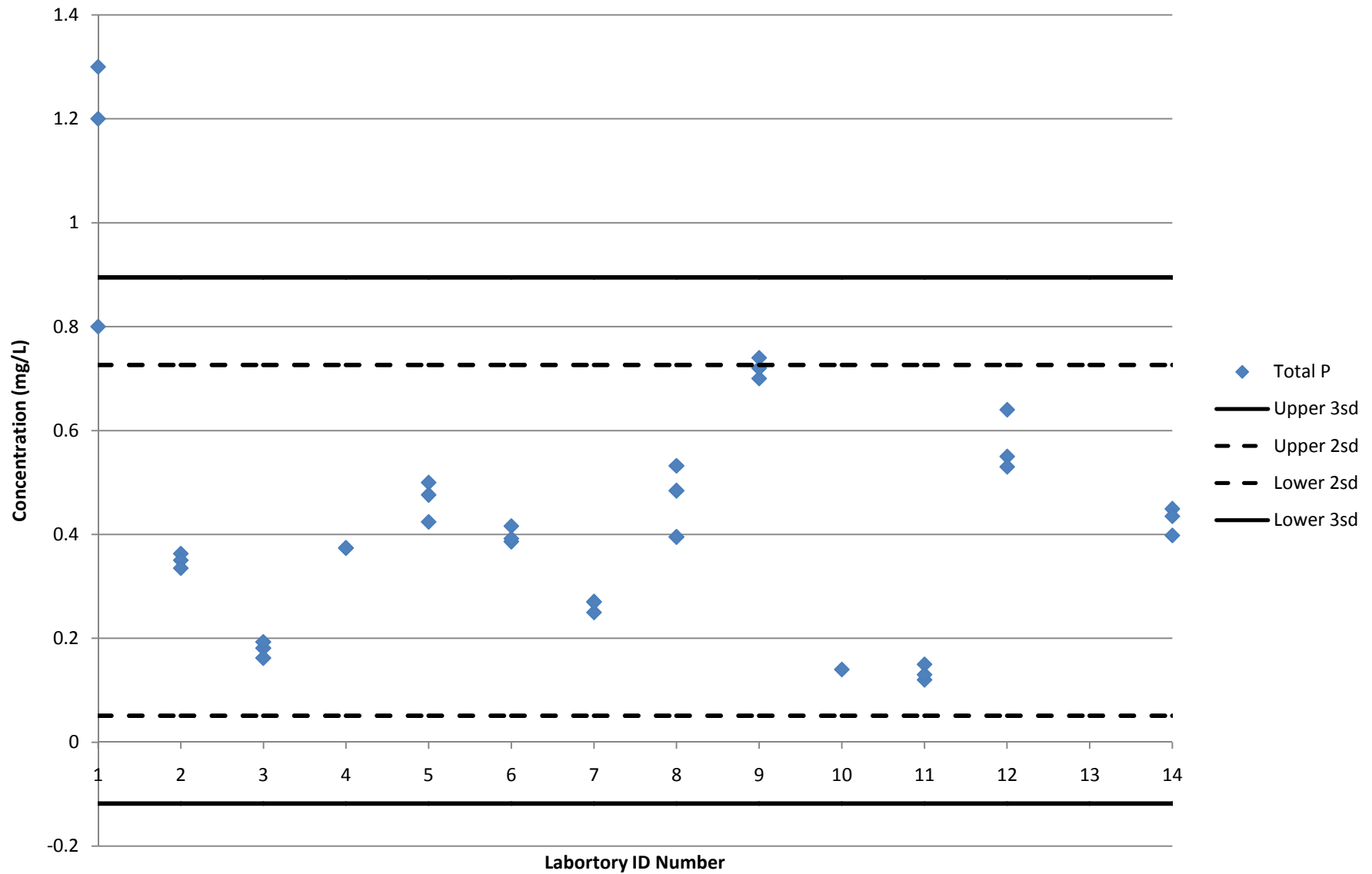
LU1: Arsenic (mean= 2.58 µg/L)
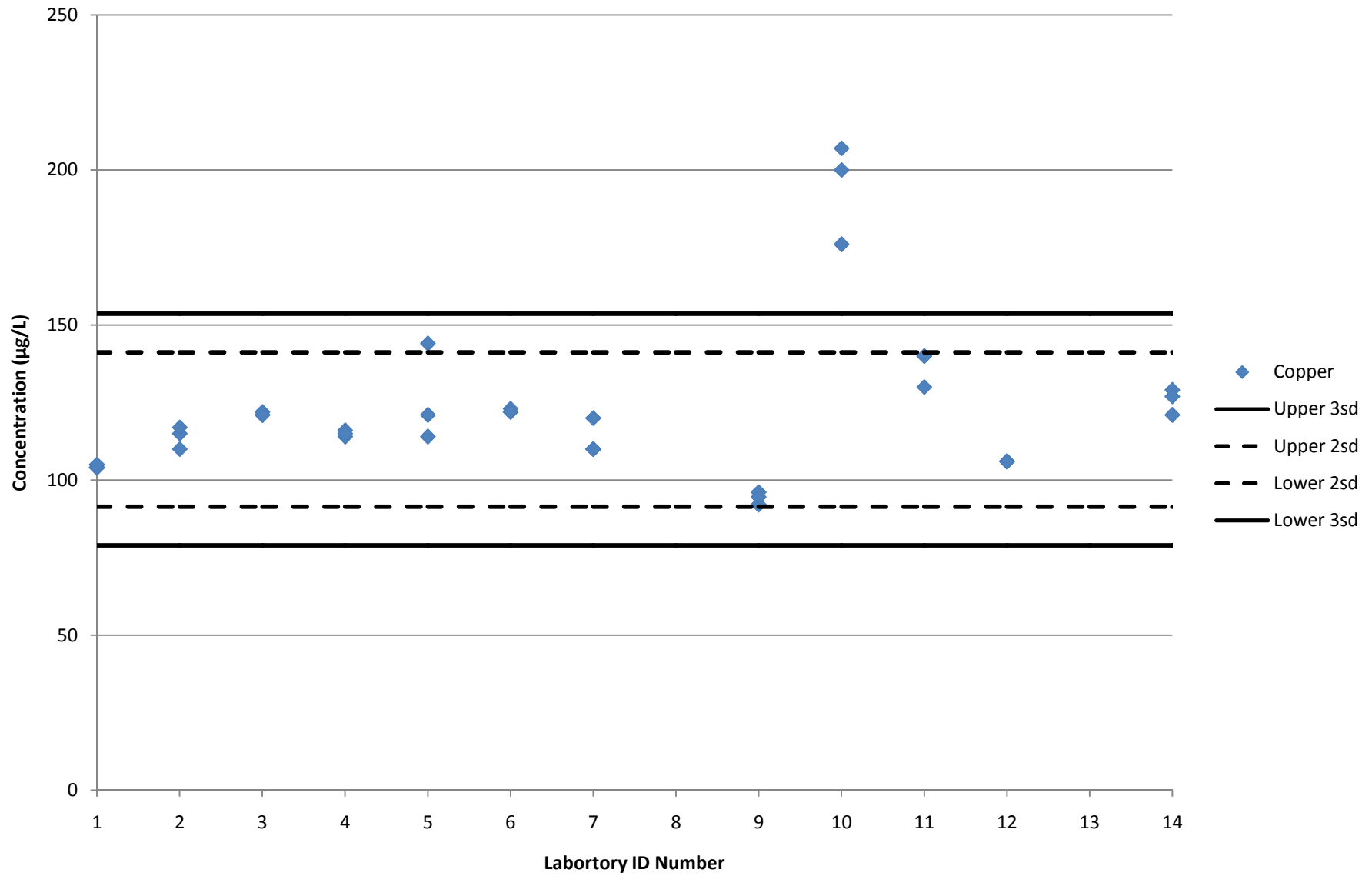(Lab 10 was ND)
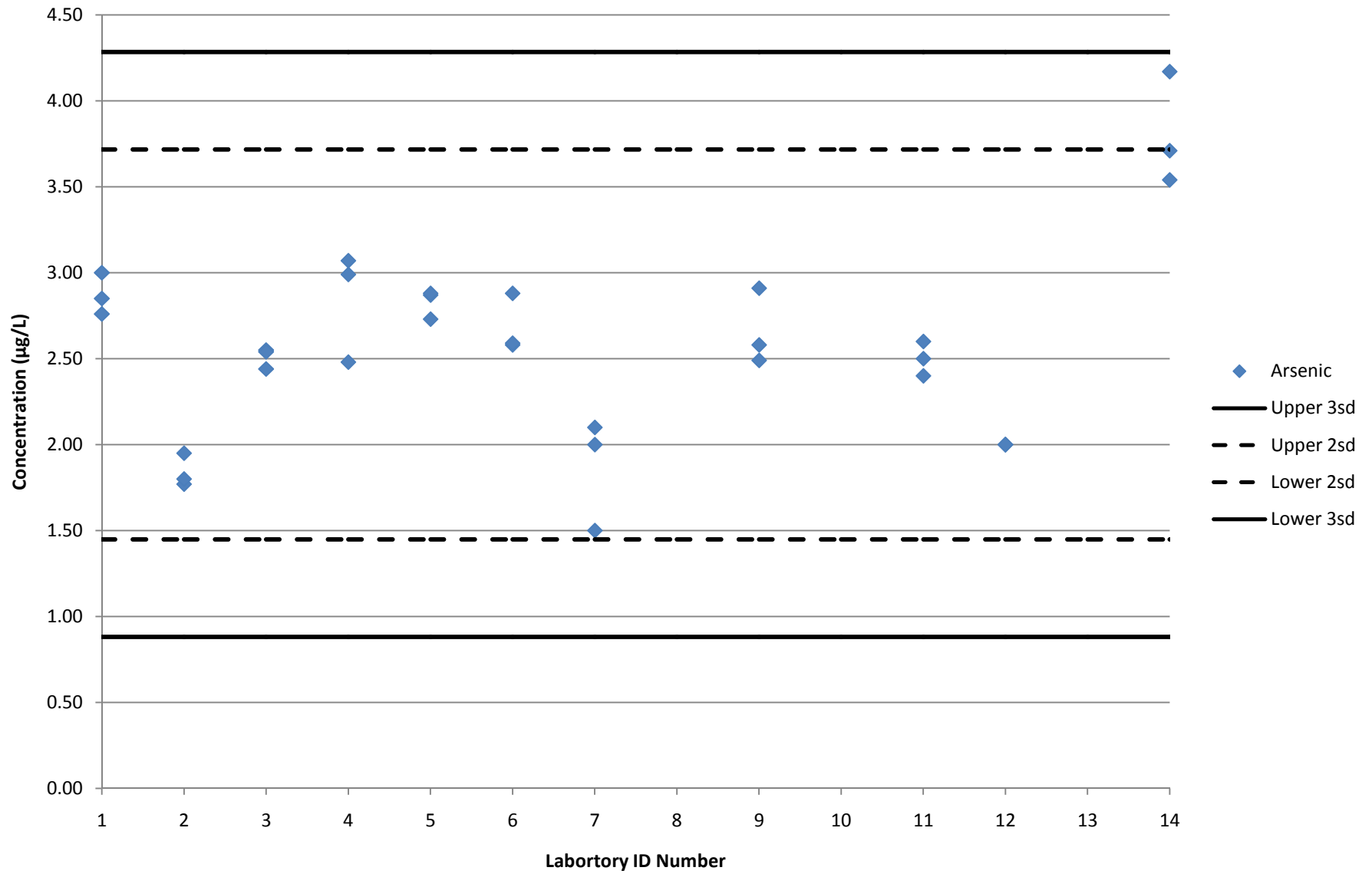
LU1: Cadmium (mean= 0.466 µg/L)
(w/o Lab 10 Data, Labs 1 and 12 were ND)
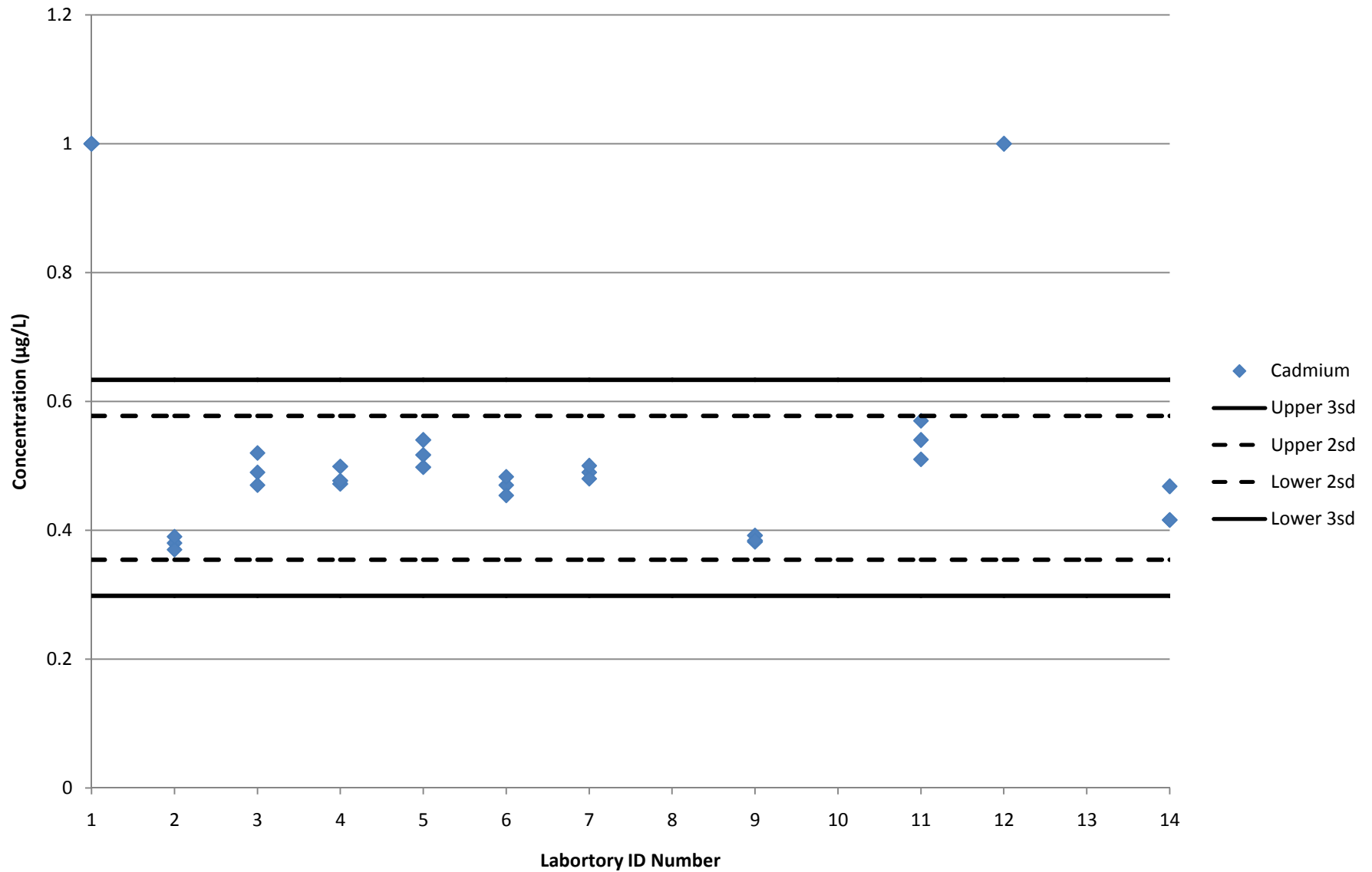
LU1: Chromium (mean= 14.2 µg/L)
(w/o Lab 10 and Lab 14 Data)
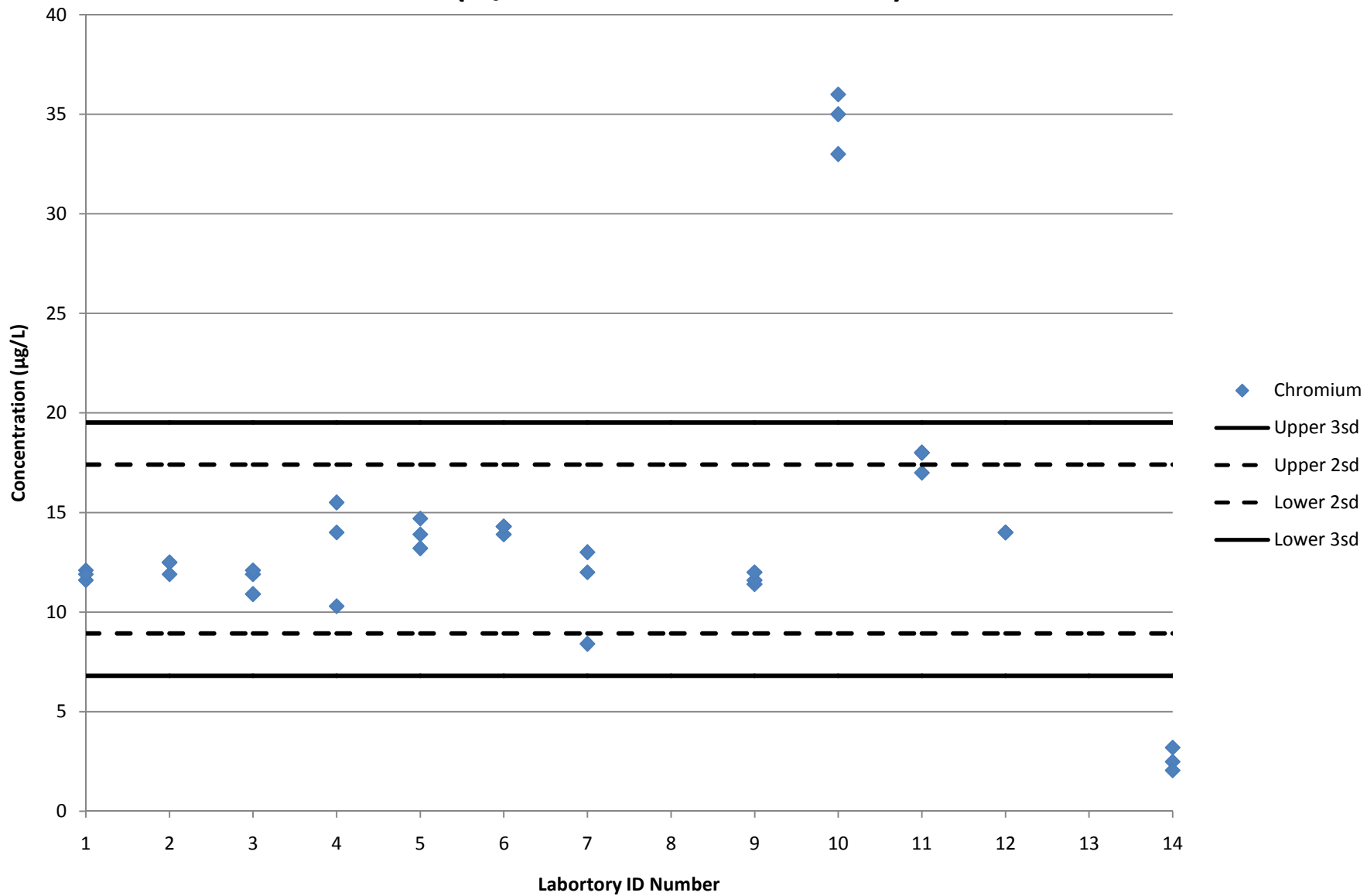
LU1: Copper (mean= 19.3 µg/L)
(w/o Lab 10 Data)
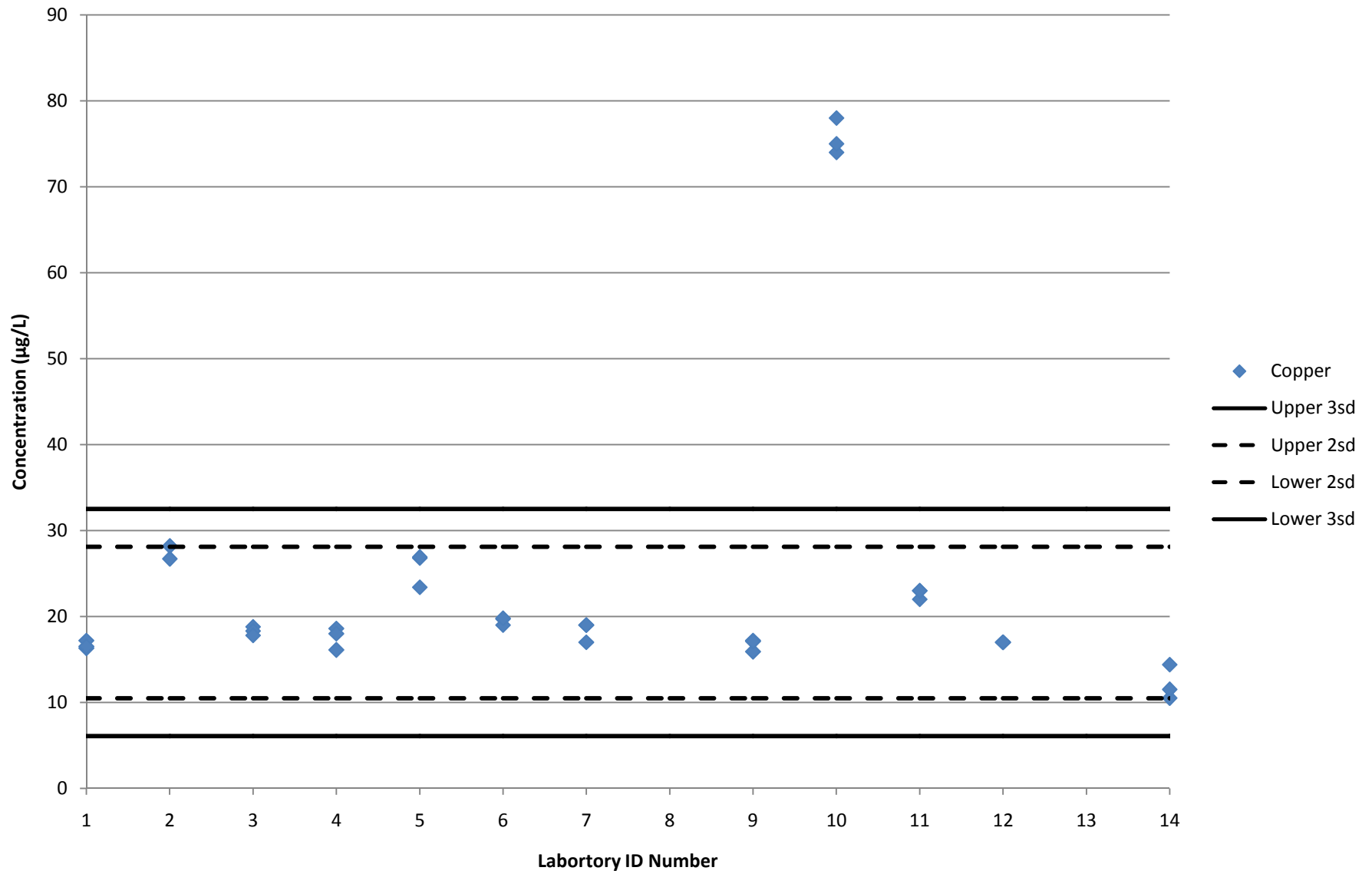
LU1: Lead (mean= 8.87 µg/L)
(Lab 10 had 2 values at ND of 20)
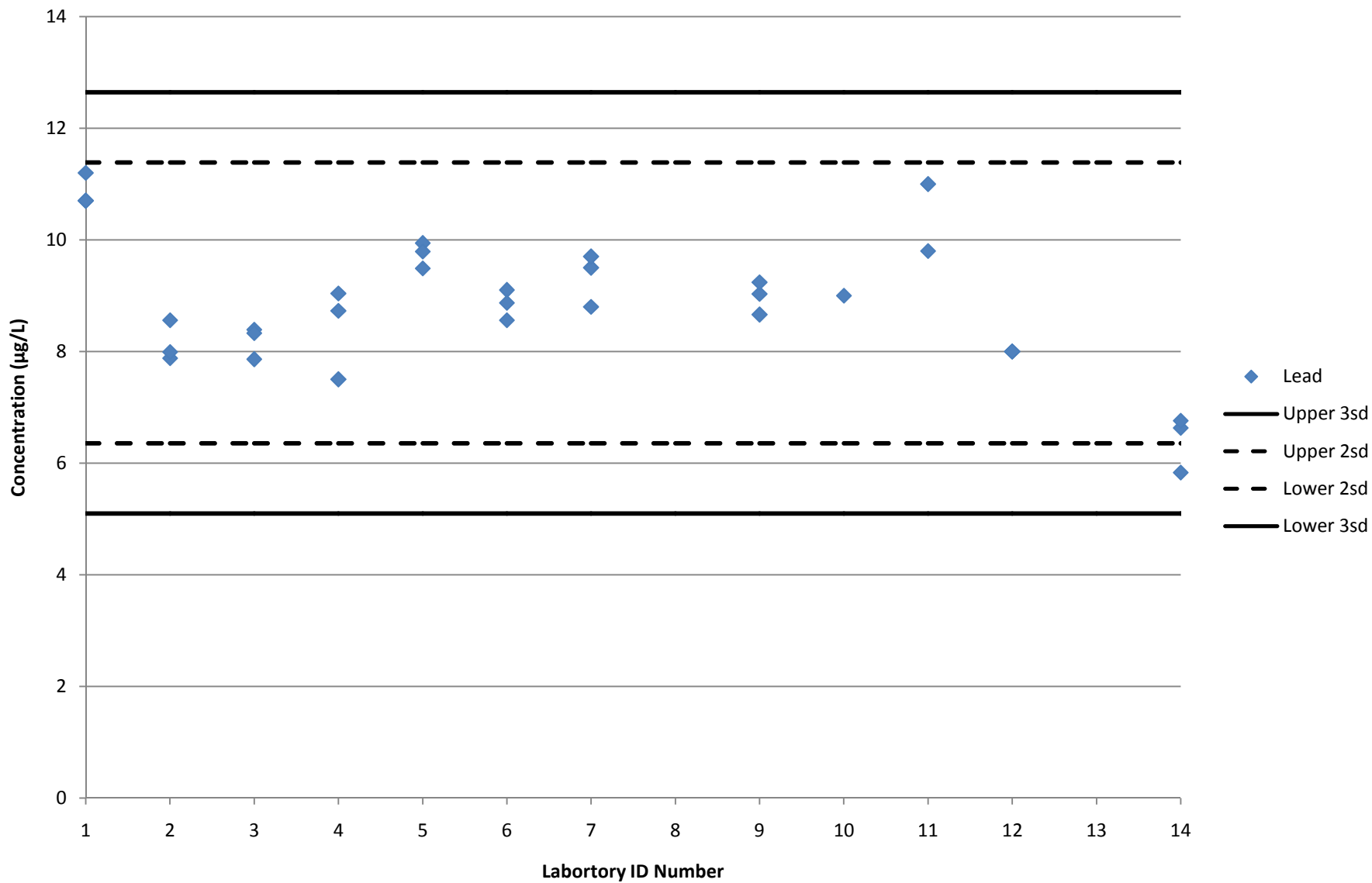
LU1: Nickel (mean= 5.08 μg/L)
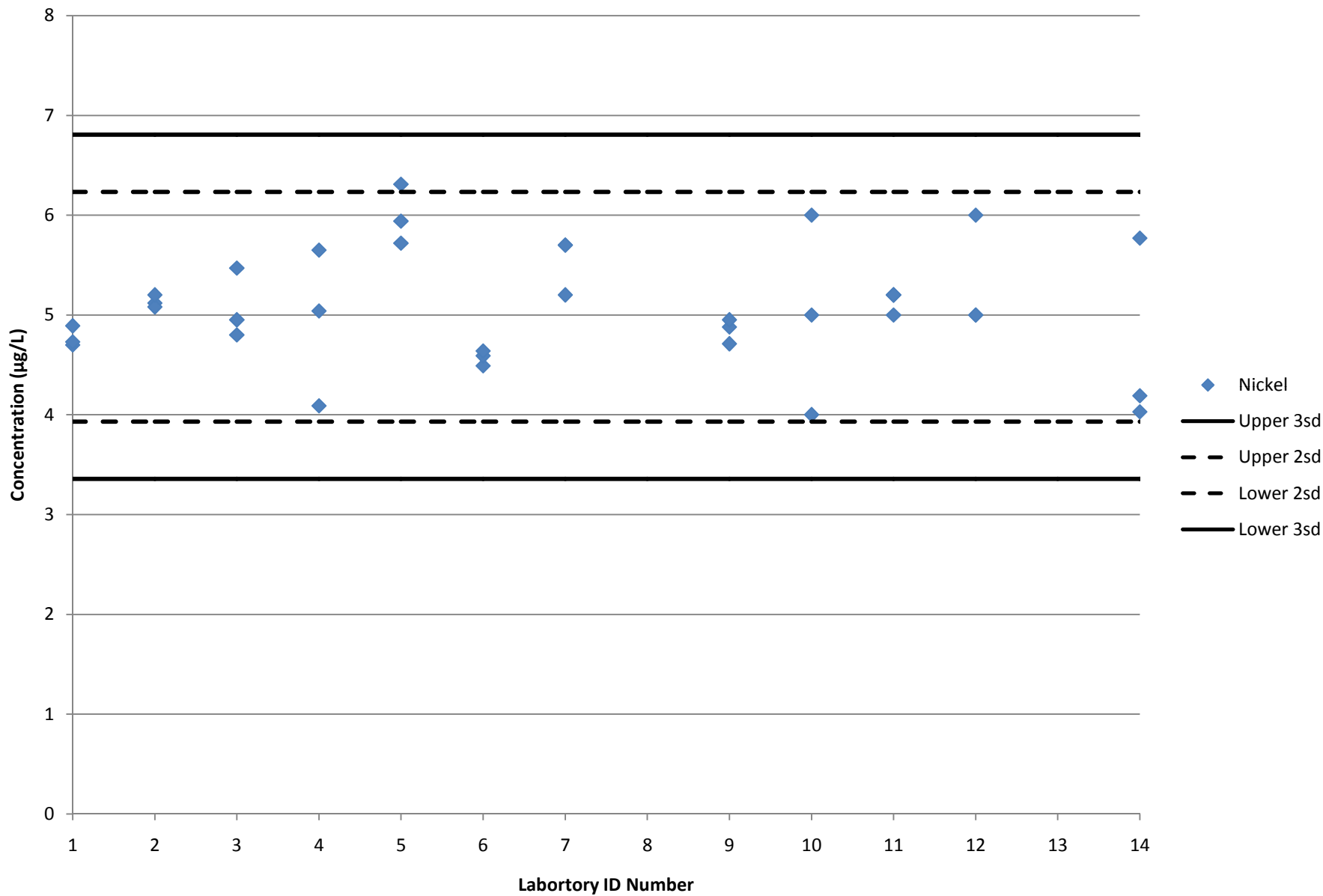
LU1: Selenium (mean = 1.44 µg/L)
(w/o Lab 10 Data, Lab 7 and 12 were ND)
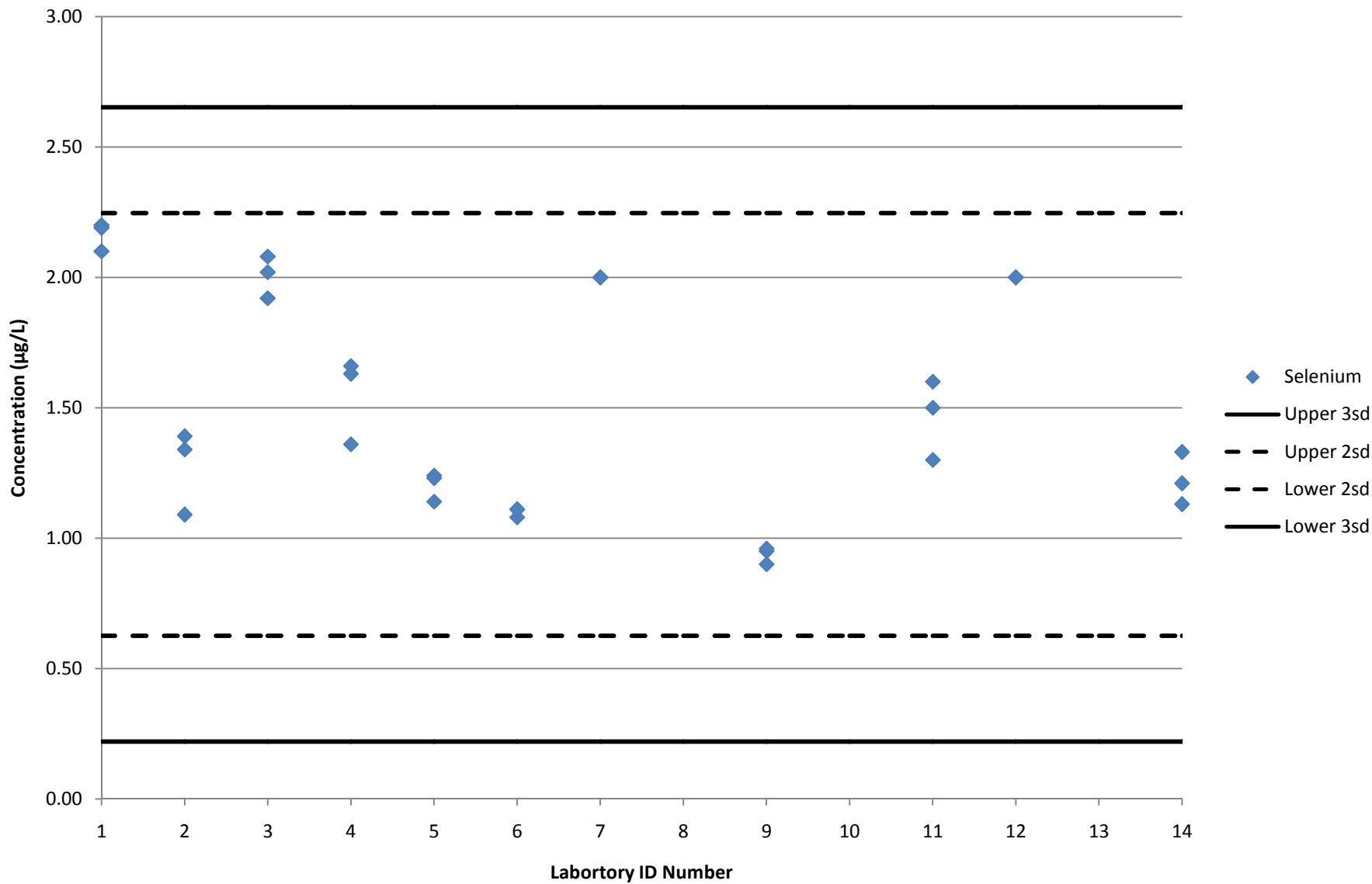
**LU1: Silver (mean= 0.069 µg/L)
(w/o Lab 10 Data, Labs 1, 3, 5, 6, 11, 12, and 14 were ND)**
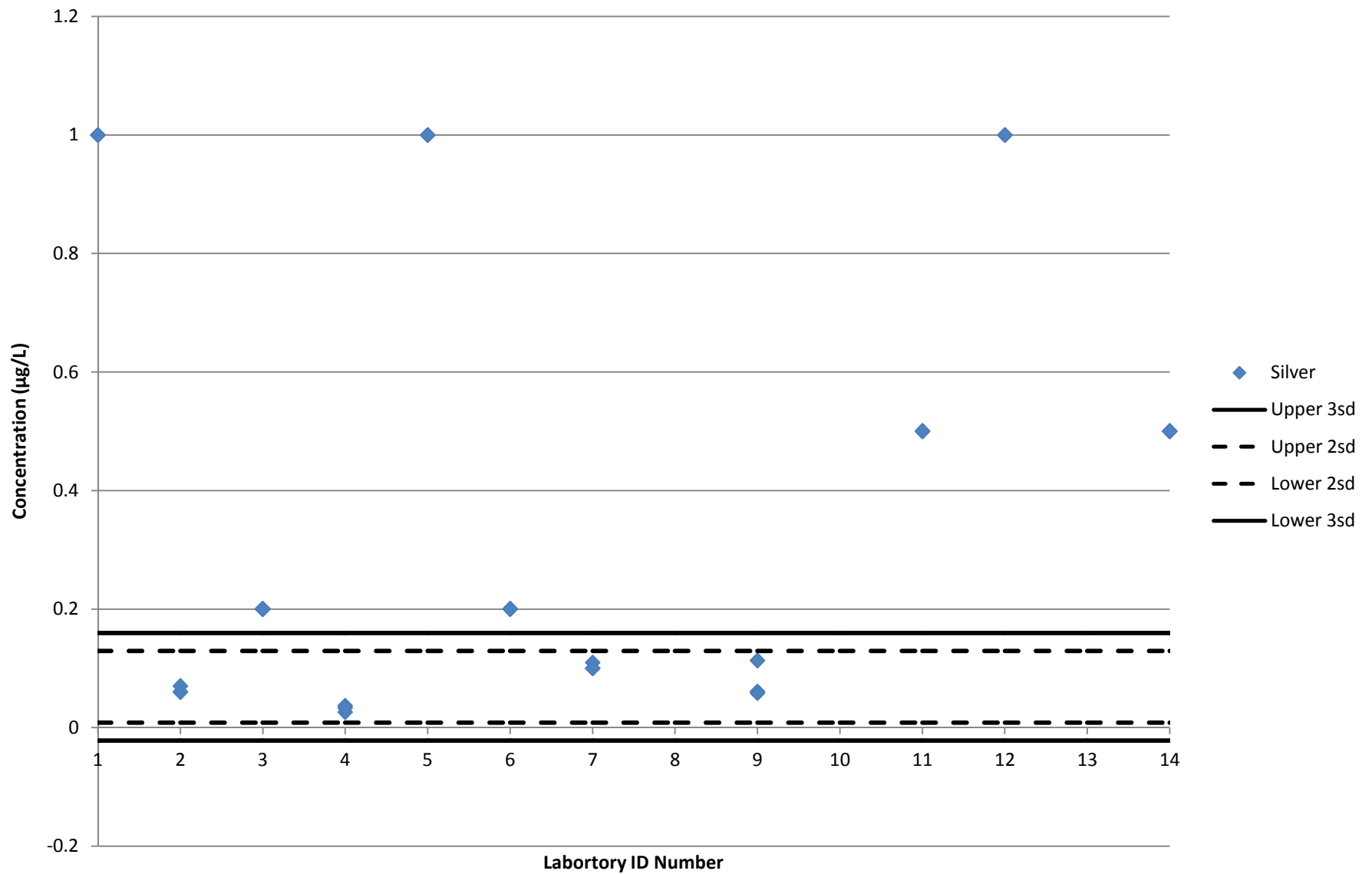
LU1: Zinc (mean = 468 µg/L)
(w/o Lab 10 Data)
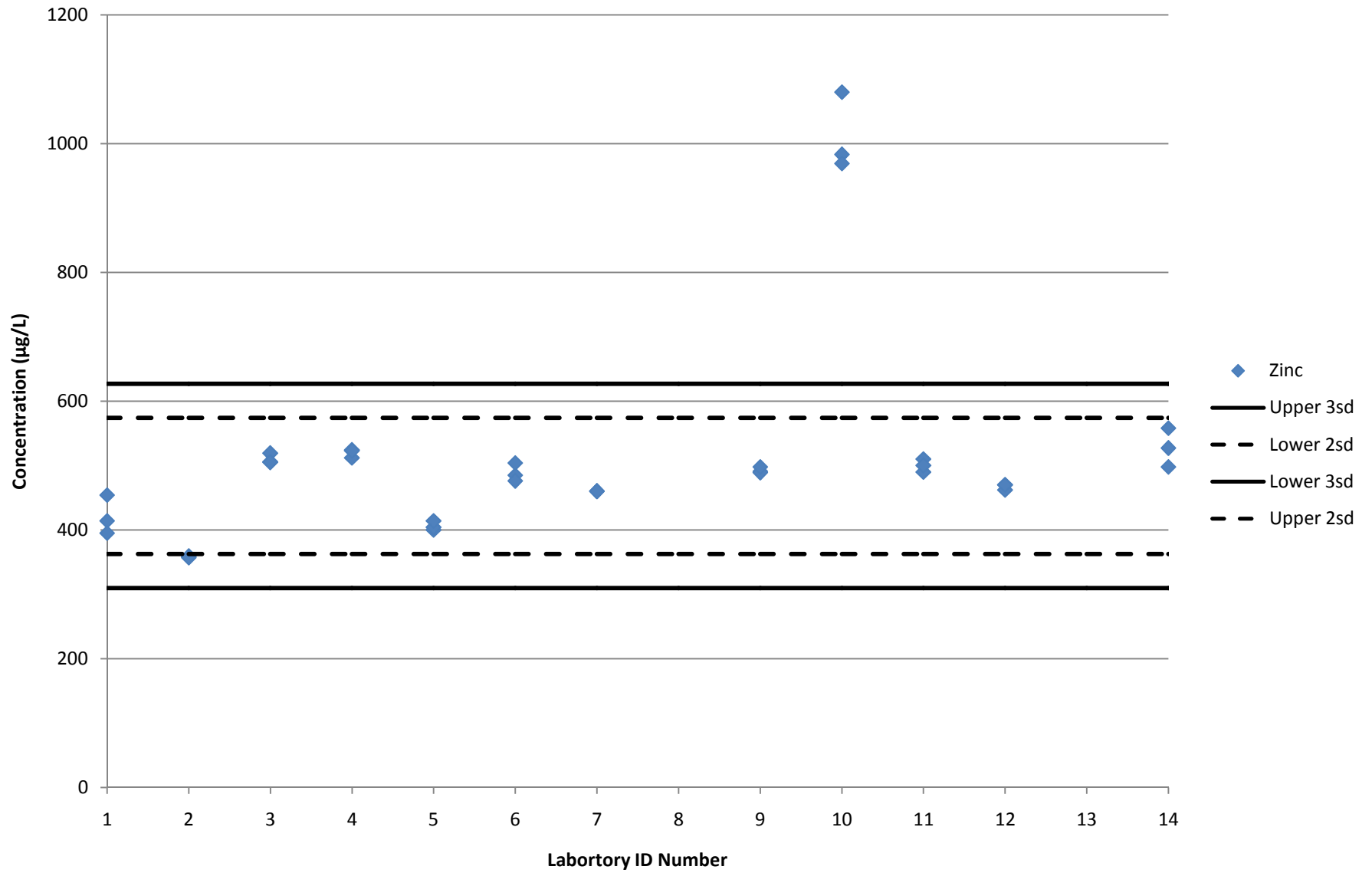
LU2: TSS (mean= 122 mg/L)
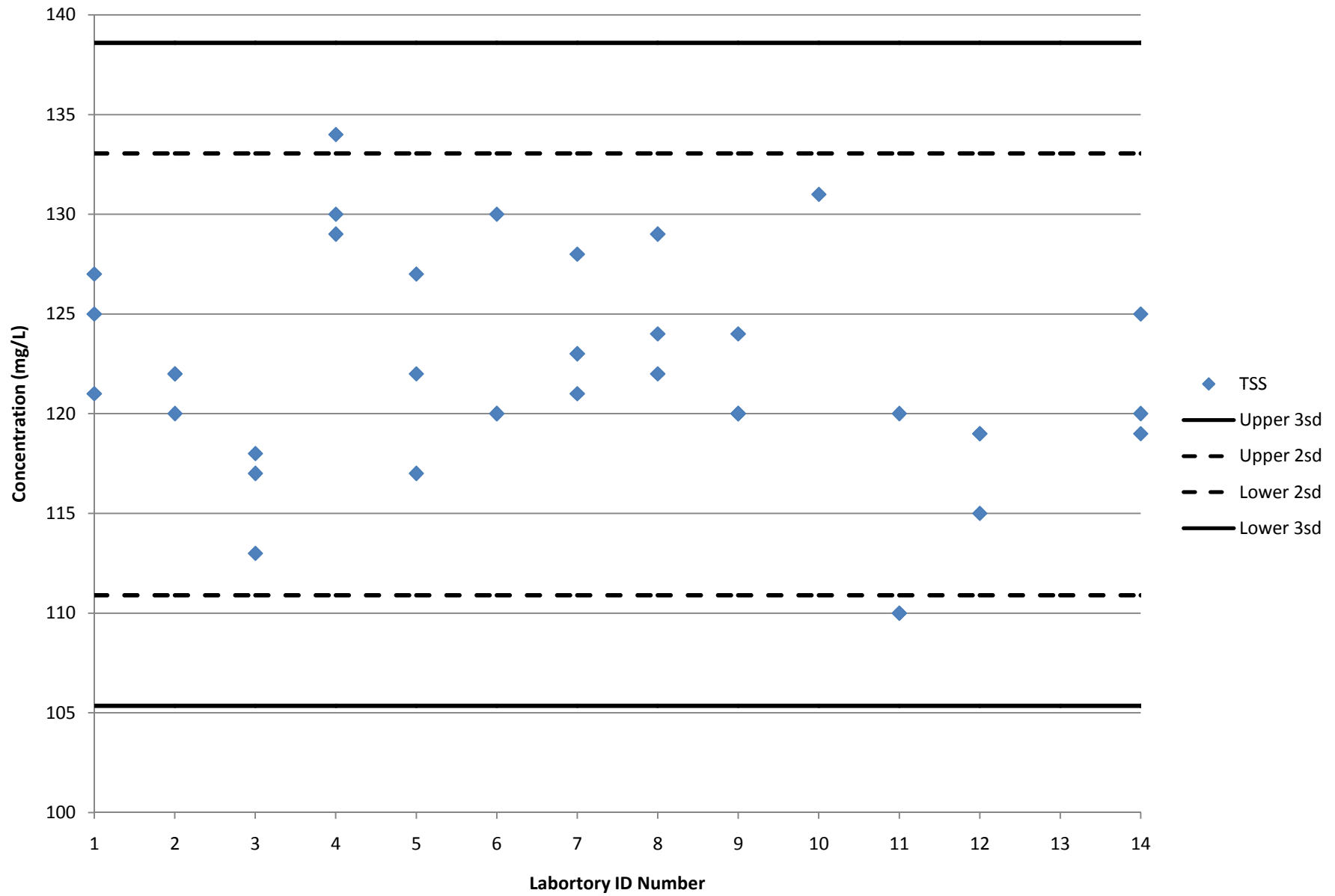
LU2: Ammonia-N (mean= 1.34 mg/L)
(Lab 6 was ND)
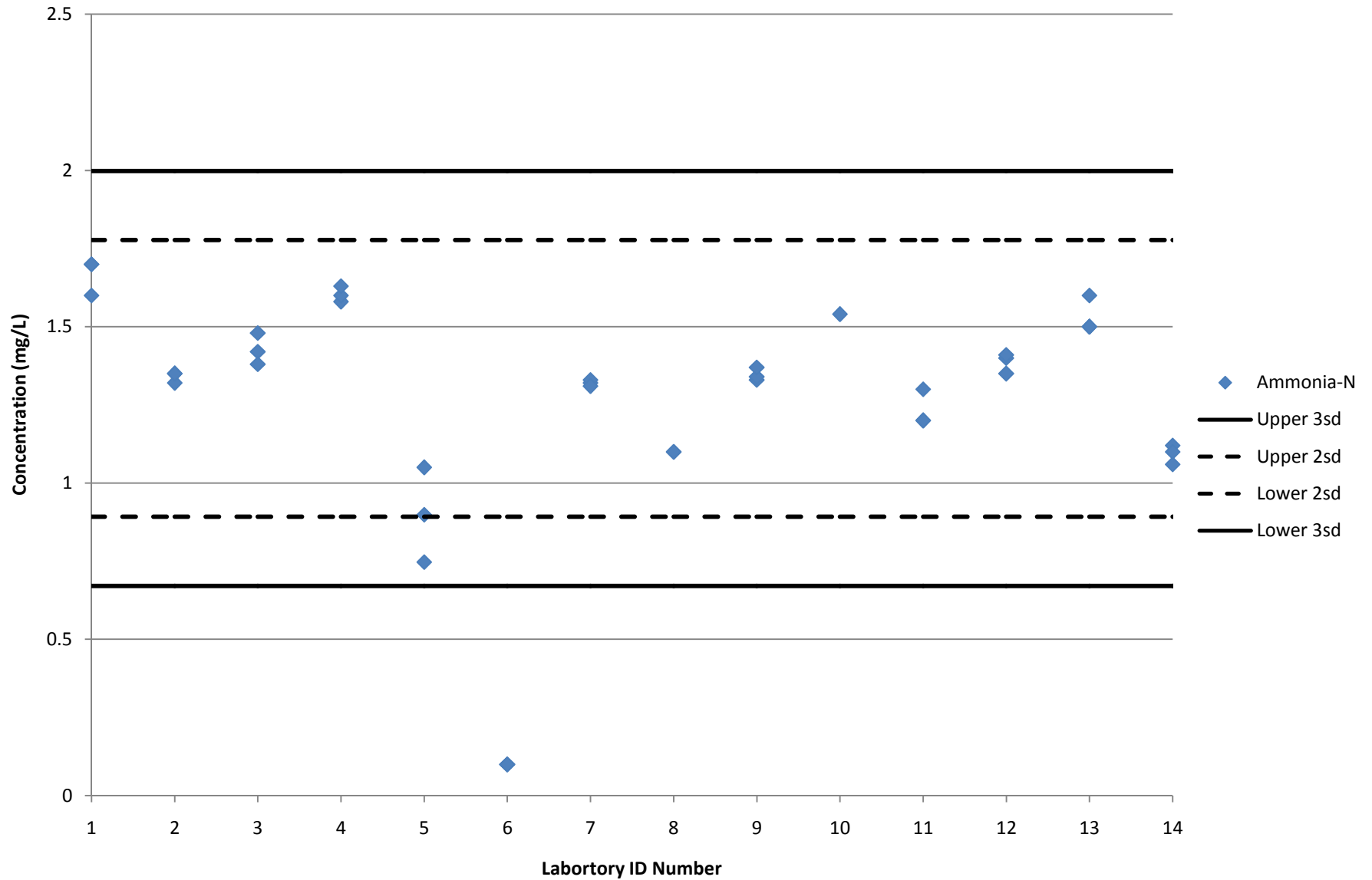
LU2: Nitrate+Nitrite-N (mean= 0.675 mg/L)
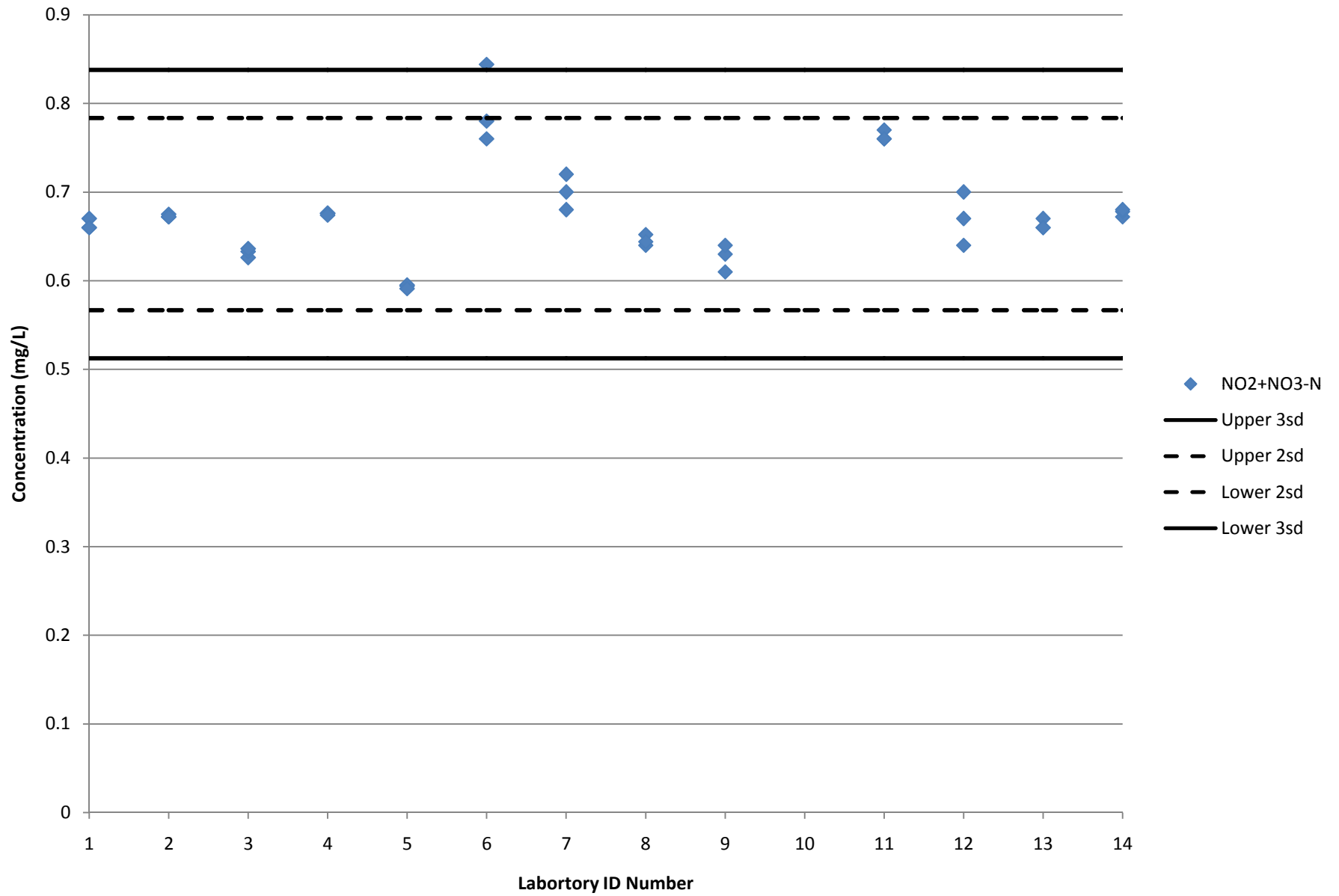
LU2: TKN (mean= 2.95 mg/L)
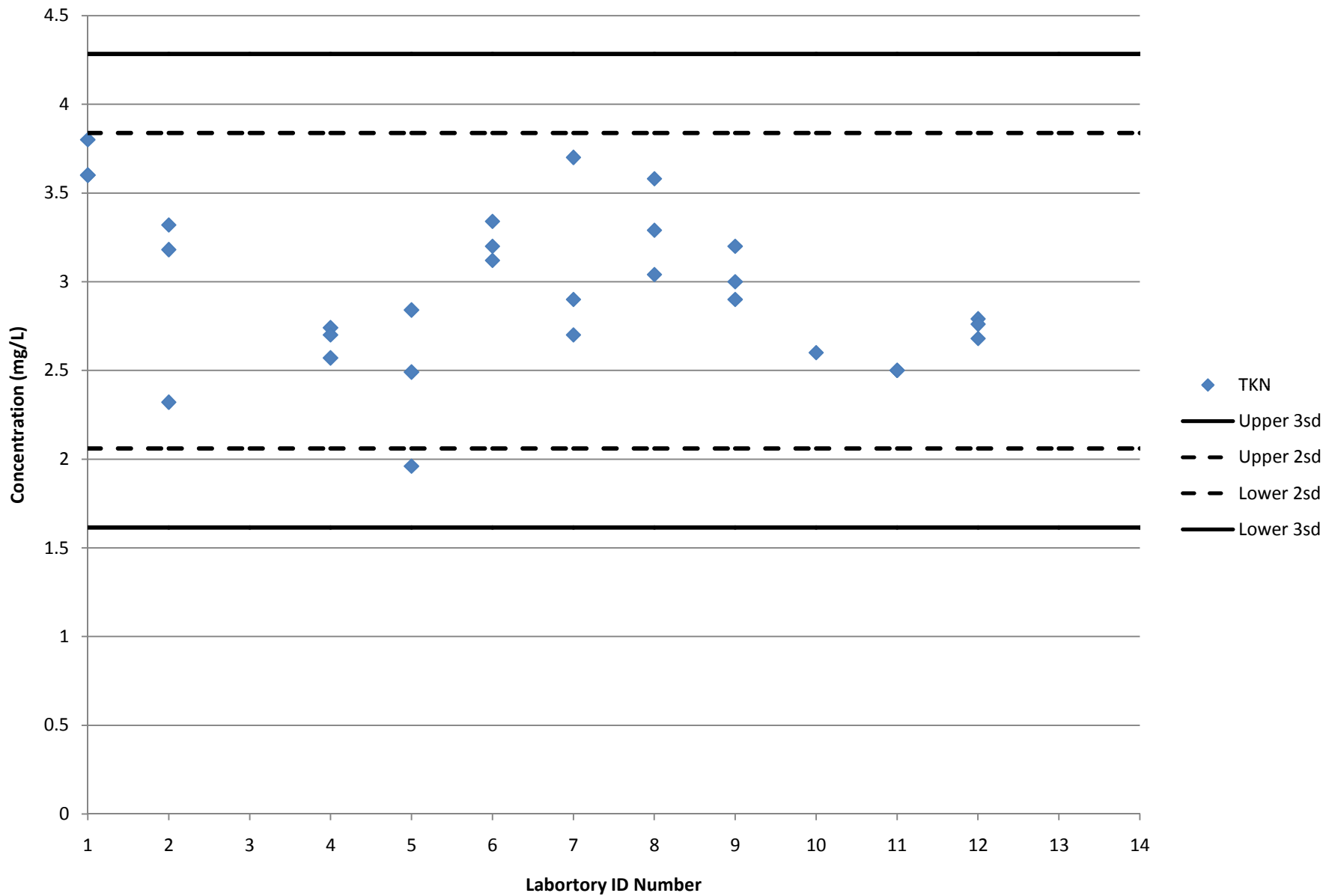
LU2: TOC (mean= 26.5 mg/L)
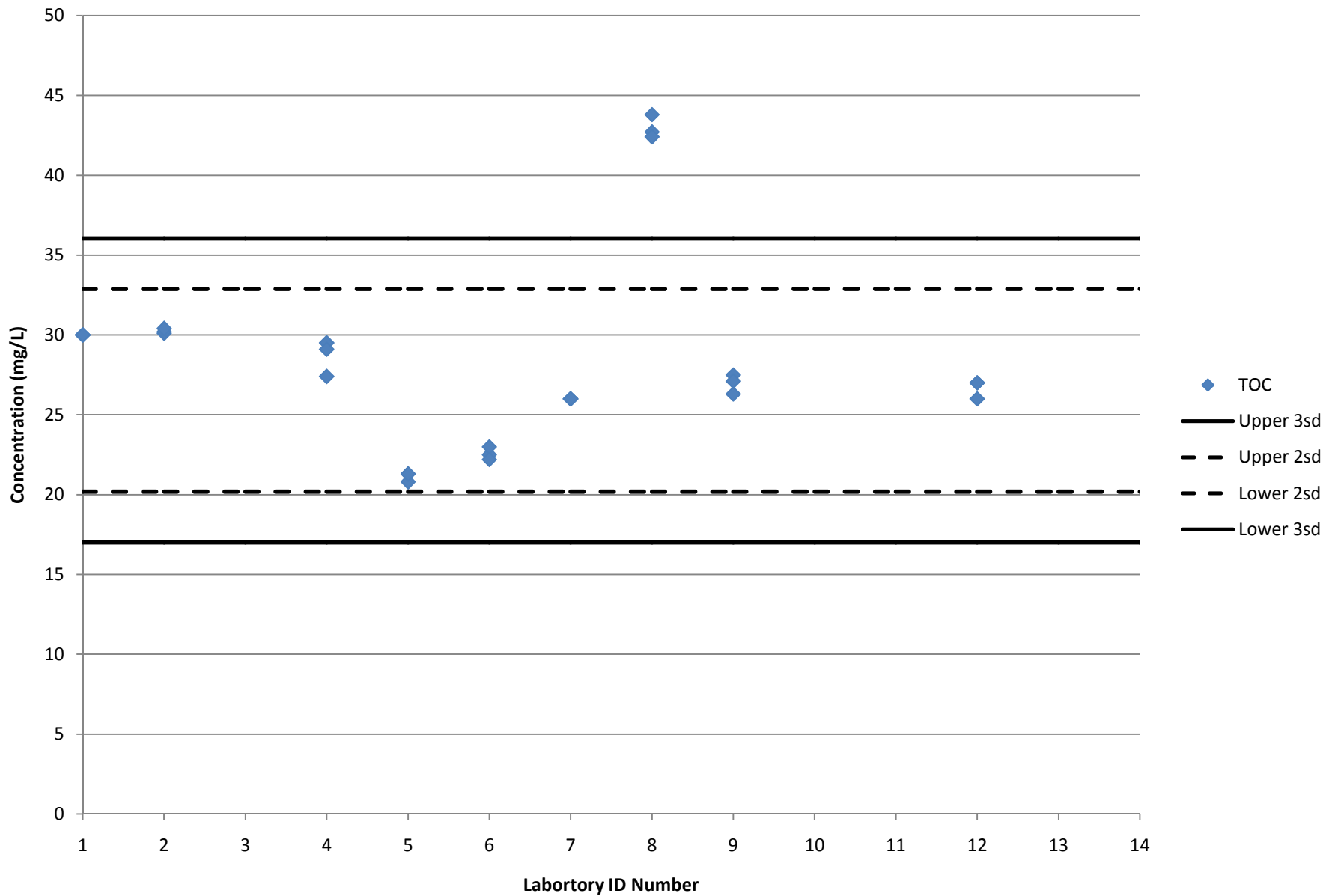
LU2: Total Phosphorus (mean= 0.288 mg/L) (w/o Lab 1 Data)

Concentration (mg/L) vs. Labortory ID Number

Legend:
- Total P
- Upper 3sd
- Upper 2sd
- Lower 2sd
- Lower 3sd

LU2: Arsenic (mean= 3.13 µg/L)
(Lab 10 was ND)
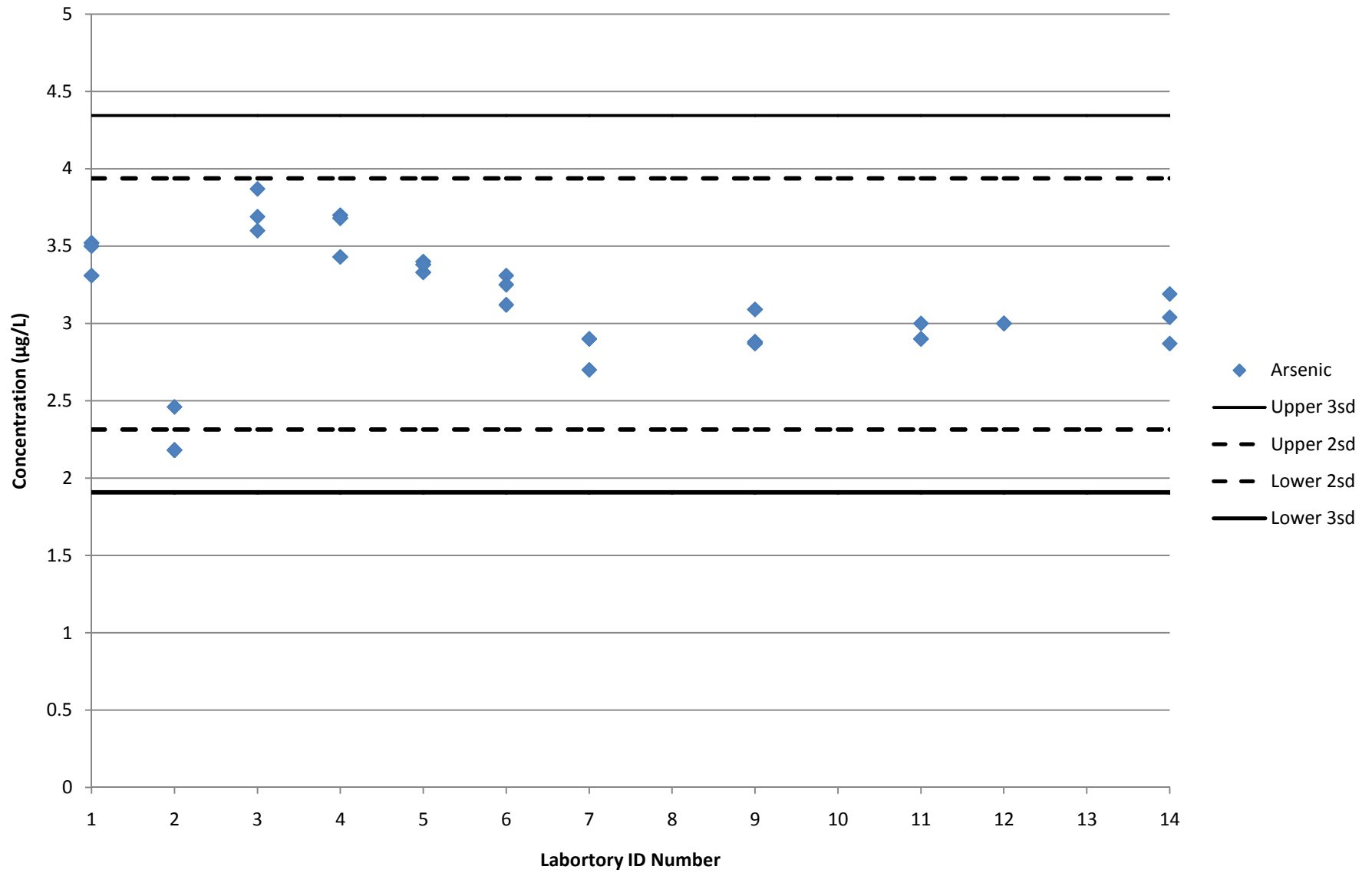
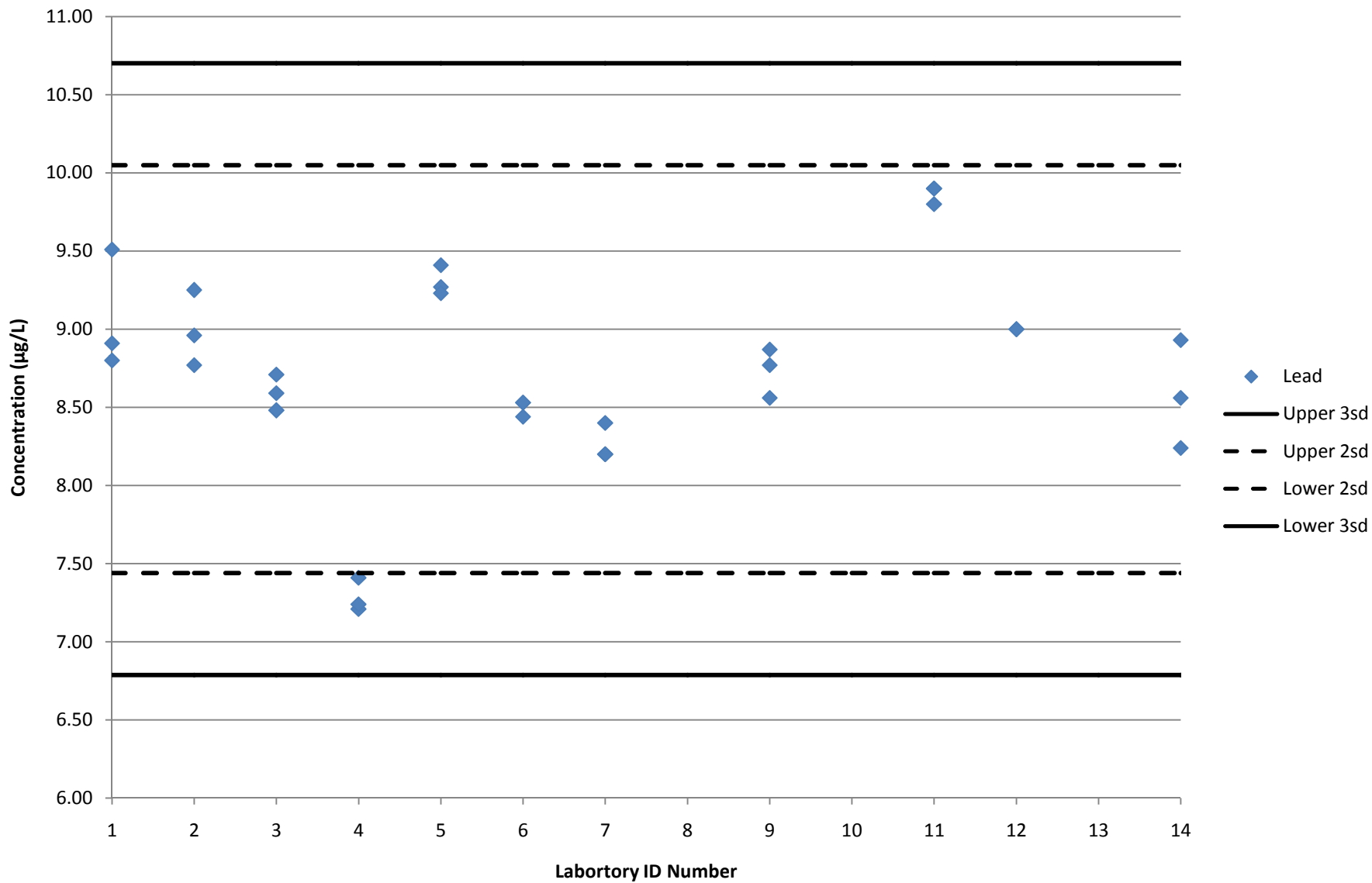LU2: Cadmium (mean= 0.306 µg/L)
(w/o Lab 10 data, Labs 1 and 12 were ND)
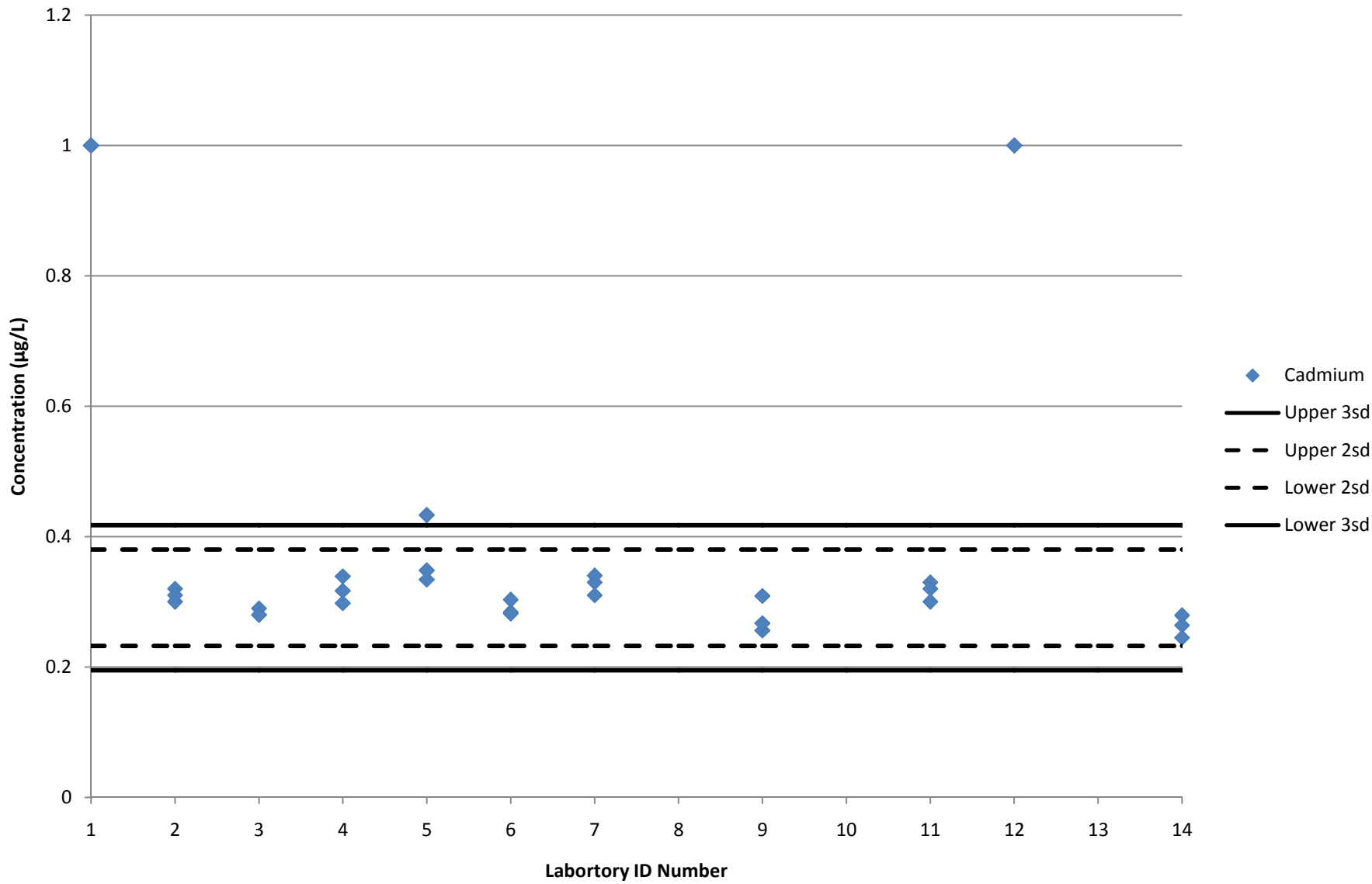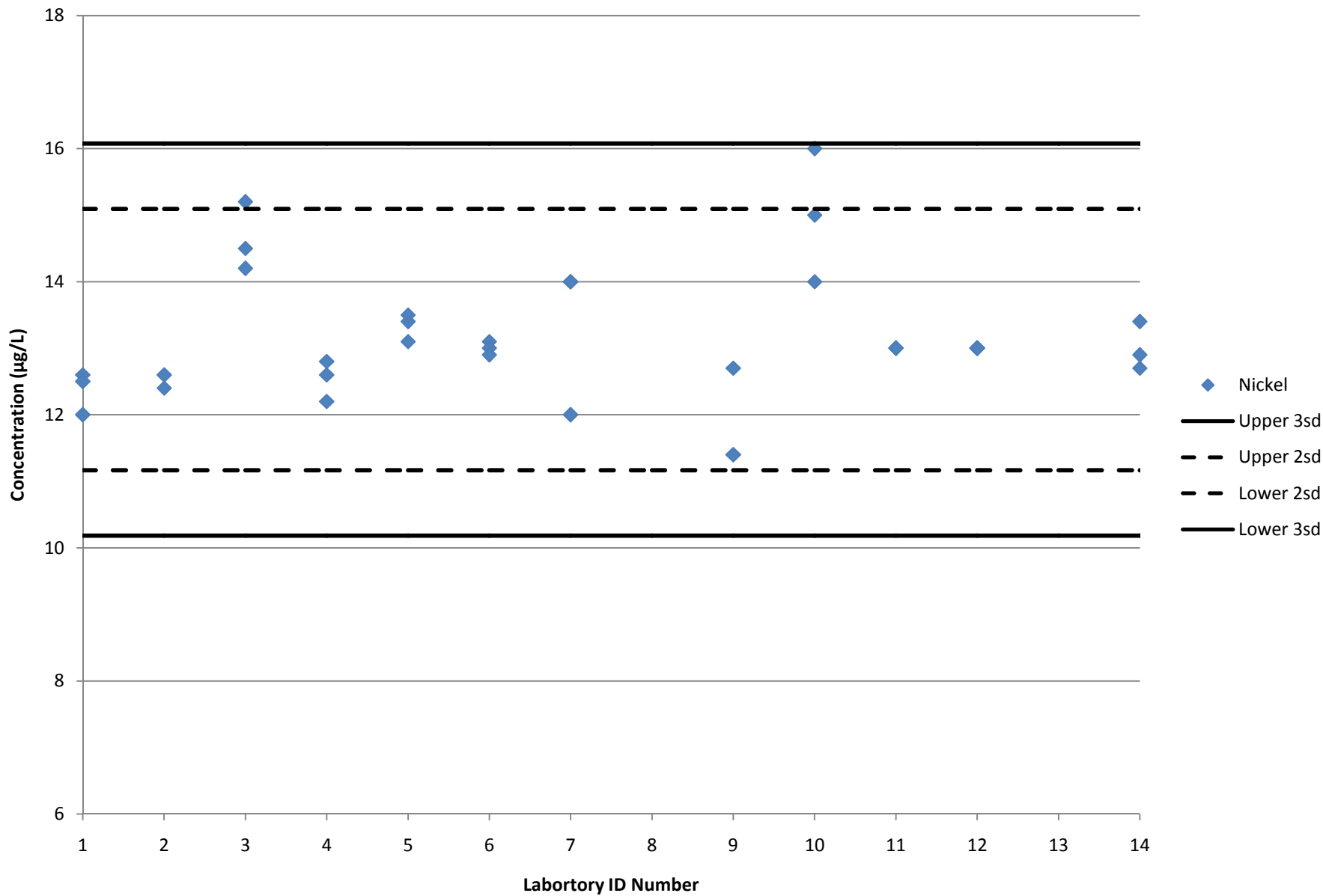
LU2: Chromium (mean= 5.50 µg/L)
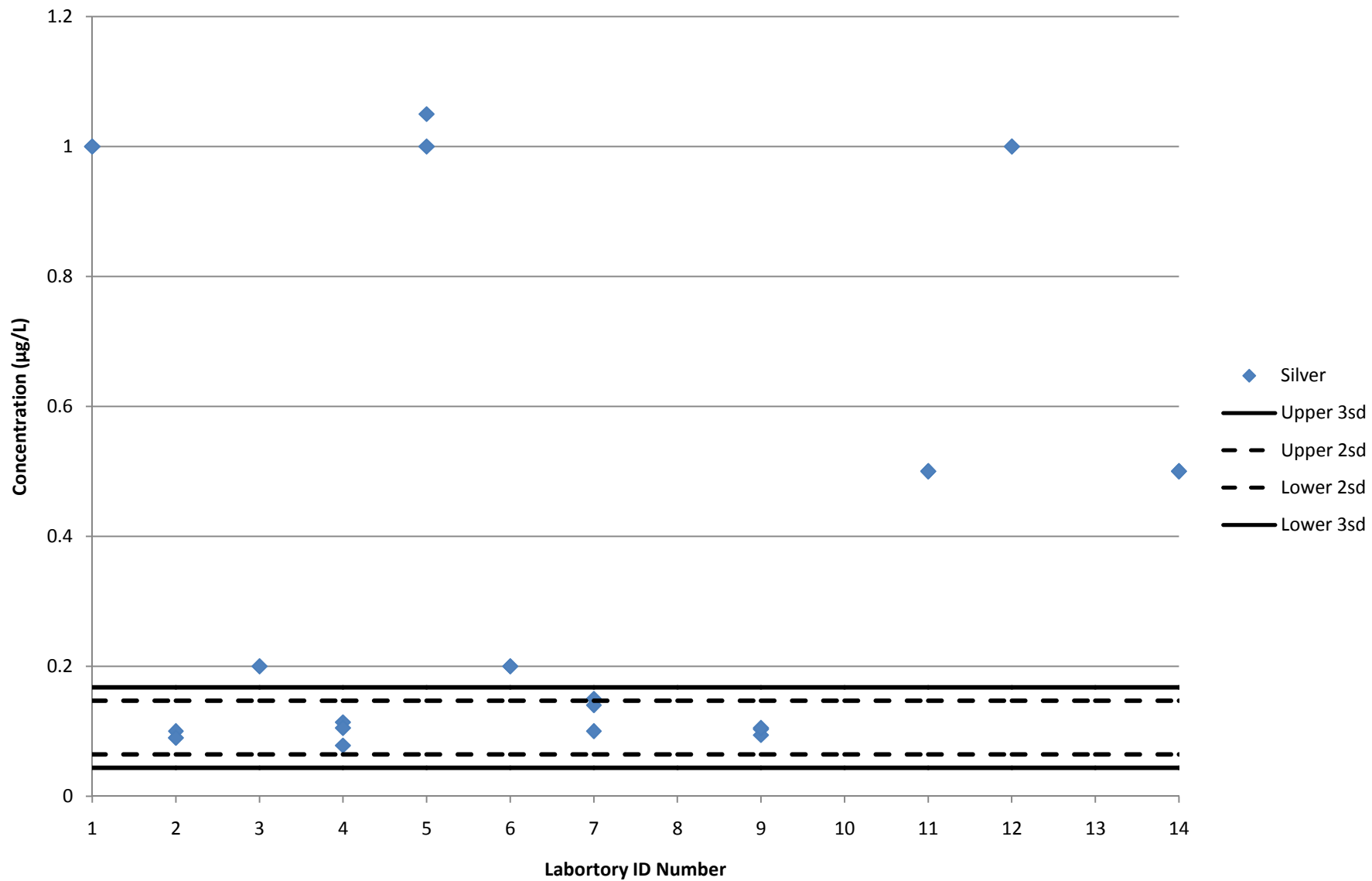(w/o Lab 10 Data)
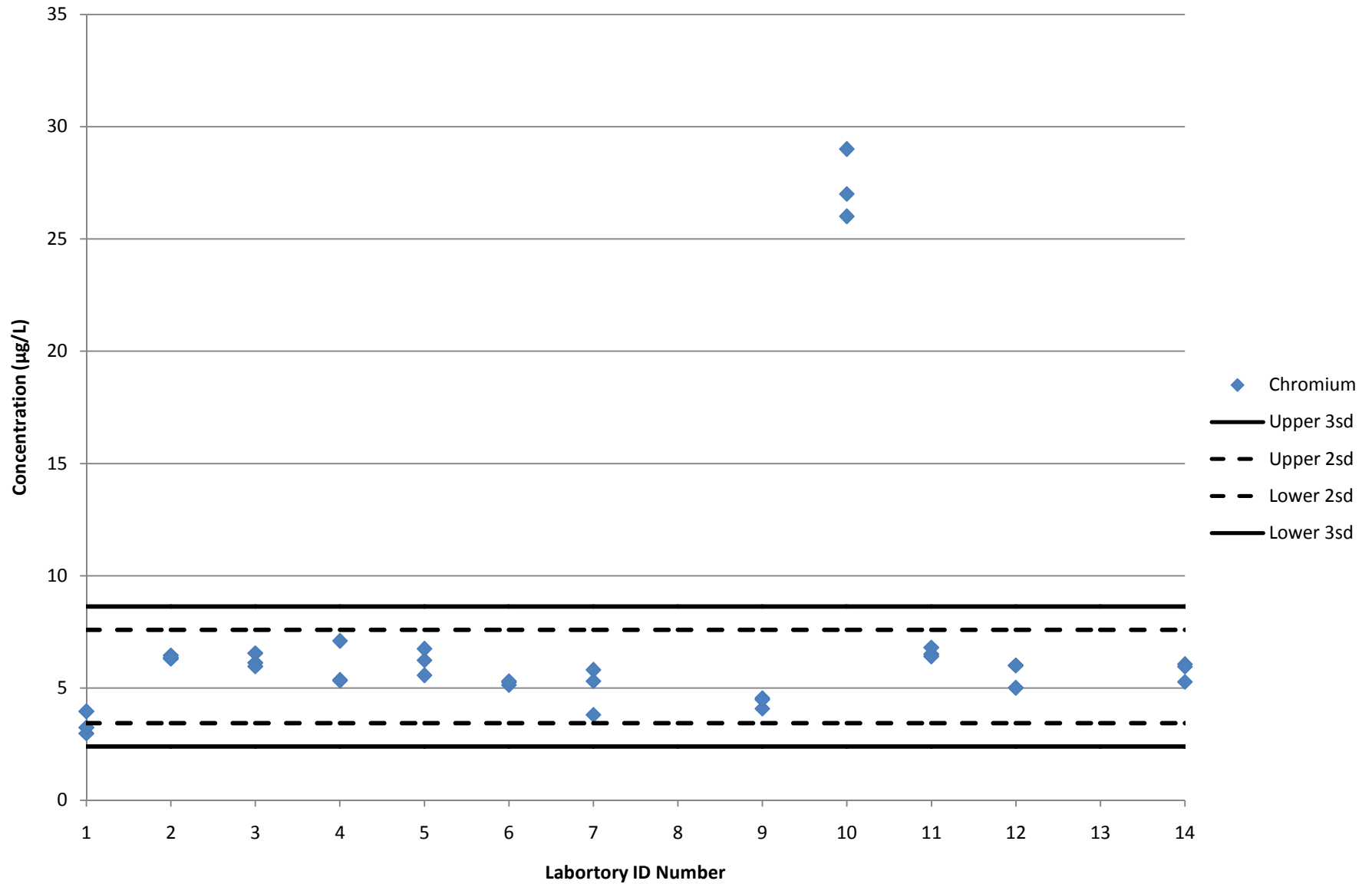
LU2: Copper (mean= 116 µg/L)
(w/o Lab 10 Data)

LU2: Lead (mean= 8.74 µg/L)
(Lab 10 was ND)

LU2: Nickel (mean= 13.1 µg/L)

LU2: Silver (mean= 0.106μg/L)
(w/o Lab 10 Data, Labs 1, 3, 5, 6, 11, 12, and 14 were ND)

LU2: Zinc (mean= 153μg/L)
(w/o Lab 10 Data)