

FINAL REPORT

EVALUATION OF PQL DETERMINATION METHODOLOGIES

CONTRACT #P33501

with

**NEW JERSEY DEPARTMENT OF ENVIRONMENTAL
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OFFICE OF SCIENCE AND RESEARCH

Project Officer: Paul Sanders

**MONTGOMERY LABORATORIES
555 EAST WALNUT ST
PASADENA, CA 91101**

Principal Investigator: Dr. Andrew Eaton

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INTRODUCTION

This report covers both the literature search included in the first progress report and the database evaluation provided in the second progress report based on data provided by individual laboratories for Method Detection Limit (MDL) determinations. The first progress report dealt with the literature available on the concept of detection and quantitation and included discussions of the EPA/ACS proposed RDL and RQL concepts. Definitions are restated below.

MDL - Method Detection Limit determined in an individual laboratory using the 40CFR136 approach.

INTERLABORATORY MDL - MDL which is the mean or median of MDLs determined in multiple individual laboratories.

EPA RDL - Reliable Detection Level; Twice the estimated interlaboratory method detection limit; That concentration where the probability of both false negatives and false positives is 1%.

PQL - A Multiplier of the MDL representing the level where most laboratories should be able to reliably quantify a compound; The multiplier may vary from compound to compound.

EPA RQL - Reliable Quantification Level; Four times the Interlaboratory MDL; That concentration where most laboratories should be able to quantify a compound. By definition, this should be above the MDL for almost all individual laboratories.

SPIKE RATIO - The median or mean of the ratios of spike level to calculated MDL from individual laboratories.

CALIBRATION RATIO - The median or mean of the ratios of the lowest calibration level to calculated MDL from individual laboratories.

DATABASE

Table 1 shows the number of "valid" data points available for each method, including the breakdown of ACTLabs members and other New Jersey certified labs. Our goal was to have at least 15-20 "valid" data points for an analyte. In the more common methods, this was not a problem. However for any of the soil matrices and for some of the less common methods, either people are not performing method detection level studies or they are not being done in a manner which allows the data to be used. Even for those methods with limited valid data points, we have discussed the data, though conclusions may be less significant.

A "valid" data point is considered to be one where the determined Method Detection Level (MDL) is less than 50 times the spike level used to determine that MDL and information provided on calibration is consistent with the cited method. EPA guidelines suggest that the

spike level should be no more than 5-10 times the MDL, but we decided to be more liberal and allow up to 50 times for a spike level to minimize the number of outliers. For some parameters, selecting a more conservative 10X multiplier would have resulted in discarding numerous data points. To test the ruggedness of this approach, we selected several analytes with large numbers of outliers using the EPA criteria and compared the statistics (Mean, Median, and Standard Deviation) using either 10X or 50X as a criterion for removing data. Appendix A contains the raw data for each compound. Data points were removed from consideration if the multiplier of spike level to calculated MDL was greater than 50 or information provided suggested that the method was not being followed (ie. calibration levels were inconsistent with the cited method). Appendix B includes selected examples after removing additional outliers using the EPA criterion of a less than ten times multiplier for the MDL determination. Table 2 demonstrates that for these data there is no significant difference between results for summary statistics using the EPA criteria versus our more liberal criteria.

The database includes whatever information was provided by the participating laboratories. In some cases this included all of the calibration levels and even the normal reporting limit (MRL) for the lab. In other cases the only calibration data provided was for the lowest point on the calibration curve, even though multipoint calibration was used.

APPROACHES TO DETERMINING QUANTIFICATION LIMITS

The principal purpose of this study was to determine whether it is feasible to calculate a simple multiplier of the MDL on a compound specific basis to determine quantitation limits (RQLs) for regulatory purposes or whether a generic multiplier such as 5X or 10X (both of which are used in the literature), or 4X (which is the EPA Proposed Reliable Quantification Level) should be used. Individual laboratory method detection limits are calculated using the procedures outlined in 40CFR136, where replicate samples spiked at a concentration 1-10 times the expected MDL are analyzed and the standard deviation of the measurement is multiplied by the appropriate Student-t value.

Our requirement for RQLs is that a result must be at a concentration for which there is finite precision and bias. To determine the appropriate concentration, we relied on the fact that a) the lowest calibration standard used by a lab represents a concentration where there is finite bias and b) the concentration used for spiking a sample to determine the MDL should be at a concentration where recoveries are measurable and therefore again represent a finite bias. Spike levels for MDL determinations are often performed below the low point on the method calibration curve because for some methods the calibration levels are specified (eg. Method 624). By definition, however, if a method detection limit is calculated from a spike, the spike

represents a level of finite precision, even below the low point on the calibration curve; therefore the calibration curve could probably be lowered to include this point. If a measured result is below a known value (eg. the lowest standard or a known spike level), it is not possible to assign a specific numerical value to it and it should not therefore be used for standard setting.

Reliable quantitation levels (RQL) are defined here as the concentration at which a majority of the laboratories could detect and quantify the compound at a concentration equivalent to the lower of the median ratio of spiking level to the MDL (Spike Ratio) or the ratio of the median calibration level to the MDL (Calibration Ratio). In addition we have compared the calculated RQL to the spike concentration and the low point on the calibration curve. We have selected the median (rather than the mean) because the median is generally a more rugged indicator of the population central tendency for these data. A simplified description of the approach is presented below.

1. Calculate the median interlaboratory spike and calibration ratios using available lab data for each compound and method of interest.
2. Select the lower of the two ratios. This is the multiplier for the interlaboratory RQL.
3. Multiply by the median interlaboratory MDL to determine the RQL.
4. Compare value to the MDLs determined for each individual laboratory. Value should be greater than 90% of the individual lab MDLs. Also determine how many labs are theoretically able to quantify at this level by comparing the value to the lower of the spike concentration or the calibration low point for each individual lab.
5. Also determine "EPA RQL" by multiplying interlaboratory MDL by 4 and compare value to individual MDLs. Also determine how many labs are theoretically able to quantify at this level by comparing the value to the lower of the spike concentration or the calibration low point for each individual lab.
6. It is worth noting that this approach does not make any assumptions about precision at the low point of the calibration curve, but merely implies that accurate quantitation should be possible if a standard is used at that level. Appendix C is a paper presented by Tim Moore and Max Grimes from RMI, Inc at the Water Environment Federation (WEF) meeting which demonstrates that additional controls on precision and accuracy are necessary at these low levels, at least for metals.

In order to specifically compare data to the proposed EPA criterion, we have always also presented comparisons to a 4X multiplier of the MDL. The RQL is shown in table form for both median and mean. RQLs are rounded to reflect appropriate significant figures.

To evaluate these criteria we determined a number of summary statistics for each compound requested, including the mean, median, maximum, minimum and standard deviation for a given data set for the MDL, the spiking level used to determine the MDL, the lowest calibration point used, the typical minimum reporting level, and the ratios of these various parameters.

Minimum reporting levels used by laboratories vary tremendously and there is no apparent systematic basis used for selecting them. In California, for drinking water the State has set a specified reporting limit for data which is reported to the State, and many labs have selected this value as their standard reporting limit for the compounds, often without regard for calibration levels or MDLs. For other compounds, labs use reporting limits which are either derived from method guidelines, are the actual calculated MDLs, or may be wishful thinking. Because reporting limits for laboratories appear to be arbitrary, this indicator was not used for statistical evaluations.

The use of summary statistics allowed us to determine on a relatively large data set whether such multipliers could be considered valid approaches. Our working hypothesis was that accurate quantitation should not occur below the lowest standard or spike concentration, in accordance with good analytical practice.

REJECTION OF OUTLIERS

No reported MDL datapoints were rejected unless the ratio of the spike level to the MDL exceeded the criteria, the reported calibration levels indicated that the referenced method was not followed (eg. low calibration point of 20 ppb for a 524.2 analysis), or the reported MDL was more than 10 times the mean MDL of the entire dataset. Use of an outlier test such as Dixon's Test could also have been used to reject data, but we elected not to perform this test because some of the variation may truly reflect interlaboratory variability. The wide standard deviations determined for some of the analytes demonstrates that data from a single lab cannot be used to assess the practicality of this approach.

Because of the wide range of MDLs reported in some cases, we selected the median as the best statistical measure to use in looking at multipliers. When a limited number of data points are available and the range of values is large, a few high or low points can significantly alter the

calculated mean. A histogram of some of the data (Figure 1) demonstrates that the median is a better measure than the mean. This minimizes the impact of a very high or very low individual value in the data sets. The mean and median are arbitrarily considered "close" to each other if the relative percent difference (RPD) between the two numbers is 25% or 0.1 ppb. For each element or compound, we have summarized the statistics describing the database and our conclusions. A database is defined as "small" if it has less than 10 valid datapoints, "intermediate" if it has 11-25 valid datapoints, and "large" if there are over 25 valid datapoints.

COMPOUND SPECIFIC EVALUATION- AQUEOUS

Copper by Method 220.2 (graphite furnace)

The database for this metal was intermediate, with 15 valid datapoints. There is a fairly wide range of reported MDLs (from 0.08 to 2.7 ppb), reinforcing the importance of using data from multiple laboratories. It is worth noting that the lab which determined the lowest MDL used a calibration point within the range used by other labs so that low level quantitation determined based on calibration should be consistent, even though MDLs may vary widely. The mean MDL was 1.1, and the median was 1.0, minimally different. The ratios of spike to MDL and low calibration point to MDL are shown in the table. In this case, using the EPA proposed ratio of 4 times the median interlaboratory MDL would provide a good measure of a level which should be quantifiable in any laboratory (4 ppb). This is higher than the individual MDL determined by any of the labs and is above the spike or calibration level for more than 60% of the labs.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	1.1	5	7	5.5	87%
Median	1	5	4	4	60%

Lead by Method 239.2 (graphite furnace)

The database for this metal was large, with 39 acceptable data points. As with copper, however, there is a very wide range of reported MDLs (from 0.07 to 5 ppb). The mean MDL (1.6 ppb) was slightly higher than the median (1.3 ppb), but still close. The median ratio of the lowest calibration point to the MDL was 4, lower than the mean of 8. The proposed RQL would be 5.2 ppb. Once again this is consistent with the EPA proposed ratio and is above the individual MDL determined by any single laboratory. 77% of the labs should be able to quantify at this level.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	1.6	6	8	9.6	77%
Median	1.3	5	4	5.2	77%

Cadmium by Method 213.2 (graphite furnace)

The database for this metal was large, with 28 acceptable data points. Again there is a wide range of individually reported MDLs (from 0.03 to 2 ppb). The mean MDL (0.37 ppb) is over twice as high as the median (0.18 ppb). The median ratio of the lowest calibration point to the MDL was 4, lower than the mean of 10. Because of the large range, we feel the median is the better statistic. Using this multiplier leads to a recommended Quantification Level of 0.7 ppb. This is consistent with the EPA proposed RQL and is above the individual MDL determined by 24 out of 28 laboratories (86%). 57% of the labs should be able to quantify at this level.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	0.37	6	10	2.2	89%
Median	0.18	4	4	0.7	57%

1,1,2-Trichloroethane by method 524.2 (GC/MS capillary column)

The database for this compound was intermediate in size, with 19 acceptable data points. Individual reported MDLs ranged from 0.03 to 1.1 ppb. The mean MDL (0.34 ppb) is close to the median MDL (0.25). The median ratio of the lowest calibration point to the MDL was 8, compared to a mean ratio of 7. In this case, the median spike ratio is a lower number, 4. This number is again consistent with the EPA proposed criterion for Quantification levels and is higher than 18 out of 19 laboratory determined MDLs (95%). 68% of the labs should be able to quantify results at this level.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	0.34	5	7	1.7	68%
Median	0.25	4	8	1.0	68%

1,1,2,2-Tetrachloroethane by method 524.2 (GC/MS capillary column)

The database for this compound was intermediate in size, with 20 acceptable data points. Individual reported MDLs ranged from 0.02 to 2.1 ppb. The mean MDL (0.41 ppb) is close to the median MDL (0.31). The median ratio of the lowest calibration point to the MDL was 7, compared to a mean ratio of 8. In this case, the median spike ratio is a lower number, 4. This number is again consistent with the EPA proposed criterion for Quantification levels and is higher than 19 out of 20 laboratory reported MDLs (95%). 65% of the labs should be able to quantify at this level.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	0.41	5	8	2.1	90%
Median	0.31	4	7	1.2	65%

1,2-Dichloropropane by 524.2 (GC/MS Capillary Column)

The database for this compound was intermediate in size, with 21 acceptable data points. Individual reported MDLs ranged from 0.04 to 0.9 ppb. The mean MDL (0.27 ppb) is close to the median MDL (0.24). The median and mean ratio of the lowest calibration point to the MDL were both 8. In this case, the median and mean spike ratios were equal at 6. This number is higher than the EPA proposed criteria of 4, but gives an apparent quantitation level which is almost twice the highest individual MDL. Using a 4X multiplier of the median gives an "EPA RQL" of 1 ppb, which is above the highest individually determined MDL. 67% of the labs should be able to provide quantitative data at this concentration.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	0.27	6	8	1.6	67%
Median	0.24	6	8	1.4	67%

Carbon Tetrachloride by 524.2 (GC/MS Capillary Column)

The database for this compound was intermediate in size, with 21 acceptable data points. Individual reported MDLs ranged from 0.05 to 0.8 ppb. The mean MDL (0.24 ppb) is close to the median MDL (0.20). The lowest ratio was the median spike ratio of 5. This number is higher than the EPA proposed criteria of 4, and gives an apparent quantitation level which is higher than each individual MDL. Using a 4X multiplier of the median gives an "EPA RQL" of 0.8 ppb, which is still above the highest individually determined MDL. 29% of the labs should be able to provide quantitative data at this concentration.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	0.24	7	11	1.7	71%
Median	0.20	5	7	1.0	71%

Chloroform by 524.2 (GC/MS Capillary Column)

The database for this compound was intermediate in size, with 20 acceptable data points. Individual reported MDLs ranged from 0.03 to 0.9 ppb. The mean MDL (0.25 ppb) is close to the median MDL (0.22). The data was very similar to that reported for TCE. The median spike ratio of 5 gives an apparent RQL which is higher than all individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 0.9 ppb, which is equal to the highest individually determined MDL. 70% of the labs should be able to quantify over 1 ppb.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	0.25	7	11	1.8	70%
Median	0.22	5	7	1.1	70%

Trichloroethylene by 524.2 (GC/MS Capillary Column)

The database for this compound was intermediate in size, with 22 acceptable data points. Individual reported MDLs ranged from 0.04 to 0.8 ppb. The mean MDL (0.26 ppb) is close to the median MDL (0.22). The lowest applicable ratio is the median spike ratio, which is 5. This number is higher than the EPA proposed criteria of 4, and gives an apparent quantitation level which is above the highest individual MDL. Using a 4X multiplier of the median gives an "EPA RQL" of 0.9 ppb, which is above the highest individually determined MDL. 68% of the labs should be able to quantify above 1 ppb. An accurate assessment of the number of labs which should be able to quantify at the "EPA RQL" is not possible because it is so close to the 1 ppb spike level used by many of the labs.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	0.26	6	11	1.6	68%
Median	0.22	5	7	1.1	68%

Chloroform by 624 (GC/MS Capillary or Packed Column)

The database for this compound was large in size, with 38 acceptable data points. Because Method 624 typically uses a high initial calibration point (5 to 20 ppb), we would expect that the spike level would provide the lower multiplier in all cases. Individual reported MDLs ranged from 0.15 to 4 ppb. The mean MDL (0.91 ppb) is close to the median MDL (0.74 ppb). The median spike ratio of 8 gives an apparent RQL which is higher than all the individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 3.0 ppb, which is still above 95% of the individual MDLs. 74% of the labs should be able to quantify above 5 ppb, but only 29% can provide quantitative data above the EPA RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	0.91	8	29	7.3	74%
Median	0.74	8	20	5.9	74%

Trichloroethylene by 624 (GC/MS Capillary or Packed Column)

The database for this compound was large, with 38 acceptable data points. Because Method 624 typically uses a high initial calibration point (5 to 20 ppb), we would expect that the spike level would provide the lower multiplier in all cases. Individual reported MDLs ranged from 0.1 to 7 ppb. The mean MDL (1.2 ppb) is close to the median MDL (0.9 ppb). The median spike ratio of 6 gives an apparent RQL which is higher than 97% of individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 3.6 ppb, which is still above 97% of the individual MDLs. 74% of the labs should be able to quantify over 5 ppb. Only 39% of the

labs used a low enough spike or standard to demonstrate quantitation at the EPA RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	1.2	7	29	8.4	74%
Median	0.89	6	17	5.4	74%

1,1,1-Trichloroethane by 624 (GC/MS Capillary or Packed Column)

The database for this compound was large, with 39 acceptable data points. Because Method 624 typically uses a high initial calibration point (5 to 20 ppb), we would expect that the spike level would provide the lower multiplier in all cases. Individual reported MDLs ranged from 0.07 to 5 ppb. The mean MDL (1.2 ppb) is close to the median MDL (0.83 ppb). The median spike ratio of 6 gives an apparent RQL which is higher than all the individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 3.3 ppb, which is still above 97% of the individual MDLs. 72% of the labs should be able to quantify over 5 ppb, but only 28% used a low enough spike or standard to demonstrate quantitation at the EPA RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	1.2	7	25	8.4	72%
Median	0.83	6	20	5.0	72%

Carbon Tetrachloride by 624 (GC/MS Capillary or Packed Column)

The database for this compound was large in size, with 38 acceptable data points. Because Method 624 typically uses a high initial calibration point (5 to 20 ppb), we would expect that the spike level would provide the lower multiplier in all cases. Individual reported MDLs ranged from 0.1 to 3.1 ppb. The mean MDL (1.0 ppb) is close to the median MDL (0.73 ppb). The median spike ratio of 7 gives an apparent RQL which is higher than all the individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 2.9 ppb, which is still above 97% of the individual MDLs. 71% should be able to quantify above 5 ppb, but only 32% can provide quantitative data at the EPA RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	1.0	7	27	7.0	71%
Median	0.73	7	19	5.1	71%

Tetrachloroethylene by 624 (GC/MS Capillary or Packed Column)

The database for this compound was large in size, with 40 acceptable data points. Because Method 624 typically uses a high initial calibration point (5 to 20 ppb), we would expect that the spike level would provide the lower multiplier in all cases. Individual reported MDLs ranged from 0.12 to 3 ppb. The mean MDL (1.1 ppb) is close to the median MDL (0.9 ppb).

The median spike ratio of 6 gives an apparent RQL which is higher than all the individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 3.6 ppb, which is still above all of the individual MDLs. 70% of the labs should be able to quantify above 5 ppb, but only 25% can provide quantitative data at the EPA RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	1.1	8	25	8.8	70%
Median	0.9	6	17	5.4	70%

Dichlorobenzenes by 624 (GC/MS Capillary or Packed Column)

The database for this compound was large in size, with 31 acceptable data points. Fewer points are available for this analyte because some labs do not include the dichlorobenzenes in method 624 and some labs did not provide data because no specific isomer was mentioned. Because Method 624 typically uses a high initial calibration point (5 to 20 ppb), we would expect that the spike level would provide the lower multiplier in all cases. Individual reported MDLs ranged from 0.13 to 5 ppb. The mean MDL (1.5 ppb) is close to the median MDL (1.0 ppb). The median spike ratio of 5 gives an apparent RQL which is higher than all of the individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 4 ppb, which is still above 87% of the individual MDLs. 61% of the labs should be able to provide quantitative data above 5 ppb, but only 35% have a spike or calibration solution at or below the EPA RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	1.5	6	22	9.0	61%
Median	1.0	5	18	5.0	61%

Diethylhexylphthalate by 625 (Extraction with GC/MS analysis of extract)

Method 625 is different from the volatiles in that it involves an additional preparation step. In addition, unlike the volatiles, the relative response of the detector varies extensively between compounds. However spiking and calibration solutions are typically prepared at a single level for all of the compounds. Thus there is the potential for a great deal more variability in results and ratios. The database for this compound was large in size, with 39 acceptable data points. Individual reported MDLs ranged from 0.4 to 13 ppb. The mean MDL (3.0 ppb) is close to the median MDL (2.7 ppb). The median spike ratio of 5 gives an apparent RQL which is higher than all of the individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 11 ppb, which is still above 97% of the individual MDLs. 74% of the labs should be able to quantify above the EPA RQL or our calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	3.0	7	12	21	100%
Median	2.7	5	7	14	74%

Benzo-a-pyrene by 625 (Extraction with GC/MS analysis of extract)

The database for this compound was large in size, with 40 acceptable data points. Individual reported MDLs ranged from 0.13 to 13 ppb. The mean MDL (2.0 ppb) is close to the median MDL (1.5 ppb). The median spike ratio of 8 gives an apparent RQL which is higher than 98% of the individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 6 ppb, which is still above 95% of the individual MDLs. 70% of the labs should be able to quantify above the calculated RQL of 12 ppb, but only 30% have a spike or calibration solution at or below the EPA RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	2.0	11	19	22	100%
Median	1.5	8	12	12	70%

Benzo(a)Anthracene by 625 (Extraction with GC/MS analysis of extract)

The database for this compound was large in size, with 38 acceptable data points. Individual reported MDLs ranged from 0.06 to 6.2 ppb. The mean MDL (1.9 ppb) is almost double the median MDL (1.1 ppb). The median spike ratio of 10 gives an apparent RQL which is higher than all of the individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 4.4 ppb, which is still above 90% of the individual MDLs. 74% of the labs should be able to quantify accurately at the calculated RQL, but only 18% have a spike or calibration solution at or below the EPA RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	1.9	11	21	21	100%
Median	1.1	10	12	11	74%

2,4-Dichlorophenol by 625 (Extraction with GC/MS analysis of extract)

One datapoint was removed from this dataset because the reported MDL was more than ten times the mean. The dataset is somewhat smaller than the other 625 compounds because in our original survey we did not properly identify the isomer and therefore some labs were not able to respond. The database for this compound was large in size, with 33 acceptable data points. Individual reported MDLs ranged from 0.13 to 9.6 ppb. The mean MDL (2.6 ppb) is much larger than the median MDL (1.3 ppb). The median spike ratio of 6 gives an apparent RQL which is higher than 97% of the individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 5.2 ppb, which is still above 82% of the individual MDLs. Only 33% of the

labs have a spike or calibration solution at or below the EPA RQL or the calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	2.6	9	14	23	100%
Median	1.3	6	10	8	33%

Pentachlorophenol by 625 (Extraction with GC/MS analysis of extract)

The database for this compound was large in size, with 37 acceptable data points. Individual reported MDLs ranged from 0.26 to 48 ppb. The mean MDL (6.2 ppb) is much larger than the median MDL (3.1 ppb). The median spike ratio of 5 gives an apparent RQL which is higher than 92% of the individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 12 ppb, which is still above 86% of the individual MDLs. Only 49% of the labs have a spike or calibration solution at or below the EPA RQL or our calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	6.2	7	11	43	100%
Median	3.1	5	6	16	49%

2,4,6-Trichlorophenol by 625 (Extraction with GC/MS analysis of extract)

One datapoint was removed from this dataset because the reported MDL was more than ten times the mean. The database for this compound was large in size, with 39 acceptable data points. Individual reported MDLs ranged from 0.18 to 12 ppb. The mean MDL (2.9 ppb) is much larger than the median MDL (1.8 ppb). The median spike ratio of 6 gives an apparent RQL which is higher than 97% of the individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 7.2 ppb, which is still above 90% of the individual MDLs. Only 28% of the labs have a spike or calibration solution at or below the EPA RQL, whereas 54% should be able to quantify accurately above the calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	2.9	9	12	26	100%
Median	1.8	6	10	11	54%

Atrazine by 507 (Extraction with GC/ECD analysis of extract)

Substantially less data was available for compounds analyzed by method 507 than for the other aqueous methods. This is largely due to the fact that not nearly as many laboratories perform this test as the others and also because the method does not clearly require the determination of a method detection limit as is required in the other methods. Out of data obtained for nine

laboratories, only 5 actually provided MDL data, with the others stating that they determined the reporting limit empirically in some form or another. As an independent test of the approach we have selected, we can also compare the RQL to the reporting limit (MRL) given by all of the surveyed labs. The database for this compound was small in size, with 5 acceptable data points. Individual reported MDLs ranged from 0.07 to 0.6 ppb. The mean MDL (0.27 ppb) is only slightly above the median MDL (0.24 ppb). The median calibration ratio of 2 gives an apparent RQL which is higher than 80% of the individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 1 ppb, which is above both all of the individual MDLs and equal to the highest reporting limit identified by any single laboratory. 67% of the labs have a spike or calibration solution at or below the EPA RQL, and only 44% of the labs should be able to quantify accurately at the calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	0.27	7	4	1.1	67%
Median	0.24	7	2	0.5	44%

Simazine by 507 (Extraction with GC/ECD analysis of extract)

The database for this compound was small in size, with 5 acceptable data points. Individual reported MDLs ranged from 0.06 to 0.75 ppb. The mean MDL (0.34 ppb) is only slightly above the median MDL (0.29 ppb). The median calibration ratio of 2 gives an apparent RQL which is higher than 80% of the individual MDLs. Using a 4X multiplier of the median gives an "EPA RQL" of 1.2 ppb, which is above both all of the individual MDLs and the highest reporting limit identified by any single laboratory. Over 89% of the labs have a spike or calibration solution at or below the EPA RQL, but only 44% of the labs should be able to quantify accurately at the calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	0.34	5	3	1.0	89%
Median	0.29	5	2	0.6	44%

Alachlor by 507 (Extraction with GC/ECD analysis of extract)

The database for this compound was even smaller than for atrazine and simazine, with only three labs reporting MDL data and six labs reporting MRL data. With a database this small, no meaningful statistics can be presented, but a comparison of the mean and median can be made to the "EPA RQL" concept. The mean MDL was 0.5 and the median was 0.3 ppb. Using a 4X multiplier, the "EPA RQL" for this compound would be 1.2 ppb, higher than all of calculated MDLs and above five out of six reporting limits.

Metolachlor and Diazinon by 507 (Extraction with GC/ECD analysis of extract)

Only one lab reported MDL data for each of these compounds, and although three laboratories reported MRL data for Diazinon, the range (100 times) of reported MRLs makes it impossible to tabulate any meaningful statistics for these compounds or even to compare them to the "EPA RQL". The most probable reason for this lack of data is that these compounds are not typically regulated and therefore most labs do not include them in their standard mix. In addition, because method 507 does not require determination of MDLs, many labs have probably not actually done the determination.

COMPOUND SPECIFIC EVALUATION- SOILS

Reported data for analyses in soil was difficult to interpret. Many laboratories did not clearly indicate on the survey forms whether data was reported in units of ug/kg or mg/kg or instead in ug/l in the final extracts. This was true for both the New Jersey labs, for which data was taken from the NJDEP database, and the California labs surveyed directly. Wherever possible if it was obvious based on the reported concentrations, we converted data to ug/kg. The other difficulty with these data is that many laboratories do not determine MDLs on soils directly, but instead determine the MDLs on aqueous samples and then convert the data to soils based on the extraction ratio (eg. 30g soil instead of 1000 ml water, equivalent to an extraction ratio of 33). This should give lower apparent MDLs because it assumes 100% extraction efficiency relative to water and doesn't adequately assess the impact of the soil matrix on the method precision. With this caveat in mind, the soils data should be examined carefully. This also helps to explain why there are markedly wide ranges on much of the soils data. Given these potential problems with the soils data, conclusions regarding these data need to be carefully considered. The database for each of these constituents is small compared to the liquid data. In spite of these caveats it is still possible to perform the same analysis on the data.

Diethylhexylphthalate by 8270 in soil (Extraction with GC/MS analysis)

The database for this analysis is small, with only 7 labs reporting MDL data and only 10 labs providing MRL data. Many labs clearly indicated that they do not perform MDL determinations, but just use the lower reporting limits shown in SW846. The mean and the median MDLs are similar (227 and 219 ppb respectively). Individual reported MDLs ranged from 80 to 560 ppb. The median calibration ratio of 3 gives an RQL which is higher than all of the individual MDLs. Because the EPA recommended RQL uses a ratio of 4, the EPA RQL would be somewhat higher (900 ppb). The median reporting limit for laboratories (365 ppb) is below any of the calculated RQLs, indicating that laboratories are reporting data well below the range of accurate quantitation. Because this is a GC/MS method, with absolute identification possible based on mass spectra, positives reported at this level are qualitatively

meaningful if labs confirm the spectra. However it is also possible that many labs are reporting false positives based on the statistics (Reliable Detection Level= twice the MDL). All of the labs have a spike or calibration solution at or below the EPA RQL, and almost 90% of the labs should be able to quantify accurately at the calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	230	6	4	900	100%
Median	220	4	3	660	89%

Benzo(a)pyrene by 8270 in soil (Extraction with GC/MS analysis)

The database for this analysis is small, with only 7 labs reporting MDL data and only 10 labs providing MRL data. The same conclusions regarding the viability of the data can be made for this analysis as for DEHP. The mean and median MDLs are similar (148 and 187 ppb respectively). Individual reported MDLs ranged from 47 to 240 ppb. The median calibration ratio of 4 yields an RQL of 760 ppb, which is well above the MDLs reported by all labs. This would be the same as the "EPA RQL". Again the median reporting limit for the dataset (330 ppb) is below the RQL or the RDL, leading to the potential for false positives being reported by labs if they are not evaluating spectra. Over 100% of the labs have a spike or calibration solution at or below the EPA RQL or the calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	150	9	6	900	100%
Median	190	5	4	760	100%

Benzo(a)anthracene by 8270 in soil (Extraction with GC/MS analysis)

The database for this analysis is small, with only 7 labs reporting MDL data and only 11 labs providing MRL data. The same conclusions regarding the viability of the data can be made for this analysis as for DEHP. The mean and median MDLs are close (156 and 101 ppb respectively). Individual reported MDLs ranged from 40 to 320 ppb. The median calibration ratio of 7 yields an RQL of 700 ppb, which is well above the MDLs reported by all labs. The "EPA RQL" would be 400 ppb, still higher than all of the individual MDLs. Because the median reporting limit for the dataset (330 ppb) is below the RQL, there is a potential for false positives being reported by labs if they are not evaluating spectra, and clearly quantitation is questionable at these levels. All of the labs have a spike or calibration solution at or below the EPA RQL, and all should be able to quantify accurately at the calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	160	8	7	1100	100%
Median	100	7	7	700	100%

2,4-Dichlorophenol by 8270 in soil (Extraction with GC/MS analysis)

The database for this analysis is small, with only 5 labs reporting MDL data and only 9 labs providing MRL data. The smaller dataset is due to the uncertainty labs had in reporting the correct isomer for dichlorophenol. The same conclusions regarding the viability of the data can be made for this analysis as for DEHP. The mean and median MDLs are close (276 and 198 ppb respectively). Individual reported MDLs ranged from 40 to 600 ppb. The median calibration ratio of 3 yields an RQL of 600 ppb, which is above the MDLs reported by all labs. The "EPA RQL" would be 800 ppb, still higher than all of the individual MDLs. Again the median reporting limit for the dataset (330 ppb) is below the RQL or the RDL, leading to the potential for false positives being reported by labs if they are not evaluating spectra. 86% of the labs have a spike or calibration solution at or below the EPA RQL but only 57% should be able to quantify accurately at the calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	280	5	6	1400	100%
Median	200	5	3	600	57%

Pentachlorophenol by 8270 in soil (Extraction with GC/MS analysis)

The database for this analysis is small, with only 7 labs reporting MDL data and only 11 labs providing MRL data. The same conclusions regarding the viability of the data can be made for this analysis as for DEHP. Pentachlorophenol has extremely wide recovery limits when extracted, leading one to expect a wide range of results from separate labs. The mean and median MDLs are substantially different (1236 and 260 ppb respectively). Individual reported MDLs ranged from 143 to 6300 ppb. The median calibration ratio of 1 yields an RQL of 300 ppb, which is below the MDL reported by 3 out of 7 labs. In contrast, the "EPA RQL" would be 1000 ppb, still higher than 6 out of 7 individual MDLs. The median reporting limit for the dataset (450 ppb) is below the "EPA RQL" or the RDL (500 ppb), leading to the potential for false positives being reported by labs if they are not evaluating spectra. It is however above the "apparent" RQL based on the median from the dataset. This inconsistency with other analyses may be due to the wide range of data and limited dataset size. Over 75% of the labs have a spike or calibration solution at or below the EPA RQL, but none of the labs should be able to quantify accurately at the calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	1240	3	2	2500	86%
Median	260	2	1	300	0%

2,4,6-Trichlorophenol by 8270 in soil (Extraction with GC/MS analysis)

The database for this analysis is small, with only 7 labs reporting MDL data and only 11 labs providing MRL data. The same conclusions regarding the viability of the data can be made for this analysis as for DEHP. The mean and median MDLs are close (356 and 329 ppb respectively). Individual reported MDLs ranged from 47 to 1100 ppb. The median calibration ratio of 2 yields an RQL of 700 ppb, substantially above the MDL reported by 6 out of 7 labs. In contrast, the "EPA RQL" would be 1300 ppb, higher than all the individual MDLs. The median reporting limit for the dataset (330 ppb) is below the "EPA RQL" or the RDL, leading to the potential for false positives being reported by labs if they are not evaluating spectra. Over 89% of the labs have a spike or calibration solution at or below the EPA RQL, but only 75% of the labs should be able to quantify accurately at the calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	360	6	5	1800	89%
Median	330	7	2	700	75%

DDT by 8080 in soil (Extraction with GC/ECD analysis)

Data for all of the pesticides in soil is difficult to interpret because of both the wide range of reported MDLs leading us to question whether units are consistent, and the range of reported calibration levels, again possibly due to inconsistency in units. No data points were removed from this dataset except for one with an MDL greater than 10 times the mean for the dataset. Additional datapoints could have been removed based on the ratio of spike level to MDL, but the data have been left in because of the uncertainty in units. The database for this analysis is small, with only 14 labs reporting MDL data and only 11 labs providing MRL data. Because we had difficulty interpreting the calibration information for this analysis, ratios are based on the spike level only. The mean and median MDLs are substantially different (1.4 and 0.3 ppb respectively). Because of the questions regarding units, the median is a much better measure of the dataset than the mean for all parameters. Individual reported MDLs ranged from 0.07 to 13 ppb. The median spike ratio of 5 yields an RQL of 1.5 ppb, which is above the MDL reported by 12 out of 14 labs (86%). The "EPA RQL" would be 1.2 ppb, also higher than 12 out of 14 individual MDLs. The median reporting limit for the dataset (6 ppb) is well above the "EPA RQL". A more careful examination of these data is required before one can draw complete conclusions.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	1.4	18	NA	25	insufficient data
Median	0.3	5	NA	1.5	insufficient data

Chlordane by 8080 in soil (Extraction with GC/ECD analysis)

Data for chlordane is based on specific isomers (alpha or gamma chlordane) and the actual MDL and calculated RQL may not be meaningful for technical chlordane, which is a mixture of numerous isomers. No data points were removed from this dataset. The database for this analysis is small, with only 10 labs reporting MDL data and only 10 labs providing MRL data. Because we had difficulty interpreting the calibration information for this analysis, ratios are based on the spike level only. The mean and median MDLs are different (2.9 and 1.0 ppb respectively). Because of the questions regarding units, the median is a much better measure of the dataset than the mean for all parameters. Individual reported MDLs ranged from 0.23 to 10 ppb. The median spike ratio of 6 yields an RQL of 6 ppb, which is above the MDL reported by 8 out of 10 labs. The "EPA RQL" would be 4 ppb, also higher than 8 out of 10 individual MDLs. The median reporting limit for the dataset (30 ppb) is well above the "EPA RQL". Because most labs report chlordane detection levels for the mixture, the comparison of reporting levels to the RQL for this compound may not be appropriate. A more careful examination of these data is required before one can draw complete conclusions.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	2.9	7	NA	21	insufficient data
Median	1.0	6	NA	6	insufficient data

Toxaphene by 8080 in soil (Extraction with GC/ECD analysis)

Toxaphene is a mixture of numerous isomers and thus provides a good parameter to evaluate the RQL concept. One data point was removed from this dataset because the MDL was more than 10 times the mean MDL. The database for this analysis is small, with only 10 labs reporting MDL data and only 10 labs providing MRL data. Because we had difficulty interpreting the calibration information for this analysis, ratios are based on the spike level only. The mean and median MDLs are close (36 and 17 ppb respectively). Because of the questions regarding units, the median is a much better measure of the dataset than the mean for all parameters. Individual reported MDLs ranged from 1 to 167 ppb. The median spike ratio of 6 yields an RQL of 102 ppb, which is above the MDL reported by 9 out of 10 labs. The "EPA RQL" would be 68 ppb, also higher than 9 out of 10 individual MDLs. The median reporting limit for the dataset (100 ppb) is above the "EPA RQL".

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	36	6	NA	220	insufficient data
Median	17	6	NA	140	insufficient data

Aldrin by 8080 in soil (Extraction with GC/ECD analysis)

The database for this analysis is small, with only 14 labs reporting MDL data and only 10 labs providing MRL data. Because we had difficulty interpreting the calibration information for this analysis, ratios are based on the spike level only. The mean and median MDLs are significantly different (1.1 and 0.3 ppb respectively). Because of the questions regarding units, the median is a much better measure of the dataset than the mean for all parameters. Individual reported MDLs ranged from 0.08 to 10 ppb. The median spike ratio of 5 yields an RQL of 1.4 ppb, which is above the MDL reported by 12 out of 14 labs. The "EPA RQL" would be 1.1 ppb, also higher than 12 out of 14 individual MDLs. The median reporting limit for the dataset (3 ppb) is above the "EPA RQL". Most labs use a reporting limit which is above the RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	1.1	11	NA	120	insufficient data
Median	0.28	5	NA	1.4	insufficient data

Dieldrin by 8080 in soil (Extraction with GC/ECD analysis)

The database for this analysis is small, with only 13 labs reporting MDL data and only 9 labs providing MRL data. Because we had difficulty interpreting the calibration information for this analysis, ratios are based on the spike level only. The mean and median MDLs are significantly different (0.7 and 0.3 ppb respectively). Because of the questions regarding units, the median is a much better measure of the dataset than the mean for all parameters. Individual reported MDLs ranged from 0.07 to 3.8 ppb. The median spike ratio of 5 yields an RQL of 1.5 ppb, which is above the MDL reported by 12 out of 13 labs. The "EPA RQL" would be 1.2 ppb, higher than 11 out of 13 individual MDLs. The median reporting limit (3.3 ppb) is above the "EPA RQL". Almost all labs use a reporting limit which is above the calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	0.7	9	NA	6.3	insufficient data
Median	0.3	5	NA	1.5	insufficient data

Lindane by 8080 in soil (Extraction with GC/ECD analysis)

The database for this analysis is small, with only 13 labs reporting MDL data and only 9 labs providing MRL data. Because we had difficulty interpreting the calibration information for this analysis, ratios are based on the spike level only. The mean and median MDLs are significantly different (2.0 and 0.3 ppb respectively). Because of the questions regarding units, the median is a much better measure of the dataset than the mean for all parameters. Individual reported MDLs ranged from 0.05 to 20 ppb. The median spike ratio of 5 yields an RQL of 1.5 ppb, which is above the MDL reported by 11 out of 13 labs. The "EPA RQL" would be 1.2 ppb,

also higher than 11 out of 13 individual MDLs. The median reporting limit (2.7 ppb) is above the "EPA RQL". Almost all labs use a reporting limit which is above the calculated RQL.

Statistic	MDL	Spike Ratio	Calibration Ratio	RQL	% quantifying at RQL
Mean	2.0	8	NA	16	insufficient data
Median	0.3	5	NA	1.5	insufficient data

CONCLUSIONS

Several conclusions are possible from these data. The concept of an RQL is defined here as the concentration above which most laboratories can reliably detect and quantify a given compound and represents a meaningful reporting limit which takes into account matrix effects. No precision information per se is included in the RQL. That is, it is not possible to state the expected precision of a given reported value at the RQL. The RQL is estimated by comparing ratios of interlaboratory data on MDLs, spike levels, and calibration levels. The median MDL is considered the best measure for calculating the RQL.

Although based on anecdotal evidence only, most MDL determinations reported by individual laboratories likely involve reagent water. The use of an interlaboratory database allows one to propose a meaningful reporting limit which is applicable to more complex matrices. Interlaboratory data based on reagent water includes some measure of the random errors also present in more complex matrices. Systematic biases due to matrix are not included in the data we have and could cause an RQL to be underestimated in these cases. It should still be noted that any individual sample may have so many interferences present that the RQL could not be achieved in any laboratory. These types of biases would be evident from analysis of spiked samples. In addition it is clear that some additional work is desirable to extend the applicability of the proposed approaches and to provide additional validation.

When sufficient data are available on interlaboratory detection limit determinations, it is viable to use a multiplier of the detection limit to estimate a reliable quantitation level (RQL). Data from as little as five (5) laboratories appears to still yield meaningful information. Comparison of spike levels or calibration levels to individual method detection limit determinations yields a variety of multipliers ranging from 2 to 11 (which would result in over a five fold difference in the proposed reliable quantitation level). To apply this approach to any regulated compound would therefore require evaluation of both MDL and calibration or spike data from a number of laboratories, which is impractical. Although this is clearly the most accurate approach (eg. a compound specific multiplier), a generic multiplier concept appears to work.

A multiplier of 3-5 appears to be a good estimator, yielding an RQL which is consistently above the majority of the MDLs calculated in any individual laboratory and falls above the low point of the calibration curve or spike concentration in most cases. Table 3 summarizes these results. As critical as the choice of multiplier is the review of the data used to generate MDL determinations. Inclusion of inadequate MDL determinations may lead to large errors in estimating the interlaboratory MDL, especially if mean MDLs are used.

The use of spike and calibration ratios pose some problems in performing calculations and data analysis in that they are inconsistently generated. In many cases the calculated interlaboratory MDL may be higher than what the method can actually achieve because the spiking level may be governed by the calibration range. For instance, this is clearly the case with method 624, which has a defined low calibration point of 5-10 ug/L, in comparison to method 524.2 which has a low calibration point of 0.5-2 ppb. Were spiking and/or calibration performed at lower concentrations, method 624 could perhaps go lower. One would inherently expect that method 624 (which uses a 5 ml purge) should have MDLs for most compounds approximately a factor of 5 higher than method 524.2, which uses a 25 ml purge. Our data suggest that the interlab MDLs for method 624 are a factor of 3-5 higher than the interlab MDLs for the same compounds analyzed by method 524.2, but calculated MDLs for either method in individual labs vary so widely that it is clear there is some inconsistency in the manner used to generate the supporting data.

Should the multiplier approach be implemented for standard setting in New Jersey, it is crucial that labs be able to demonstrate adequate quantitation at the RQL. The State should therefore require that labs include a standard or check sample at the RQL to verify quantitation. Ideally such a requirement should be included in the methods themselves, but it is not currently included in most methods.

Using a multiplier would require evaluation only of interlaboratory MDL determinations, which can be extracted from a variety of sources including Performance Evaluation samples (PE studies), as long as true values are relatively close (less than 50 times) the MDL. Again, data from as few as five laboratories appears to yield meaningful results. Table 3 summarizes data on RQLs for all compounds studied.

Soils data requires further evaluation because most MDL determinations on soil have not used actual spiked soils and therefore involve many assumptions. In spite of these caveats, the use of a multiplier of 3-5 appears to be applicable even to soils, at least based on comparisons of individual laboratory determined MDLs on soils to a proposed RQL.

RECOMMENDATIONS

To extend this work, we recommend that additional MDL data be gathered on soils and a firm statistical evaluation of the number of laboratories required to generate reliable datasets be performed. It should be possible to take some of the larger datasets (eg. volatiles) and censor random data to determine when the use of a 3-5X multiplier no longer provided a reliable estimate. We also recommend that the State require MDL data of the sort used for this analysis for all reportable parameters from certified laboratories in order to insure that labs are reporting data at meaningful levels. Evaluation of the data presented in this study shows that many individual labs report quantitative data well below the calibration curve, although this is not good science. By requiring the use of RQL check samples on all analytical runs, the State would be able to increase the confidence that reliable data were being generated at this concentration. This would put New Jersey in the forefront of States with reliable data to support regulatory compliance limits.

Table 1: Summary of "Acceptable MDL" Datapoints by Source

Analysis parameter	Method	Matrix	# ACTL	# NJLabs	Total
Copper	220.2	water	4	11	15
Lead	239.2	water	10	29	39
Cadmium	213.2	water	8	20	28
1,1,2-trichloroethane	524.2	water	6	13	19
1,1,2,2-tetrachloroethane	524.2	water	7	13	20
1,2-dichloropropane	524.2	water	7	14	21
carbon tetrachloride	524.2	water	7	14	21
trichloroethylene	524.2	water	8	14	22
chloroform	524.2	water	6	14	20
trichloroethylene	624	wastewater	8	30	38
1,1,1-trichloroethane	624	wastewater	9	30	39
chloroform	624	wastewater	8	30	38
carbon tetrachloride	624	wastewater	8	30	38
tetrachloroethylene	624	wastewater	10	30	40
dichlorobenzene	624	wastewater	7	24	31
bis(2-ethylhexyl)phthalate	625	water	10	29	39
benzo(a)pyrene	625	water	10	30	40
benzo(a)anthracene	625	water	9	29	38
2,4-dichlorophenol	625	water	4	29	33
pentachlorophenol	625	water	9	28	37
2,4,6-trichlorophenol	625	water	10	29	39
atrazine	507	water	4	1	5
simazine	507	water	4	1	5
alachlor	507	water	3	0	3
metolachlor	507	water	1	0	1
Diazinon	507	water	1	0	1
bis(2-ethylhexyl)phthalate	8270	soil	6	1	7
benzo(a)pyrene	8270	soil	6	1	7
benzo(a)anthracene	8270	soil	6	1	7
2,4-dichlorophenol	8270	soil	4	1	5
pentachlorophenol	8270	soil	6	1	7
2,4,6-trichlorophenol	8270	soil	6	1	7
DDT	8080	soil	8	6	14
chlordan	8080	soil	3	7	10
toxaphene	8080	soil	4	7	11
aldrin	8080	soil	7	7	14
dieldrin	8080	soil	5	7	12
lindane	8080	soil	6	7	13

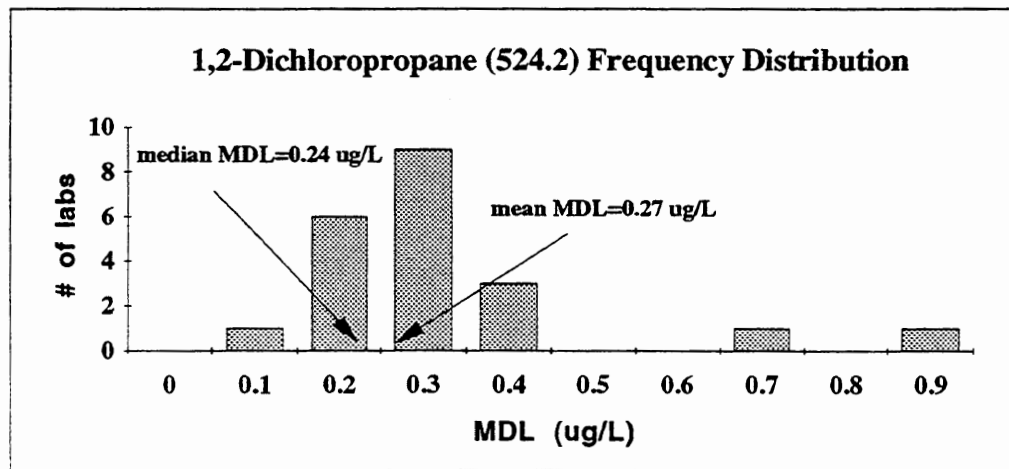
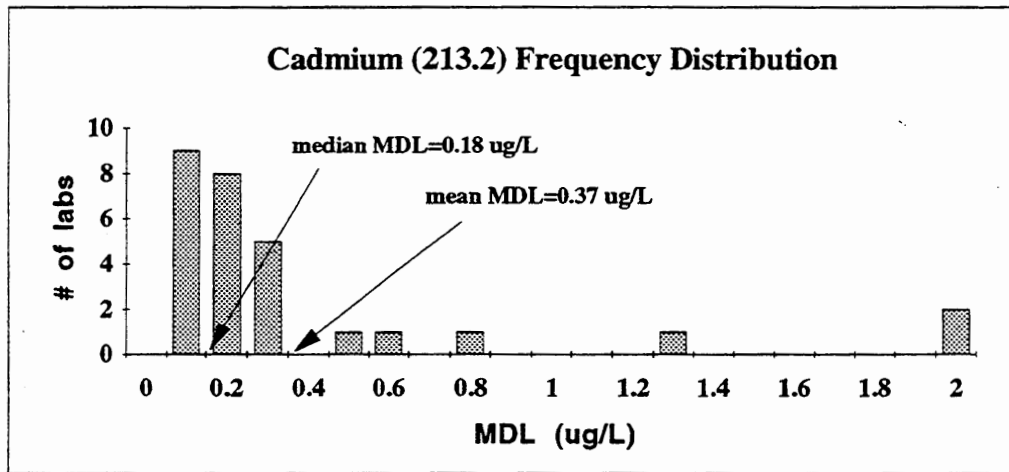
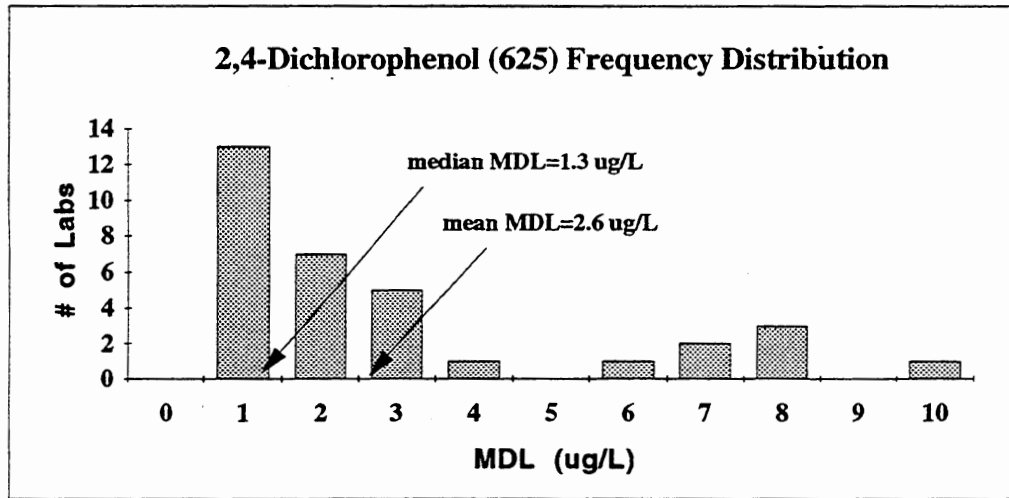
Table 2: Comparison Statistics for Database

Compound	Mean	Median	Standard Dev	Variance	F Value	t statistic	Significance
Cadmium	0.4	0.18	0.53	0.2809	1.28	0.00	none
Cadmium no outliers	0.4	0.2	0.6	0.36			
TCE 524	0.3	0.22	0.18	0.0324	1.00	0.00	none
TCE 524 no outliers	0.3	0.24	0.18	0.0324			
TCE 624	1.2	0.9	1.2	1.44	1.17	-0.33	none
TCE 624 no outliers	1.3	0.9	1.3	1.69			
CCl4 624	1	0.73	0.77	0.5929	1.08	-0.53	none
CCl4 624 no outliers	1.1	0.95	0.8	0.64			
DEHP 625	3	2.7	3	9	1.14	-0.67	none
DEHP 625 no outliers	3.5	2.9	3.2	10.24			
BAP 625	2	1.5	2.3	5.29	1.38	-0.83	none
BAP 625 no outliers	2.5	1.9	2.7	7.29			
DDT 8080	4.6	0.3	13	169	1.33	-0.08	none
DDT 8080 no outliers	5.1	0.4	15	225			

Table 3: Summary of MDLs, RQLs, and Percent of Labs meeting RQL

Method	Compound	Interlab MDL (ug/L)	Median Spike Level	Median Low Calibration Level	Calculated RQL (ug/L)	EPA RQL (ug/L)	% of Labs theoretically able to quantify at EPA RQL	% of Labs theoretically able to quantify at Calculated RQL
220.2	Copper	1	5	5	4	4	60%	60%
239.2	Lead	1.3	6	5	5.2	5.2	77%	77%
213.2	Cadmium	0.18	1	1	0.7	0.7	57%	57%
524.2	1,1,2-Trichloroethane	0.25	1	2	1	1	68%	68%
524.2	1,1,2,2-tetrachloroethane	0.31	1	2	1.2	1.2	65%	65%
524.2	1,2-dichloropropane	0.24	1	2	1.4	1	67%	67%
524.2	Carbon Tetrachloride	0.2	1	2	1	0.8	29%	71%
524.2	TCE	0.22	1	2	1.1	0.9	32%	68%
524.2	Chloroform	0.22	1	2	1.1	0.9	30%	70%
624	TCE	0.89	5	20	5.4	3.6	32%	74%
624	1,1,1-Trichloroethane	0.83	5	20	5	3.3	31%	72%
624	Chloroform	0.74	5	20	5.9	3	29%	74%
624	Carbon Tetrachloride	0.73	5	20	5.1	2.9	32%	71%
624	Tetrachloroethene	0.9	5	20	5.4	3.6	28%	70%
624	Dichlorobenzenes	1	5	20	5	4	35%	61%
625	DEHP	2.7	10	20	14	11	77%	74%
625	benzo(a)pyrene	1.5	10	20	12	6	33%	70%
625	benzo(a)anthracene	1.1	10	20	11	4.4	18%	74%
625	2,4-Dichlorophenol	1.3	10	20	8	5.2	33%	33%
625	Pentachlorophenol	3.1	20	20	16	12	49%	49%
625	2,4,6-Trichlorophenol	1.8	20	20	11	7.2	28%	54%
507	Atrazine	0.24	2.3	0.8	0.5	1	75%	44%
507	Simazine	0.29	2.3	0.95	0.6	1.2	88%	44%
8270	DEHP	220	835	670	660	900	100%	89%
8270	Benzo(a)pyrene	190	835	670	760	760	89%	100%
8270	Benzo(a)anthracene	100	665	670	700	400	44%	100%
8270	2,4-Dichlorophenol	200	500	670	600	800	86%	57%
8270	Pentachlorophenol	260	1165	670	300	1000	78%	0%
8270	2,4,6-Trichlorophenol	330	830	670	700	1300	78%	6%
8080	DDT	0.3	2	4.5	1.5	1.2	insufficient data	insufficient data
8080	Chlordane	1	4	4	6	4	insufficient data	insufficient data
8080	Toxaphene	17	83	-	100	68	insufficient data	insufficient data
8080	Aldrin	0.28	2	2	1.4	1.1	insufficient data	insufficient data
8080	Dieldrin	0.3	1.7	2.5	1.5	1.3	insufficient data	insufficient data
8080	Lindane	0.3	1.4	2.5	1.5	1.2	insufficient data	insufficient data

Figure 1: Cumulative Frequency Distributions for Selected Tests



2,4 Dichlorophenol and Cadmium have very different mean and median MDLs, while 1,2-Dichloropropane has a similar mean and median MDL.

APPENDIX A

RAW DATA FOR MDL SURVEY

njdep cu
2/9/93

MDL/RDL/PQL database form

#	Parameter	Method	Matrix	Tot #								
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
	Copper	220.2	Water	15								
N	01289	0.08	0.5	1						6	13	
N	77903	0.14	1	3						7	21	
N	77319	0.20	0.5	0.3	0.5	1	3			3	2	
C	C001	0.35	5	1	10	25			1	14	3	1
N	77166	0.77	2.5	25						3	32	
C	C002	0.79	6	5	25	50			2	8	6	0.4
C	C003	0.88	10						1	11		
N	77360	1.0	5	5						5	5	
N	16107	1.1	1	5						1	5	
C	C004	1.2	2.5	5	10	20	30	40	10	2	4	2.0
N	77886	1.2	6	5						5	4	
N	84890	1.7	5	5						3	3	
N	08235	1.7	5	2						3	1	
N	07673	2.0	10	10						5	5	
N	77434	2.7	10	2						4	1	
	MEAN	1.1	4.7	5.3	11	24	17	40	4	5	7	1.1
	MEDIAN	1.0	5	5	10	23	17	40	2	5	4	1.0
	MAXIMUM	2.7	10	25	25	50	30	40	10	14	32	2.0
	MINIMUM	0.08	0.5	0.3	1	1	3	40	1	1	1	0.4
	STANDARD DEVIATION	0.7	3.4	6.2	10	20	19		4	4	9	0.8

#	Parameter	Method	Matrix	Tot #								
	Lead	239.2	Water	39								
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
N	77319	0.07	0.5	0.5	1	3	10	30		7	7	
N	84890	0.28	2.5	2.5						9	9	
N	61667	0.32	1	1						3	3	
N	77903	0.35	2.5	10						7	29	
C	C001	0.35	5	1	10	25			1	14	3	1
N	20044	0.68	2	5						3	7	
N	01289	0.75	2	10						3	13	
C	C005	0.8	2	1	25	100			1	3	1	1.0
N	81446	0.9	5	2.5						6	3	
C	C006	0.9	10	20	40	50	60		5	11	22	0.3
C	C004	0.9	2	4	8	10	20	30	5	2	4	1.3
N	77166	0.96	2	10						2	10	
N	77360	1	5	10						5	10	
N	54457	1	10	5	10	20	30	50	5	10	5	1.0
N	11118	1	10	25						10	25	
N	73361	1	5	3						5	3	
C	C007	1	10	50	100				5	10	50	0.1
N	18725	1.2	5	20						4	17	
N	49529	1.3	5	5						4	4	
N	73581	1.3	10	4						8	3	
C	C002	1.3	6	3	30	60			2	5	2	0.7
N	77175	1.4	10	2						7	1	
N	55735	1.4	10	5						7	4	
N	77600	1.6	10	3						6	2	
C	C008	1.7	20	25	50	100			5	12	15	0.2
N	73771	1.8	20	25						11	14	
N	07673	2	10	10						5	5	
N	08235	2	5	5						3	3	
C	C009	2	10	2	5	10	15	20	2	5	1	1.0
N	16107	2.1	2	2						1	1	
N	02046	2.3	10	5						4	2	
N	73812	2.4	10	25						4	10	
N	07059	2.5	2	5						1	2	
C	C010	2.5	10	5	10	15	20	50	5	4	2	1.0
N	77434	3.2	20	2						6	1	
N	77886	3.3	6	5						2	2	
N	12543	3.5	25	25						7	7	
C	C003	4	10						5	3		
N	73469	5	10	5						2	1	
MEAN		1.6	8	9	26	39	26	36	4	6	8	0.7
MEDIAN		1.3	6	5	10	23	20	30	5	5	4	1.0
MAXIMUM		5	25	50	100	100	60	50	5	14	50	1.3
MINIMUM		0.07	0.5	0.5	1	3	10	20	1	0.8	1	0.1
STANDARD DEVIATION		1.1	6	10	29	37	18	13	2	3	10	0.4
Data Points Removed												
C	C011	2	2000	2	5	10	20		2	1000	1	1.0

#	Parameter	Method	Matrix	Tot #								
	Cadmium	213.2	Water	28								
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
N	01289	0.03	0.1	0.5						3	17	
N	77319	0.03	0.05	0.05	0.1	0.3	0.5	1		1	1	
N	61667	0.05	0.25	0.25						5	5	
N	20044	0.07	0.25	0.25						4	4	
C	C001	0.07	1	0.25	0.5	1	2.5		0.5	14	4	2
C	C007	0.09	1	5	10				1	11	56	0.2
N	77360	0.1	1.5	1						15	10	
N	11118	0.1	1	2.5						10	25	
C	C002	0.1	0.5	1	2	3			0.1	5	10	0.1
N	49529	0.12	0.5	0.5						4	4	
N	77903	0.12	1.5	1						13	8	
N	77166	0.13	0.5	1.25						4	10	
N	18725	0.15	1	2						7	13	
N	77886	0.16	0.3	0.5						2	3	
N	54457	0.2	1	0.5	1	2	3	5	1	5	3	2.0
C	C005	0.2	0.5	10	25				0.5	3	50	0.1
C	C008	0.2	2	0.5	1	2			1	10	3	2.0
N	84890	0.24	0.5	0.5						2	2	
N	55735	0.26	1	1						4	4	
N	16107	0.26	0.5	0.5						2	2	
N	73361	0.3	5	2.5						17	8	
C	C004	0.3	0.4	0.8	1	2	4	6	1	1	3	1.3
C	C009	0.5	2	0.5	1	2			1	4	1	2.0
N	08235	0.56	2	2						4	4	
C	C003	0.8	10						1	13		
N	77434	1.3	5	2						4	2	
N	07673	2	10	25						5	13	
N	73771	2	2	5						1	3	
MEAN		0.37	2	2	5	2	2.5		0.8	6	10	1.2
MEDIAN		0.18	1	1	1	2	2.75		1	4	4	1.6
MAXIMUM		2	10	25	25	3	4		1	17	56	2.0
MINIMUM		0.03	0.05	0.05	0.1	0.3	0.5		0.1	0.5	1	0.1
STANDARD DEVIATION		0.53	2.6	5.0	8.2	0.9	1.5		0.34	5	14	0.9
Data Points Removed												
C	C011	0.6	2000	0.5	1	2	4		0.6	3333	1	1.2

#	Parameter	Method	Matrix	Tot #								
	1,1,2-Trichloroethane	524.2	Water	19								
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
C	C010	0.03	0.1	0.5	2.5	5	10	30	0.1	3	17	0.2
C	C005	0.13	1	0.5	1	2	5	10	0.5	8	4	1.0
N	55735	0.14	1	2						7	14	
N	01289	0.16	2	2						13	13	
N	74603	0.2	1	1						5	5	
N	61667	0.21	0.5	2						2	10	
N	07059	0.22	1	2						5	9	
N	77360	0.23	2	2						9	9	
C	C009	0.23	2	2	4	10	20	40	0.5	9	9	0.3
N	18725	0.25	1	2						4	8	
C	C002	0.33	1	2	4	10	20	30	0.5	3	6	0.3
N	73331	0.34	2	0.5						6	1	
N	49529	0.41	1	1						2	2	
N	77434	0.42	1	4						2	10	
C	C001	0.44	1	1	2	5	10	20	0.5	2	2	0.5
N	20044	0.47	0.4	0.5						1	1	
C	C007	0.55	2	5	10	15	30	40	0.5	4	9	0.1
N	77166	0.59	2	2	5	10	25	50		3	3	
N	73469	1.1	4	4						4	4	
MEAN		0.34	1	2	4	8	17	31	0.4	5	7	0.4
MEDIAN		0.25	1	2	4	10	20	30	0.5	4	8	0.3
MAXIMUM		1.1	4	5	10	15	30	50	0.5	13	17	1.0
MINIMUM		0.03	0.1	0.5	1	2	5	10	0.1	0.9	1	0.1
STANDARD DEVIATION		0.24	0.9	1	3	4	9	13	0.16	3	4	0.3
Data Points Removed												
C	C003	0.009	0.5	2	5	10	20		0.1	56	222	0.1
C	C012	0.13	10	4	10	20	30	40	1	77	31	0.3
C	C006	8	50	20	50	100	150	200	10	6	3	0.5
N	77175	0.16	5	20						31	125	

#	Parameter	Method	Matrix	Tot #								
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
	1,1,2,2-Tetrachloroethane	524.2	Water	20								
C	C010	0.02	0.1	0.5	2.5	5	10	30	0.1	5	25	0.2
C	C002	0.14	1	2	4	10	20	30	0.5	7	14	0.3
N	77360	0.15	2	2						13	13	
N	18725	0.16	1	2						6	13	
N	01289	0.17	2	2						12	12	
N	55735	0.21	1	2						5	10	
C	C012	0.21	4	4	10	20	30	40	1	19	19	0.3
N	20044	0.26	0.4	0.5						2	2	
C	C007	0.29	2	5	10	15	30	40	0.5	7	17	0.1
N	61667	0.3	0.5	2						2	7	
C	C009	0.31	2	2	4	10	20	40	0.5	6	6	0.3
N	77434	0.39	1	4						3	10	
C	C001	0.39	1	1	2	5	10	20	0.5	3	3	0.5
N	73331	0.41	2	0.5						5	1	
N	77166	0.48	2	2	5	10	25	50		4	4	
C	C005	0.49	1	0.5	1	2	5	10	0.5	2	1	1.0
N	07059	0.51	1	2						2	4	
N	49529	0.61	1	1						2	2	
N	74603	0.64	1	3						2	5	
N	73469	2.1	4	4						2	2	
	MEAN	0.41	2	2	5	10	19	33	0.5	5	8	0.4
	MEDIAN	0.31	1	2	4	10	20	35	0.5	4	7	0.3
	MAXIMUM	2.1	4	5	10	20	30	50	1	19	25	1.0
	MINIMUM	0.02	0.1	0.5	1	2	5	10	0.1	2	1	0.1
	STANDARD DEVIATION	0.43	1.0	1.3	3.4	5.8	9.5	12.8	0.3	5	7	0.3
Data Points Removed												
C	C003	0.008	0.5	2	5	10	20		0.04	63	250	0.0
C	C006	6	50	20	50	100	150	200	20	8	3	1.0
N	77175	0.33	5	20						15	61	

Parameter		Method	Matrix	Tot #								
1,2-Dichloropropane		524.2	Water	21								
#	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
C	C010	0.04	0.1	0.5	2.5	5	10	30	0.1	3	13	0.2
N	07059	0.11	1	2						9	18	
N	55735	0.15	1	2						7	13	
N	49529	0.15	1	1						7	7	
N	77360	0.17	2	2						12	12	
C	C005	0.18	1	0.5	1	2	5	10	0.5	6	3	1.0
N	01289	0.19	2	2						11	11	
N	16107	0.21	1	0.3						5	1	
N	18725	0.22	1	2						5	9	
C	C009	0.23	2	2	4	10	20	40	0.5	9	9	0.3
N	73331	0.24	2	0.5						8	2	
N	20044	0.24	0.4	0.5						2	2	
N	77434	0.25	1	4						4	16	
C	C012	0.25	4	4	10	20	30	40	1	16	16	0.3
C	C002	0.26	1	2	4	10	20	30	0.5	4	8	0.3
N	61667	0.27	0.5	2						2	7	
C	C007	0.32	2	5	10	15	30	40	0.5	6	16	0.1
N	77166	0.36	2	2	5	10	25	50		6	6	
C	C001	0.37	1	1	2	5	10	20	0.5	3	3	0.5
N	74603	0.64	1	1						2	2	
N	73469	0.9	4	4						4	4	
MEAN		0.27	1	2	5	10	19	33	0.5	6	8	0.4
MEDIAN		0.24	1	2	4	10	20	35	0.5	6	8	0.3
MAXIMUM		0.9	4	5	10	20	30	50	1	16	18	1.0
MINIMUM		0.04	0.1	0.3	1	2	5	10	0.1	1.6	1	0.1
STANDARD DEVIATION		0.19	1.0	1	3	6	10	13	0	4	5	0.3
Data Points Removed												
C	C003	0.01	0.5	2	5	10	20		0.02	50	200	0.0
N	77175	0.05	5	20						100	400	
C	C006	4	50	20	50	100	150	200	20	13	5	1.0

#	Parameter	Method	Matrix	Tot #								
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
	Carbon Tetrachloride	524.2	Water	21								
C	C010	0.05	0.1	0.5	2.5	5	10	30	0.1	2	10	0.2
C	C005	0.067	1	0.5	1	2	5	10	0.5	15	7	1.0
N	77434	0.07	1	4						14	57	
N	18725	0.09	1	2						11	22	
N	07059	0.1	1	2						10	20	
N	20044	0.12	0.4	0.5						3	4	
N	74603	0.16	1	1						6	6	
N	55735	0.16	1	2						6	13	
C	C007	0.16	2	5	10	15	30	40	0.5	13	31	0.1
C	C003	0.18	0.5	2	5	10	20		0.21	3	11	0.1
N	77360	0.2	2	2						10	10	
N	61667	0.2	0.5	2						3	10	
N	16107	0.24	1	0.3						4	1	
N	73331	0.24	2	0.5						8	2	
C	C002	0.26	1	2	4	10	20	30	0.5	4	8	0.3
C	C001	0.27	1	1	2	5	10	20	0.5	4	4	0.5
C	C009	0.36	2	2	4	10	20	40	0.5	6	6	0.3
N	01289	0.396	2	2						5	5	
N	49529	0.4	1	1						3	3	
N	77166	0.49	2	2	5	10	25	50		4	4	
N	73469	0.8	4	4						5	5	
	MEAN	0.24	1	2	4	8	18	31	0.4	7	11	0.3
	MEDIAN	0.20	1	2	4	10	20	30	0.5	5	7	0.3
	MAXIMUM	0.8	4	5	10	15	30	50	0.5	15	57	1.0
	MINIMUM	0.05	0.1	0.3	1	2	5	10	0.1	2.0	1	0.1
	STANDARD DEVIATION	0.18	0.9	1.2	3	4	8	13	0.17	4	13	0.3
Data Points Removed												
N	77175	0.07	5	20						71	286	
C	C012	0.17	10	4	10	20	30	40	1	59	24	0.3
C	C006	12	50	20	50	100	150	200	10	4	2	0.5

#	Parameter	Method	Matrix	Tot #								
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
	TCE	524.2	Water	22								
C	C010	0.04	0.1	0.5	2.5	5	10	30	0.1	3	13	0.2
N	77434	0.07	1	4						14	57	
N	18725	0.09	1	2						11	22	
C	C003	0.1	0.5	2	5	10	20		0.19	5	20	0.1
N	07059	0.1	1	2						10	20	
N	20044	0.12	0.4	0.5						3	4	
N	74603	0.16	1	1						6	6	
N	55735	0.16	1	2						6	13	
C	C005	0.19	1	0.5	1	2	5	10	0.5	5	3	1.0
N	77360	0.2	2	2						10	10	
N	61667	0.2	0.5	2						3	10	
C	C002	0.23	1	2	4	10	20	30	0.5	4	9	0.3
N	16107	0.24	1	0.3						4	1	
N	73331	0.24	2	0.5						8	2	
C	C001	0.29	1	1	2	5	10	20	0.5	3	3	0.5
N	01289	0.4	2	2						5	5	
N	49529	0.4	1	1						3	3	
C	C008	0.41	2	5	10	20			0.5	5	12	0.1
C	C009	0.43	2	2	4	10	20	40	0.5	5	5	0.3
C	C007	0.46	2	5	10	15	30	40	0.5	4	11	0.1
N	77166	0.49	2	2	5	10	25	50		4	4	
N	73469	0.8	4	4						5	5	
	MEAN	0.26	1	2	5	10	18	31	0.4	6	11	0.3
	MEDIAN	0.22	1	2	4	10	20	30	0.5	5	7	0.2
	MAXIMUM	0.8	4	5	10	20	30	50	0.5	14	57	1.0
	MINIMUM	0.04	0.1	0.3	1	2	5	10	0.1	2.5	1	0.1
	STANDARD DEVIATION	0.18	0.8	1.4	3.2	5.5	8.5	13.5	0.17	3	12	0.3
Data Points Removed												
N	77175	0.07	5	20						71	286	
C	C012	0.18	10	4	10	20	30	40	1	56	22	0.3
C	C006	7	50	20	50	100	150	200	10	7	3	0.5

#	Parameter	Method	Matrix	Tot #								
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
	Chloroform	524.2	Water	20								
C	C010	0.03	0.1	0.5	2.5	5	10	30	0.1	3	17	0.2
N	49529	0.08	1	1						13	13	
C	C005	0.08	1	0.5	1	2	5	10	0.5	13	6	1.0
N	77434	0.09	1	4						11	44	
N	20044	0.12	0.4	0.5						3	4	
C	C007	0.12	2	5	10	15	30	40	0.5	17	42	0.1
N	74603	0.13	1	1						8	8	
N	55735	0.16	1	2						6	13	
N	07059	0.17	1	2						6	12	
C	C001	0.2	1	1	2	5	10	20	0.5	5	5	0.5
N	16107	0.24	1	0.3						4	1	
C	C002	0.24	1	2	4	10	20	30	0.5	4	8	0.3
N	18725	0.25	1	2						4	8	
N	61667	0.26	0.5	2						2	8	
N	73331	0.27	2	0.5						7	2	
N	01289	0.28	2	2						7	7	
C	C009	0.41	2	2	4	10	20	40	0.5	5	5	0.3
N	77166	0.42	2	2	5	10	25	50		5	5	
N	77360	0.61	2	2						3	3	
N	73469	0.9	4	4						4	4	
	MEAN	0.25	1	2	4	8	17	31	0.4	7	11	0.4
	MEDIAN	0.22	1	2	4	10	20	30	0.5	5	7	0.3
	MAXIMUM	0.9	4	5	10	15	30	50	0.5	17	44	1.0
	MINIMUM	0.03	0.1	0.3	1	2	5	10	0.1	1.9	1	0.10
	STANDARD DEVIATION	0.21	0.9	1	3	4	9	13	0.16	4	12	0.3
Data Points Removed												
C	C012	0.17	10	4	10	20	30	40	1	59	24	0.3
C	C003	0.007	0.5	2	5	10	20		0.03	71	286	0.0
N	77175	0.05	5	20						100	400	
C	C006	4	50	20	50	100	150	200	10	13	5	0.5

#	Parameter	Method	Matrix	Tot #								
	Trichloroethylene	624	Water	38								
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
N	07059	0.1	2	5						20	50	
N	49529	0.11	2	20						18	182	
C	C002	0.13	1	10	20	50	100	200	1	8	77	0.1
N	74487	0.16	1	20						6	125	
C	C010	0.2	0.5	0.5	2.5	5	10	30	0.5	3	3	1.0
N	02046	0.24	2	20	50					8	83	
N	64777	0.3	2	10						7	33	
N	12543	0.34	5	10						15	29	
N	77434	0.4	5	20						13	50	
N	73771	0.4	5	20						13	50	
N	18725	0.47	2	20						4	43	
N	61667	0.49	2	20						4	41	
C	C013	0.61	0.5	20	50	100	150	200		1	33	
N	79795	0.7	5	10						7	14	
N	88608	0.7	5	10						7	14	
N	77443	0.71	2	20						3	28	
N	81446	0.72	4	10						6	14	
N	84861	0.8	2	20						3	25	
N	77903	0.88	5	5						6	6	
N	73581	0.9	10	5						11	6	
C	C001	0.92	5	20	50	100	150	200	5	5	22	0.25
N	73469	0.92	10	20						11	22	
N	73723	0.93	5	20						5	22	
N	55735	0.94	5	20						5	21	
N	77175	0.98	5	20						5	20	
C	C011	1	5	10	20	50	100	200	1	5	10	0.1
N	82313	1.04	10	10						10	10	
N	07633	1.3	5	5	20					4	4	
N	20044	1.43	4.5	5						3	3	
N	77600	1.7	20	20						12	12	
C	C009	1.8	10	20	50	100	150	200	5	6	11	0.3
N	02565	2	5	20						3	10	
N	73331	2.03	10	20						5	10	
C	C008	2.1	10	25	50	100			5	5	12	0.2
N	11118	2.7	10	10						4	4	
N	54720	2.8	20	20						7	7	
N	77166	2.9	20	20	100	200				7	7	
C	C006	7	50	20	50	100	150	200	20	7	3	1.0
MEAN		1.2	7	15	42	89	116	176	5.4	7	29	0.4
MEDIAN		0.89	5	20	50	100	150	200	5	6	17	0.3
MAXIMUM		7	50	25	100	200	150	200	20	20	182	1.0
MINIMUM		0.1	0.5	0.5	2.5	5	10	30	0.5	0.8	3	0.1
STANDARD DEVIATION		1.24	8.8	7	26	54	52	64	6.79	4	36	0.4
Data Points Removed												
C	C003	0.009	15	20	50	100	150	200	4.1	1667	2222	0.2

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MDL/RDL/PQL database form

#	Parameter		Method	Matrix	Tot #							
	1,1,1-Trichloroethane		624	Water	39							
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
C	C002	0.07	1	10	20	50	100	200	1	14	143	0.1
N	07059	0.1	1	2						10	20	
C	C010	0.1	0.5	0.5	2.5	5	10	30	0.5	5	5	1.0
N	64777	0.2	2	10						10	50	
N	73771	0.3	5	20						17	67	
N	81446	0.33	4	10						12	30	
N	12543	0.34	5	10						15	29	
N	77434	0.38	5	20						13	53	
N	88608	0.4	5	10						13	25	
C	C013	0.41	0.5	20	50	100	150	200		1	49	
N	61667	0.43	2	20						5	47	
C	C001	0.52	5	20	50	100	150	200	5	10	38	0.25
N	49529	0.53	2	20						4	38	
N	18725	0.57	2	20						4	35	
N	84861	0.57	2	20						4	35	
N	73723	0.63	5	20						8	32	
N	79795	0.68	5	10						7	15	
N	73469	0.78	10	20						13	26	
N	77903	0.82	5	5						6	6	
N	55735	0.83	5	20						6	24	
N	82313	0.85	10	10						12	12	
N	74487	0.9	1	20						1	22	
N	02046	0.94	2	20	50					2	21	
C	C014	0.94	10	20	50	100	150	200	2	11	21	0.1
C	C011	1	5	10	20	50	100	200	1	5	10	0.1
N	77443	1.1	2	20						2	18	
N	73581	1.3	10	5						8	4	
N	20044	1.5	4.5	5						3	3	
N	77175	1.5	5	20						3	13	
C	C009	1.5	10	20	50	100	150	200	5	7	13	0.3
N	07633	1.6	5	5	20					3	3	
N	11118	1.8	10	10						6	6	
N	02565	2	5	20						3	10	
N	73331	2.1	10	20						5	10	
N	77166	2.6	20	20	100	200				8	8	
C	C008	3.1	10	25	50	100			5	3	8	0.2
N	54720	3.3	20	20						6	6	
N	77600	3.3	20	20						6	6	
C	C006	5	50	20	50	100	150	200	20	10	4	1.0
	MEAN	1.2	7	15	43	91	120	179	4.9	7	25	0.4
	MEDIAN	0.83	5	20	50	100	150	200	3.5	6	20	0.2
	MAXIMUM	5	50	25	100	200	150	200	20	17	143	1.0
	MINIMUM	0.07	0.5	0.5	2.5	5	10	30	0.5	1.1	3	0.1
	STANDARD DEVIATION	1.07	8.7	6.6	25	51	50	60	6.39	4	25	0.4
Data Points Removed												
C	C012	0.25	50	20	50	100	150	200	5	200	80	0.3
C	C003	0.01	15	20	50	100	150	200	4.1	1500	2000	0.2

#	Parameter		Method	Matrix	Tot #							
	Chloroform		624	Water	38							
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
N	02046	0.15	2	20	50					13	133	
N	07059	0.17	1	2						6	12	
C	C002	0.17	1	10	20	50	100	200	1	6	59	0.1
N	49529	0.18	2	20						11	111	
C	C010	0.2	0.5	0.5	2.5	5	10	30	0.5	3	3	1.0
N	74487	0.21	1	20						5	95	
C	C013	0.29	0.5	20	50	100	150	200		2	69	
N	79795	0.3	5	10						17	33	
N	81446	0.34	4	10						12	29	
N	12543	0.35	5	10						14	29	
N	88608	0.4	5	10						13	25	
N	77434	0.42	5	20						12	48	
N	18725	0.44	2	20						5	45	
N	20044	0.48	4.5	5						9	10	
N	55735	0.51	5	20						10	39	
N	64777	0.6	2	10						3	17	
N	73771	0.6	5	20						8	33	
N	77903	0.61	5	5						8	8	
C	C001	0.72	5	20	50	100	150	200	5	7	28	0.25
N	11118	0.76	10	10						13	13	
N	77175	0.78	5	20						6	26	
N	73723	0.85	5	20						6	24	
C	C014	0.85	10	20	50	100	150	200	2	12	24	0.1
N	07633	0.92	5	5	20					5	5	
N	84861	0.96	2	20						2	21	
N	77443	0.98	2	20						2	20	
N	73581	0.98	10	5						10	5	
N	02565	1	5	20						5	20	
C	C011	1	5	10	20	50	100	200	1	5	10	0.1
N	73469	1.2	10	20						8	17	
N	61667	1.2	2	20						2	17	
N	82313	1.2	10	10						8	8	
C	C009	1.2	10	20	50	100	150	200	5	8	17	0.3
N	77166	1.9	20	20	100	200				11	11	
N	77600	2	20	20						10	10	
N	73331	2.5	10	20						4	8	
N	54720	3.1	20	20						6	6	
C	C006	4	50	20	50	100	150	200	20	13	5	1.0
MEAN		0.91	7	15	42	89	120	179	4.9	8	29	0.4
MEDIAN		0.74	5	20	50	100	150	200	2	8	20	0.3
MAXIMUM		4	50	20	100	200	150	200	20	17	133	1.0
MINIMUM		0.15	0.5	0.5	2.5	5	10	30	0.5	1.7	3	0.1
STANDARD DEVIATION		0.83	8.8	6.5	26	54	50	60	6.9	4	30	0.4

Data Points Removed

C	C003	0.16	15	20	50	100	150	200	4.1	94	125	0.2
C	C012	0.96	50	20	50	100	150	200	5	52	21	0.3

#	Parameter		Method	Matrix	Tot #							
	Carbon Tetrachloride		624	Water	38							
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
N	07059	0.1	1	2						10	20	
C	C002	0.12	1	10	20	50	100	200	1	8	83	0.1
N	74487	0.19	1	20						5	105	
N	02046	0.26	2	20	50					8	77	
N	12543	0.28	5	10						18	36	
N	49529	0.29	2	20						7	69	
C	C010	0.3	0.5	0.5	2.5	5	10	30	0.5	2	2	1.0
N	79795	0.3	5	10						17	33	
N	64777	0.3	2	10						7	33	
N	73771	0.4	5	20						13	50	
N	61667	0.4	2	20						5	50	
N	77434	0.42	5	20						12	48	
N	84861	0.46	2	20						4	43	
C	C013	0.48	0.5	20	50	100	150	200		1	42	
N	88608	0.5	5	10						10	20	
C	C001	0.51	5	20	50	100	150	200	5	10	39	0.25
N	20044	0.63	4.5	5						7	8	
N	18725	0.66	2	20						3	30	
N	77903	0.66	5	5						8	8	
N	73469	0.8	10	20						13	25	
N	82313	0.85	10	10						12	12	
N	55735	0.9	5	20						6	22	
C	C011	1	5	10	20	50	100	200	1	5	10	0.1
C	C003	1	15	20	50	100	150	200	2.8	15	20	0.1
N	73723	1.1	5	20						5	18	
N	77443	1.1	2	20						2	18	
C	C014	1.2	10	20	50	100	150	200	2	8	17	0.1
C	C009	1.2	10	20	50	100	150	200	5	8	17	0.3
N	81446	1.3	4	10						3	8	
N	73581	1.3	10	5						8	4	
N	11118	1.39	10	10						7	7	
N	77175	1.7	5	20						3	12	
N	73331	1.8	10	20						6	11	
N	07633	1.9	5	5	20					3	3	
N	02565	2	5	20						3	10	
N	54720	2.7	20	20						7	7	
N	77600	2.9	20	20						7	7	
N	77166	3.1	20	20	100	200				6	6	
	MEAN	1.0	6	15	42	89	120	179	2.5	7	27	0.3
	MEDIAN	0.73	5	20	50	100	150	200	2	7	19	0.1
	MAXIMUM	3.1	20	20	100	200	150	200	5	18	105	1.0
	MINIMUM	0.1	0.5	0.5	2.5	5	10	30	0.5	1.0	2	0.1
	STANDARD DEVIATION	0.77	5.3	6.5	26	54	50	60	1.9	4	24	0.3
Data Points Removed												
C	C012	0.56	50	20	50	100	150	200	5	89	36	0.3
C	C006	12	50	20	50	100	150	200	20	4	2	1.0

MDL/RDL/PQL database form

#	Parameter		Method	Matrix	Tot #							
	Tetrachloroethylene		624	Water	40							
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
C	C002	0.12	1	10	20	50	100	200	1	8	83	0.1
N	49529	0.15	2	20						13	133	
N	64777	0.2	2	10						10	50	
N	02046	0.25	2	20	50					8	80	
N	74487	0.26	1	20						4	77	
N	12543	0.28	5	10						18	36	
N	07059	0.3	2	5						7	17	
C	C010	0.3	0.5	0.5	2.5	5	10	30	0.5	2	2	1.0
N	73771	0.4	5	20						13	50	
N	81446	0.42	4	10						10	24	
N	79795	0.5	5	10						10	20	
N	18725	0.53	2	20						4	38	
C	C013	0.54	0.5	20	50	100	150	200		1	37	
N	84861	0.6	2	20						3	33	
C	C001	0.74	5	20	50	100	150	200	5	7	27	0.25
N	20044	0.76	4.5	5						6	7	
N	73581	0.77	10	5						13	6	
N	77903	0.8	5	5						6	6	
N	77434	0.84	5	20						6	24	
N	77443	0.89	2	20						2	22	
N	73723	0.9	5	20						6	22	
C	C011	1	5	10	20	50	100	200	1	5	10	0.1
N	61667	1.1	5	20						5	18	
N	88608	1.1	5	10						5	9	
N	73331	1.1	10	20						9	18	
C	C014	1.2	10	20	50	100	150	200	2	8	17	0.1
C	C009	1.2	10	20	50	100	150	200	5	8	17	0.3
N	77175	1.3	5	20						4	15	
N	11118	1.4	10	10						7	7	
N	55735	1.5	5	20						3	13	
C	C012	1.5	50	20	50	100	150	200	5	33	13	0.3
N	77600	1.6	20	20						13	13	
N	82313	1.7	10	10						6	6	
N	02565	2	5	20						3	10	
C	C003	2.5	15	20	50	100	150	200	4.1	6	8	0.2
N	07633	2.5	5	5	20					2	2	
N	77166	2.7	20	20	100	200				7	7	
N	54720	2.9	20	20						7	7	
N	73469	3	10	20						3	7	
C	C006	3	50	20	50	100	150	200	10	17	7	0.5
	MEAN	1.1	9	15	43	91	126	183	3.7	8	25	0.3
	MEDIAN	0.9	5	20	50	100	150	200	4.1	6	17	0.3
	MAXIMUM	3	50	20	100	200	150	200	10	33	133	1.0
	MINIMUM	0.12	0.5	0.5	2.5	5	10	30	0.5	0.9	2	0.1
	STANDARD DEVIATION	0.84	10.9	6.3	24	48	46	54	3.0	6	27	0.3

Parameter		Method	Matrix	Tot #								
Dichlorobenzenes		624	Water	31								
#	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
C	C002	0.13	1	10	20	50	100	200	1	8	77	0.1
C	C010	0.2	0.5	0.5	2.5	5	10	30	0.5	3	3	1.0
N	07059	0.2	2	5						10	25	
N	74487	0.28	1	20						4	71	
N	81446	0.3	4	10						13	33	
N	02046	0.3	2	20	50					7	67	
N	18725	0.5	2	20						4	40	
N	64777	0.5	2	10						4	20	
N	77175	0.5	5	20						10	40	
N	79795	0.5	5	10						10	20	
N	73723	0.5	5	20						10	40	
C	C013	0.54	0.5	20	50	100	150	200		1	37	
N	77903	0.7	5	5						7	7	
N	88608	0.7	5	10						7	14	
N	73331	0.8	10	20						13	25	
N	02565	1	5	20						5	20	
N	77443	1.1	2	20						2	18	
N	84861	1.2	2	20						2	17	
N	20044	1.4	4.5	5						3	4	
N	77434	1.4	10	40						7	29	
C	C014	1.4	10	20	50	100	150	200	2	7	14	0.1
N	07633	1.5	5	5	20					3	3	
N	55735	1.6	10	40						6	25	
N	73581	1.6	10	5						6	3	
N	77166	2.2	20	20	100	200				9	9	
N	82313	2.3	10	10						4	4	
C	C009	3.8	10	20	50	100	150	200	5	3	5	0.3
C	C008	4.1	10	25	50	100			5	2	6	0.2
N	54720	4.3	20	20						5	5	
N	11118	4.7	10	10						2	2	
C	C011	5	10	10	20	50	100	200	5	2	2	0.5
MEAN		1.5	6	16	41	88	110	172	3.1	6	22	0.4
MEDIAN		1	5	20	50	100	125	200	3.5	5	18	0.2
MAXIMUM		5	20	40	100	200	150	200	5	13	77	1.0
MINIMUM		0.13	0.5	0.5	2.5	5	10	30	0.5	0.9	2	0.1
STANDARD DEVIATION		1.43	5.1	9	27	57	55	69	2.2	3	21	0.3

#	Parameter		Method	Matrix	Tot #							
	Bis(2-ethylhexyl)phthalate		625	Water	39							
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
N	77443	0.4	1	1						3	3	
C	C014	0.56	10	20	50	80	120	160	10	18	36	0.5
N	49529	0.57	2	20						4	35	
N	61667	0.7	2	20						3	29	
N	79795	0.71	5	20						7	28	
N	12543	0.77	10	10						25	25	
N	77903	0.79	20	20						25	25	
N	73771	0.8	5	20						6	25	
N	64777	0.8	10	20						13	25	
N	73723	0.85	5	20						6	24	
N	20044	0.86	20	5						23	6	
N	07633	0.96	2	5	20	50	80	120		2	5	
N	84861	0.96	10	20						10	21	
C	C011	1	10	20	50	80	120	160	10	10	20	0.5
N	02565	1	20	20						20	20	
N	73331	1.1	20	20						18	18	
N	77166	1.4	10	20	50	80	120	160		7	14	
N	77434	1.6	10	20						6	13	
C	C003	2.4	20	20	50	80	120	160	2.5	8	8	0.1
N	73812	2.7	10	20						4	7	
N	02046	2.9	4	20	50	80	120	160		1	7	
N	74487	2.9	10	20						3	7	
C	C002	2.9	20	20	50	80	120	160	10	7	7	0.5
C	C008	3	3	25	50	100			10	1	8	0.4
N	54720	3	5	5						2	2	
C	C001	3	40	20	50	80	120	160	10	13	7	0.5
N	07059	3.2	10	20						3	6	
N	55735	3.3	10	20						3	6	
N	18725	3.5	10	20						3	6	
N	73361	3.7	10	20						3	5	
C	C005	4	10	10	20	40	60	80	20	3	3	2.0
N	73469	4.2	20	20						5	5	
C	C010	4.4	20	20	40	75	100	200	20	5	5	1.0
N	73581	5.5	20	5						4	1	
C	C012	6.9	20	20	50	80	120	16	10	3	3	0.5
C	C009	7.6	20	20	50	80	120	160	10	3	3	0.5
N	77175	9.9	10	20						1	2	
N	81446	11	50	0.5						5	0	
N	82625	13	10	20						1	2	
	MEAN	3.0	13	17	45	76	110	141	11.3	7	12	0.7
	MEDIAN	2.7	10	20	50	80	120	160	10	5	7	0.5
	MAXIMUM	13	50	25	50	100	120	200	20	25	36	2.0
	MINIMUM	0.4	1	0.5	20	40	60	16	2.5	0.8	0	0.1
	STANDARD DEVIATION	3.0	9.9	6.4	11	15	20	49	5.2	7	10	0.5

#	Parameter		Method	Matrix	Tot #							
	Benzo-a-pyrene		625	Water	40							
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
N	07633	0.13	2	5	20	50	80	120		15	38	
C	C014	0.24	10	20	50	80	120	160	10	42	83	0.5
N	77443	0.37	1	1						3	3	
N	49529	0.37	2	20						5	54	
N	64777	0.4	10	20						25	50	
N	79795	0.48	5	20						10	42	
N	73723	0.5	5	20						10	40	
N	73331	0.5	20	20						40	40	
C	C009	0.55	20	20	50	80	120	160	10	36	36	0.5
N	73771	0.7	5	20						7	29	
N	77903	0.7	20	20						29	29	
N	12543	0.78	10	10						13	25	
N	84861	0.8	10	20						13	25	
C	C008	0.87	3	25	50	100			10	3	29	0.4
N	54720	1	5	5						5	5	
N	73361	1	10	20						10	20	
C	C011	1	10	20	50	80	120	160	10	10	20	0.5
N	73469	1	20	20						20	20	
N	77434	1.1	10	20						9	18	
C	C005	1.4	10	10	20	40	60	80	20	7	7	2.0
C	C002	1.5	20	20	50	80	120	160	10	13	13	0.5
C	C003	1.5	20	20	50	80	120	160	2.5	13	13	0.1
N	20044	1.6	20	20						13	13	
N	73581	1.6	20	5						13	3	
N	02046	1.8	4	20	50	80	120	160		2	11	
N	73812	1.9	10	20						5	11	
N	61667	2.1	2	20						1	10	
N	18725	2.1	10	20						5	10	
N	07059	2.5	10	20						4	8	
N	82625	2.7	10	20						4	7	
C	C010	2.8	20	20	40	75	100	200	20	7	7	1.0
C	C001	2.8	40	20	50	80	120	160	10	14	7	0.5
N	77166	3	10	20	50	80	120	160		3	7	
N	55735	3.2	10	20						3	6	
N	77175	3.6	10	20						3	6	
N	74487	3.6	10	20						3	6	
C	C012	3.7	100	20	50	80	120	16	10	27	5	0.5
N	77600	5.3	20	20						3	3	
N	02565	7	20	20						3	3	
N	81446	13	50	0.5						4	0	
MEAN		2.0	15	18	45	76	110	141	11	11	19	0.7
MEDIAN		1.5	10	20	50	80	120	160	10	8	12	0.5
MAXIMUM		13	100	25	50	100	120	200	20	42	83	2.0
MINIMUM		0.13	1	0.5	20	40	60	16	2.5	1.0	0	0.1
STANDARD DEVIATION		2.3	17	6.0	11	15	20	49	5.2	11	18	0.5

#	Parameter		Method	Matrix	Tot #							
	Benzo(a)Anthracene		625	Water	38							
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
N	77443	0.06	1	1						17	17	
N	07633	0.09	2	5	20	50	80	120		22	56	
C	C008	0.23	3	25	50	100			10	13	109	0.4
C	C014	0.32	10	20	50	80	120	160	10	31	63	0.5
N	49529	0.33	2	20						6	61	
N	73723	0.34	5	20						15	59	
N	79795	0.5	5	20						10	40	
N	61667	0.66	2	20						3	30	
N	64777	0.7	10	20						14	29	
N	12543	0.7	10	10						25	25	
N	73331	0.8	20	20						25	25	
N	84861	0.84	10	20						12	24	
C	C002	0.86	20	20	50	80	120	160	5	23	23	0.3
N	20044	0.9	20	20						22	22	
C	C003	0.99	20	20	50	80	120	160	2.5	20	20	0.1
C	C005	0.99	10	10	20	40	60	80	5	10	10	0.5
N	77434	1	10	20						10	20	
C	C011	1	10	20	50	80	120	160	10	10	20	0.5
N	54720	1	5	5						5	5	
N	73361	1.1	10	20						9	18	
N	73469	1.5	20	20						13	13	
N	73581	1.6	20	5						13	3	
N	55735	1.9	10	20						5	11	
N	02046	2.1	4	20	50	80	120	160		2	10	
N	82625	2.3	10	20						4	9	
N	18725	2.5	10	20						4	8	
N	07059	2.6	10	20						4	8	
N	77166	2.8	10	20	50	80	120	160		4	7	
N	74487	2.9	10	20						3	7	
C	C001	3	40	20	50	80	120	160	10	13	7	0.5
C	C010	3	20	20	40	75	100	200	20	7	7	1.0
C	C012	3.1	100	20	50	80	120	16	10	32	6	0.5
N	77175	3.8	10	20						3	5	
N	73812	3.8	10	20						3	5	
N	77600	4.6	20	20						4	4	
N	02565	5	20	20						4	4	
N	73771	5.1	5	20						1	4	
N	81446	6.2	50	0.5						8	0	
MEAN		1.9	15	17	44	75	109	140	9.2	11	21	0.5
MEDIAN		1.1	10	20	50	80	120	160	10	10	12	0.5
MAXIMUM		6.2	100	25	50	100	120	200	20	32	109	1.0
MINIMUM		0.06	1	0.5	20	40	60	16	2.5	1.0	0	0.1
STANDARD DEVIATION		1.58	17.3	6.1	12	16	21	51	5.00	9	22	0.2
Data Points Removed												
N	77903	0.16	20	20						125	125	
C	C009	0.3	20	20	50	80	120	160	10	67	67	0.5

Parameter		Method	Matrix	Tot #								
2,4-Dichlorophenol		625	Water	33								
#	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
N	77443	0.13	3	1						23	8	
N	49529	0.36	2	20						6	56	
C	C014	0.6	10	20	50	80	120	160	10	17	33	0.5
N	73723	0.67	5	20						7	30	
N	64777	0.7	10	20						14	29	
N	73771	0.7	5	20						7	29	
N	07633	0.71	2	5	20	50	80	120		3	7	
N	20044	0.88	20	20						23	23	
N	73469	0.9	20	20						22	22	
N	54720	1	5	5						5	5	
N	02046	1	4	20	50	80	120	160		4	20	
N	79795	1	5	20						5	20	
C	C011	1	10	20	50	80	120	160	10	10	20	0.5
N	73331	1.1	20	20						18	18	
N	12543	1.1	10	10						15	4	
N	73581	1.3	20	5						15	4	
C	C003	1.3	20	20	50	80	120	160	2.5	15	15	0.1
N	73361	1.4	10	20						7	14	
N	74487	1.5	20	20						13	13	
N	84861	1.8	10	20						6	11	
C	C010	2.2	20	20	40	75	100	200	20	9	9	1.0
N	77903	2.3	20	20						9	9	
N	61667	2.5	2	20						1	8	
N	73812	2.6	10	20						4	8	
N	82625	2.7	10	20						4	7	
N	77600	3.8	20	20						4	10	
N	77434	5.2	20	50						4	10	
N	55735	6.1	20	20						3	3	
N	77166	6.7	20	20	50	80	120	160		3	3	
N	07059	7.1	10	20						1	3	
N	18725	7.6	40	20						5	3	
N	02565	8	20	20						3	3	
N	81446	9.6	50	0.5						5	0	
MEAN		2.6	14	18	44	75	111	160	10.6	9	14	0.5
MEDIAN		1.3	10	20	50	80	120	160	10	6	10	0.5
MAXIMUM		9.6	50	50	50	80	120	200	20	23	56	1.0
MINIMUM		0.13	2	0.5	20	50	80	120	2.5	0.8	0	0.1
STANDARD DEVIATION		3	11	8	11	11	16	23	7	7	12	0.4

Data Points Removed

N	77175	39	50	20						1	1	
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#	Parameter		Method	Matrix	Tot #							
	Pentachlorophenol		625	Water	37							
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
C	C014	0.26	10	20	50	80	120	160	10	38	77	0.5
N	49529	0.43	2	20						5	47	
N	77443	0.6	3	2						5	3	
N	64777	0.8	10	20						13	25	
N	07633	0.99	2	5	20	50	80	120		2	5	
N	73469	1	20	20						20	20	
N	84861	1	10	20						10	20	
C	C011	1	10	20	50	80	120	160	10	10	20	0.5
N	20044	1.2	20	20						17	17	
N	73361	1.2	10	20						8	17	
C	C005	1.3	10	10	20	40	60	80	20	8	8	2.0
N	73723	1.5	10	50						7	33	
N	79795	1.7	5	20						3	12	
N	74487	1.9	20	20						11	11	
C	C003	1.9	20	20	50	80	120	160	2.5	11	11	0.1
N	73331	2.2	20	20						9	9	
N	61667	2.3	10	50						4	22	
N	73581	2.8	20	5						7	2	
N	07059	3.1	20	20						6	6	
N	82625	3.1	10	20						3	6	
N	77600	3.3	20	20						6	6	
N	55735	3.6	20	20						6	6	
C	C009	3.8	40	20	50	80	120	160	20	11	5	1.0
N	77166	4.9	20	20	50	80	120	160		4	4	
C	C008	5	2	50	100	150			10	0	10	0.2
N	54720	7	25	10						4	1	
C	C002	7.6	20	20	50	80	120	160	10	3	3	0.5
N	12543	7.9	20	10						3	3	
N	02046	8	20	20	50	80	120	160		3	3	
N	77434	10	20	50						2	5	
N	02565	10	20	20						2	2	
N	73771	12	25	20						2	2	
C	C001	13	40	20	50	80	120	160	10	3	2	0.5
C	C010	15	50	20	40	75	100	200	20	3	1	1.0
N	18725	20	40	20						2	1	
N	81446	20	50	5						3	0	
N	77175	48	50	20						1	0	
	MEAN	6.2	20	21	48	80	109.09	153	12.5	7	11	0.7
	MEDIAN	3.1	20	20	50	80	120	160	10	5	6	0.5
	MAXIMUM	48	50	50	100	150	120	200	20	38	77	2.0
	MINIMUM	0.26	2	2	20	40	60	80	2.5	0.4	0	0.1
	STANDARD DEVIATION	8.82	13.3	11.6	20	26	21	30	6.12	7	15	0.6
Data points removed												
C	C012	190	200	20	50	80	120	16	10	1	0	0.5

#	Parameter		Method	Matrix	Tot #							
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
N	77443	0.18	3	1						17	6	
N	73723	0.5	5	20						10	40	
N	49529	0.53	2	20						4	38	
N	64777	0.7	10	20						14	29	
N	73469	0.8	20	20						25	25	
N	73331	0.8	20	20						25	25	
N	79795	0.86	5	20						6	23	
N	07633	0.9	2	5	20	50	80	120		2	6	
C	C002	0.9	20	20	50	80	120	160	10	22	22	0.5
C	C011	1	10	20	50	80	120	160	10	10	20	0.5
N	73771	1.1	5	20						5	18	
C	C014	1.1	10	20	50	80	120	160	2	9	18	0.1
N	55735	1.2	20	20						17	17	
N	12543	1.2	20	10						3	15	
N	02046	1.3	4	20	50	80	120	160		3	15	
C	C003	1.3	20	20	50	80	120	160	2.5	15	15	0.1
N	73581	1.6	20	5						13	3	
N	74487	1.7	20	20						12	12	
N	73361	1.7	10	20						6	12	
N	20044	1.8	20	20						11	11	
C	C005	1.8	10	10	20	40	60	80	10	6	6	1.0
N	73812	1.9	10	20						5	11	
N	54720	2	5	5						3	3	
N	84861	2	10	20						5	10	
C	C010	2	20	20	40	75	100	200	20	10	10	1.0
N	61667	2.3	2	20						1	9	
N	77903	2.3	20	20						9	9	
N	82625	2.8	10	20						4	7	
C	C007	3.4	50	20	50	80	120	160		15	6	
C	C009	3.8	20	20	50	80	120	160	5	5	5	0.3
N	77600	4.9	20	20						4	4	
N	77434	5.6	20	20						4	4	
N	18725	5.6	40	20						7	4	
N	77166	6.2	20	20	50	80	120	160		3	3	
N	07059	7	10	20						1	3	
C	C001	7.4	40	20	50	80	120	160	10	5	3	0.5
N	02565	10	20	20						2	2	
C	C012	10	200	20	50	80	120	16	10	20	2	0.5
N	81446	12	50	0.5						4	0	
	MEAN	2.9	21	17	45	74	111	143	9	9	12	0.5
	MEDIAN	1.8	20	20	50	80	120	160	10	6	10	0.5
	MAXIMUM	12	200	20	50	80	120	200	20	25	40	1.0
	MINIMUM	0.18	2	0.5	20	40	60	16	2	0.9	0.04	0.1
	STANDARD DEVIATION	2.9	32	6	11	13	19	47	5	7	10	0.3
Data Points Removed												
N	77175	44	50	20						1	0	

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

MDL/RDL/PQL database form

[illegible]

[illegible]

[illegible]

[illegible]

MDL/RDL/PQL database form

[illegible]

[illegible]

Data Points Removed

N	73361	1000	20000	200						20	0.2	
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C	C005	0.07	5	2	5	10	15	20	4	75	30	2.0
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MDL/RDL/PQL database form

[illegible]

C	C005	0.1	10	4	10	20	30	40	4	100	40	1.0
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C	C012	0.04	10	2.5	5	25	50		0.1	250	63	0.04
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APPENDIX B

SELECTED RAW DATA WITH ADDITIONAL OUTLIERS REMOVED

#	Parameter	Method	Matrix	Tot #								
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
	Cadmium	213.2	Water	22								
N	01289	0.03	0.1	0.5						3	17	
N	77319	0.03	0.05	0.05	0.1	0.3	0.5	1		1	1	
N	61667	0.05	0.25	0.25						5	5	
N	20044	0.07	0.25	0.25						4	4	
N	11118	0.1	1	2.5						10	25	
C	C002	0.1	0.5	1	2	3			0.1	5	10	0.1
N	49529	0.12	0.5	0.5						4	4	
N	77166	0.13	0.5	1.25						4	10	
N	18725	0.15	1	2						7	13	
N	77886	0.16	0.3	0.5						2	3	
N	54457	0.2	1	0.5	1	2	3	5	1	5	3	2.0
C	C005	0.2	0.5	10	25				0.5	3	50	0.1
C	C008	0.2	2	0.5	1	2			1	10	3	2.0
N	84890	0.24	0.5	0.5						2	2	
N	55735	0.26	1	1						4	4	
N	16107	0.26	0.5	0.5						2	2	
C	C004	0.3	0.4	0.8	1	2	4	6	1	1	3	1.3
C	C009	0.5	2	0.5	1	2			1	4	1	2.0
N	08235	0.56	2	2						4	4	
N	77434	1.3	5	2						4	2	
N	07673	2	10	25						5	13	
N	73771	2	2	5						1	3	
	MEAN	0.4	1	3	4	2			0.8	4	8	1.2
	MEDIAN	0.2	0.5	0.65	1	2			1	4	4	1.6
	MAXIMUM	2	10	25	25	3			1	10	50	2.0
	MINIMUM	0.03	0.05	0.05	0.1	0.3			0.1	0.5	1	0.1
	STANDARD DEVIATION	0.58	2.2	5.5	9.1	0.9			0.38	2	11	0.9
Data Points Removed												
C	C011	0.6	2000	0.5	1	2	4		0.6	3333	1	1.2

#	Parameter	Method	Matrix	Tot #								
	TCE	524.2	Water	20								
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
C	C010	0.04	0.1	0.5	2.5	5	10	30	0.1	3	13	0.2
C	C003	0.1	0.5	2	5	10	20		0.19	5	20	0.1
N	07059	0.1	1	2						10	20	
N	20044	0.12	0.4	0.5						3	4	
N	74603	0.16	1	1						6	6	
N	55735	0.16	1	2						6	13	
C	C005	0.19	1	0.5	1	2	5	10	0.5	5	3	1.0
N	77360	0.2	2	2						10	10	
N	61667	0.2	0.5	2						3	10	
C	C002	0.23	1	2	4	10	20	30	0.5	4	9	0.3
N	16107	0.24	1	0.3						4	1	
N	73331	0.24	2	0.5						8	2	
C	C001	0.29	1	1	2	5	10	20	0.5	3	3	0.5
N	01289	0.4	2	2						5	5	
N	49529	0.4	1	1						3	3	
C	C008	0.41	2	5	10	20			0.5	5	12	0.1
C	C009	0.43	2	2	4	10	20	40	0.5	5	5	0.3
C	C007	0.46	2	5	10	15	30	40	0.5	4	11	0.1
N	77166	0.49	2	2	5	10	25	50		4	4	
N	73469	0.8	4	4						5	5	
MEAN		0.3	1	2	5	10	18	31	0.4	5	8	0.3
MEDIAN		0.235	1	2	4	10	20	30	0.5	5	6	0.2
MAXIMUM		0.8	4	5	10	20	30	50	0.5	10	20	1.0
MINIMUM		0.04	0.1	0.3	1	2	5	10	0.1	2.5	1	0.1
STANDARD DEVIATION		0.18	0.9	1.4	3.2	5.5	8.5	13.5	0.17	2	6	0.3
Data Points Removed												
N	77175	0.07	5	20						71	286	
C	C012	0.18	10	4	10	20	30	40	1	56	22	0.3
C	C006	7	50	20	50	100	150	200	10	7	3	0.5

#	Parameter	Method	Matrix	Tot #								
	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/MDL	Calib level/MDL	MRL/Calib Low
C	C002	0.13	1	10	20	50	100	200	1	8	77	0.1
N	74487	0.16	1	20						6	125	
C	C010	0.2	0.5	0.5	2.5	5	10	30	0.5	3	3	1.0
N	02046	0.24	2	20	50					8	83	
N	64777	0.3	2	10						7	33	
N	18725	0.47	2	20						4	43	
N	61667	0.49	2	20						4	41	
C	C013	0.61	0.5	20	50	100	150	200		1	33	
N	79795	0.7	5	10						7	14	
N	88608	0.7	5	10						7	14	
N	77443	0.71	2	20						3	28	
N	81446	0.72	4	10						6	14	
N	84861	0.8	2	20						3	25	
N	77903	0.88	5	5						6	6	
C	C001	0.92	5	20	50	100	150	200	5	5	22	0.25
N	73723	0.93	5	20						5	22	
N	55735	0.94	5	20						5	21	
N	77175	0.98	5	20						5	20	
C	C011	1	5	10	20	50	100	200	1	5	10	0.1
N	82313	1.04	10	10						10	10	
N	07633	1.3	5	5	20					4	4	
N	20044	1.43	4.5	5						3	3	
C	C009	1.8	10	20	50	100	150	200	5	6	11	0.3
N	02565	2	5	20						3	10	
N	73331	2.03	10	20						5	10	
C	C008	2.1	10	25	50	100			5	5	12	0.2
N	11118	2.7	10	10						4	4	
N	54720	2.8	20	20						7	7	
N	77166	2.9	20	20	100	200				7	7	
C	C006	7	50	20	50	100	150	200	20	7	3	1.0
	MEAN	1.3	7	15	42	89	116	176	5.4	5	24	0.4
	MEDIAN	0.925	5	20	50	100	150	200	5	5	14	0.3
	MAXIMUM	7	50	25	100	200	150	200	20	10	125	1.0
	MINIMUM	0.13	0.5	0.5	2.5	5	10	30	0.5	0.8	3	0.1
	STANDARD DEVIATION	1.33	9.5	7	26	54	52	64	6.79	2	27	0.4
Data Points Removed												
C	C003	0.009	15	20	50	100	150	200	4.1	1667	2222	0.2

Parameter		Method	Matrix	Tot #								
Carbon Tetrachloride		624	Water	32								
#	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
N	07059	0.1	1	2						10	20	
N	12543	0.28	5	10						18	36	
C	C010	0.3	0.5	0.5	2.5	5	10	30	0.5	2	2	1.0
N	79795	0.3	5	10						17	33	
N	64777	0.3	2	10						7	33	
N	77434	0.42	5	20						12	48	
N	84861	0.46	2	20						4	43	
C	C013	0.48	0.5	20	50	100	150	200		1	42	
N	88608	0.5	5	10						10	20	
C	C001	0.51	5	20	50	100	150	200	5	10	39	0.25
N	20044	0.63	4.5	5						7	8	
N	18725	0.66	2	20						3	30	
N	77903	0.66	5	5						8	8	
N	73469	0.8	10	20						13	25	
N	82313	0.85	10	10						12	12	
N	55735	0.9	5	20						6	22	
C	C011	1	5	10	20	50	100	200	1	5	10	0.1
C	C003	1	15	20	50	100	150	200	2.8	15	20	0.1
N	73723	1.1	5	20						5	18	
N	77443	1.1	2	20						2	18	
C	C014	1.2	10	20	50	100	150	200	2	8	17	0.1
C	C009	1.2	10	20	50	100	150	200	5	8	17	0.3
N	81446	1.3	4	10						3	8	
N	73581	1.3	10	5						8	4	
N	11118	1.39	10	10						7	7	
N	77175	1.7	5	20						3	12	
N	73331	1.8	10	20						6	11	
N	07633	1.9	5	5	20					3	3	
N	02565	2	5	20						3	10	
N	54720	2.7	20	20						7	7	
N	77600	2.9	20	20						7	7	
N	77166	3.1	20	20	100	200				6	6	
	MEAN	1.1	7	14	44	94	123	176	2.7	7	19	0.3
	MEDIAN	0.95	5	20	50	100	150	200	2.4	7	17	0.2
	MAXIMUM	3.1	20	20	100	200	150	200	5	18	48	1.0
	MINIMUM	0.1	0.5	0.5	2.5	5	10	30	0.5	1.0	2	0.1
	STANDARD DEVIATION	0.78	5.4	6.8	28	55	53	64	1.9	4	13	0.3

Data Points Removed

C	C012	0.56	50	20	50	100	150	200	5	89	36	0.3
C	C006	12	50	20	50	100	150	200	20	4	2	1.0
C	C002	0.12	1	10	20	50	100	200	1	8	83	0.1
N	74487	0.19	1	20						5	105	
N	02046	0.26	2	20	50					8	77	
N	49529	0.29	2	20						7	69	
N	73771	0.4	5	20						13	50	
N	61667	0.4	2	20						5	50	

Parameter		Method	Matrix	Tot #								
Bis(2-ethylhexyl)phthalate		625	Water	31								
#	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
N	77443	0.4	1	1						3	3	
N	49529	0.57	2	20						4	35	
N	61667	0.7	2	20						3	29	
N	79795	0.71	5	20						7	28	
N	73771	0.8	5	20						6	25	
N	73723	0.85	5	20						6	24	
N	07633	0.96	2	5	20	50	80	120		2	5	
N	84861	0.96	10	20						10	21	
C	C011	1	10	20	50	80	120	160	10	10	20	0.5
N	77166	1.4	10	20	50	80	120	160		7	14	
N	77434	1.6	10	20						6	13	
C	C003	2.4	20	20	50	80	120	160	2.5	8	8	0.1
N	73812	2.7	10	20						4	7	
N	02046	2.9	4	20	50	80	120	160		1	7	
N	74487	2.9	10	20						3	7	
C	C002	2.9	20	20	50	80	120	160	10	7	7	0.5
C	C008	3	3	25	50	100			10	1	8	0.4
N	54720	3	5	5						2	2	
N	07059	3.2	10	20						3	6	
N	55735	3.3	10	20						3	6	
N	18725	3.5	10	20						3	6	
N	73361	3.7	10	20						3	5	
C	C005	4	10	10	20	40	60	80	20	3	3	2.0
N	73469	4.2	20	20						5	5	
C	C010	4.4	20	20	40	75	100	200	20	5	5	1.0
N	73581	5.5	20	5						4	1	
C	C012	6.9	20	20	50	80	120	16	10	3	3	0.5
C	C009	7.6	20	20	50	80	120	160	10	3	3	0.5
N	77175	9.9	10	20						1	2	
N	81446	11	50	0.5						5	0	
N	82625	13	10	20						1	2	
	MEAN	3.5	11	17	44	75	108	138	11.6	4	10	0.7
	MEDIAN	2.9	10	20	50	80	120	160	10	3	6	0.5
	MAXIMUM	13	50	25	50	100	120	200	20	10	35	2.0
	MINIMUM	0.4	1	0.5	20	40	60	16	2.5	0.8	0	0.1
	STANDARD DEVIATION	3.2	9.5	6.6	12	16	21	53	5.8	3	10	0.6

Parameter		Method	Matrix	Tot #								
Benzo-a-pyrene		625	Water	25								
#	Lab Code	MDL (ug/L)	MDL Spike level	Calib low Point	Calib Conc 2	Calib Conc 3	Calib Conc 4	Calib Conc 5	Normal Reporting Limit (MRL)	MDL Spike/ MDL	Calib level/ MDL	MRL/ Calib Low
N	77443	0.37	1	1						3	3	
N	49529	0.37	2	20						5	54	
N	79795	0.48	5	20						10	42	
N	73723	0.5	5	20						10	40	
N	73771	0.7	5	20						7	29	
C	C008	0.87	3	25	50	100			10	3	29	0.4
N	54720	1	5	5						5	5	
N	73361	1	10	20						10	20	
C	C011	1	10	20	50	80	120	160	10	10	20	0.5
N	77434	1.1	10	20						9	18	
C	C005	1.4	10	10	20	40	60	80	20	7	7	2.0
N	02046	1.8	4	20	50	80	120	160		2	11	
N	73812	1.9	10	20						5	11	
N	61667	2.1	2	20						1	10	
N	18725	2.1	10	20						5	10	
N	07059	2.5	10	20						4	8	
N	82625	2.7	10	20						4	7	
C	C010	2.8	20	20	40	75	100	200	20	7	7	1.0
N	77166	3	10	20	50	80	120	160		3	7	
N	55735	3.2	10	20						3	6	
N	77175	3.6	10	20						3	6	
N	74487	3.6	10	20						3	6	
N	77600	5.3	20	20						3	3	
N	02565	7	20	20						3	3	
N	81446	13	50	0.5						4	0	
	MEAN	2.5	10	18	43	76	104	152		5	14	
	MEDIAN	1.9	10	20	50	80	120	160		4	8	
	MAXIMUM	13	50	25	50	100	120	200		10	54	
	MINIMUM	0.37	1	0.5	20	40	60	80		1.0	0	
	STANDARD DEVIATION	2.7	10	6.3	12	20	26	44		3	14	

[illegible]

APPENDIX C

**WEF MANUSCRIPT ON PQLS
(Moore and Grimes, 1992)**

A STUDY TO DETERMINE THE PERFORMANCE OF EPA APPROVED METHODS AT CONCENTRATIONS BETWEEN THE MDL AND PQL

**T. F. Moore, Risk Sciences
6190 Lehman Drive, Suite 108
Colorado Springs, CO 80918**

**M. M. Grimes, Director of Technical Services
Regulatory Management, Inc. Colorado Springs, CO 80918**

ABSTRACT

The use of Gold Book numbers for stream standards has created a numeric standard driven process which results in stream standards and permit limits that are often at or below analytical detection capability. The use of Gold Book standards requires regulatory, permitting and compliance decisions to be based on measurements that are in the Method Detection Level (MDL) - Practical Quantitation Level, (PQL) range. This study determined the performance of certified laboratories, using EPA approved methods, at concentrations near the PQL level. An eight laboratory performance evaluation study was performed for silver, cadmium, copper, selenium and lead in an artificial sample matrix representative of selected water reclamation plant effluents. Samples were submitted in triplicate, at three concentrations plus a blank. The study was conducted entirely in the blind. The prepared samples, in the artificial matrix, were added to bottles supplied by the laboratories, labeled as real samples and shipped to the laboratories for analysis.

KEY WORDS

Method Detection Limit, Practical Quantitation Level, Matrix

INTRODUCTION

Recent federal and state water quality regulation is strongly focused on eliminating toxics, especially heavy metals, ammonia and chlorine. Often the substance concentration deemed to be toxic is at the lower limit of available detection technologies.

Nevertheless, initiatives such as EPA's new toxics rule (published in November, 1991), and California's Inland Surface Waters Plan will require NPDES permittee to certify compliance with water quality criteria set in the low parts-per-billion range.

Are the laboratory analyses accurate enough to make such certifications? The EPA and the laboratories say yes. However, EPA surveys of lab performance often use samples spiked to levels more than 1000% of the recommended water quality objectives. In addition, the EPA spikes are made into reagent water rather than a more complicated effluent-type matrix.

The internal MDL/PQL studies performed by most labs also suffer from being conducted

in near-pure water rather than effluent. Moreover, such studies are always conducted with knowledge as to what the "real" value should be. Errors are immediately detected and remedied. When a sample's true value is unknown there is no opportunity to make such corrections.

The critical question is how accurate and reliable are commercial laboratories when presented with complex water samples spiked near their claimed PQLs. What is their real world performance?

The purpose of the study was to determine the performance of certified commercial laboratories, using EPA approved methods, in a synthetic matrix, at the level designated by the Santa Ana Regional Board, to be the PQL for cadmium, copper, lead, selenium and silver. The California Inland Surface Waters Plan, the ISWP, defines PQL in the following manner: "Practical Quantitation Level, PQL, is the lowest concentration of a substance which can be determined within ± 20 percent of the true concentration by 75 percent of the analytical laboratories tested in a performance evaluation study... A performance evaluation study of eight laboratories was performed to directly evaluate the variability of laboratory measurements for the methods specified, at the PQL concentrations specified, for each metal. Known samples were submitted to each laboratory, at 80 percent of the PQL, the PQL; and 120 percent of the PQL. Each sample was submitted in triplicate. The known samples were prepared in a matrix that approximated the major cations and anions present in the effluents of typical dischargers in the Santa Ana region. The PQL will be considered to have been set at the correct concentration if six out of the eight laboratories are within ± 20 percent of the true concentration. The study also included ammonia at a concentration significantly above the PQL. A single concentration, 2.5 mg/L was analyzed over 100 times to provide an accurate measure of the variability for a parameter present at a concentration that is in the "Region of Certain Quantification". The definition of PQL implicitly makes the assumption that variability is concentration dependent and that measurements above the PQL have less variability. The ammonia results should have a variability that is substantially less than ± 20 percent, since the known concentration of 2.5 mg/L, is over ten times the PQL.

The second objective was to test the reliability of the entire analytical system at the PQL level for each of the five metals. This study was designed to simulate an actual effluent study, performed by a commercial laboratory, for determining NPDES compliance. The study used a real sample matrix, bottles and preservatives supplied by the laboratories and standard courier service between the customer and the laboratories. The study was initiated with a letter to each laboratory explaining that this was an important study related to the NPDES permit program and that the sample matrix was effluent. The letter specified the EPA methods to be used and the expected concentration of each analyte. The laboratory was instructed to provide appropriate bottles, preservatives and any special instructions needed. The samples were shipped to the labs, by courier on different days of the week to simulate normal temporal trends in a NPDES study. No special sample handling was requested. The true nature of the study was not divulged to the laboratories. The performance evaluation study was conducted under the identical conditions to any well coordinated monitoring effort using a commercial laboratory. The results of the performance evaluation study are an

accurate representation of the ability of the eight laboratories studied to correctly determine compliance with standards that are set near the PQL.

STUDY PROCEDURES

Laboratory selection

Six of the laboratories were selected based on their participation in the process used by the Santa Ana Regional board to establish the PQLs for NPDES permits. Two additional laboratories were added. All of the laboratories are experienced environmental laboratories, familiar with compliance monitoring and are certified by the State of California and numerous other programs. The laboratories are all from a single geographical area, are routinely used by dischargers and are familiar with compliance monitoring.

Study implementation

The study was designed and coordinated by an outside consultant. The study was initiated by a letter which indicated that a discharger needed analytical services for a special study requested by the Regional Board for the NPDES renewal process. The samples were identified as effluents and the analytical methods required by the Regional Board in the PQL determination study were specified. The expected concentration range for each element was given. The letter specified the detection limits and reporting procedures for the study. Sample containers, preservation and sample handling procedures were specified. Each laboratory received an identical copy of this letter. The laboratories were aware of the importance of the study, the matrix, the methods to be used and the expected concentration range.

Sample matrix

The study was conducted in a synthetic matrix that approximated the composition of the dischargers in the Santa Ana Region. The synthetic water was based on a natural bottled water, supplemented by commercially prepared ammonia, phosphorous and glucose-glutamic acid standards. High purity inorganic salts, certified to be 99.99+ were used to fine tune the major cations and anions. The synthetic water used the BOD standard, glucose-glutamic acid, to provide a simple non refractory organic component and included zinc at 50 µg/L as a potential matrix interference, since zinc was present in all effluent samples measured. The composition of the synthetic water matched the average effluent concentration of the six dischargers within 10 percent for all of the major cations and anions except sodium, potassium and phosphorous. These three parameters were present at lower concentrations in the synthetic water than the average effluent concentration. The synthetic water contains all of the common analytical interferences. However, the matrix of the synthetic water is not as complex as the actual effluent matrix.

Table I

Parameter	Synthetic water measured concentration	Low of the six WRPs *	Mean of the Six WRPs	High of the six WRPs
Calcium	59 mg/L	46 mg/L	62 mg/L	73 mg/L
Magnesium	11 mg/L	8 mg/L	11 mg/L	12 mg/L
Hardness	192 mg/L as CaCO ₃	149 mg/L as CaCO ₃	199 mg/L as CaCO ₃	231 mg/L as CaCO ₃
Sodium	74 mg/L	66 mg/L	88 mg/L	120 mg/L
Potassium	5.5 mg/L	12 mg/L	14 mg/L	15 mg/L
Zinc	58 µg/L	40 µg/L	54 µg/L	86 µg/L
BOD	9 (Calculated)			
Ammonia	2.5 mg/L	.1 mg/L	2.6 mg/L	8.2 mg/L
Chloride	82 mg/L	55 mg/L	78 mg/L	100 mg/L
Phosphorous	4.4 mg/L	3.7 mg/L	6.1 mg/L	7.9 mg/L
Sulfate	98 mg/L	76 mg/L	89 mg/L	97 mg/L

*WRP values are quarterly values measured during a special study in 1990 and 1991.

Preparation of the samples

The synthetic water was made in a single 100 liter batch. A new 113 liter HDPE tank with cover and spigot was used for the preparation of the synthetic water. The new tank was rinsed with tap water and filled with deionized water. The tank sat for a total of 12 days, filled with D.I water. The tank was emptied and refilled with deionized water every 3 days during the 12 day period to clean and condition the new container. The commercial mineral water, the ammonia stock solution, the glucose glutamic acid BOD standard and the phosphorous standard were all added in the liquid form. All liquid measurements were made to graduated cylinder accuracy. Sodium carbonate, magnesium chloride hexahydrate, calcium chloride dihydrate and sodium sulfate were weighed to 0.1 mg, dissolved in a two liter volumetric flask and transferred to the tank. The tank was brought to the desired volume with 18 meg ohm deionized water. The total measured volume of liquid added to the tank was 99,950 milliliters. All of the transfers, except the ammonia standard were done with a single 4 liter graduated cylinder. The graduated cylinder used to measure the solutions was calibrated by weight with a balance capable of weighing to 0.1 grams. The measurement error was 17 grams out of 4000 or .42 percent. Based on these procedures, the nominal volume of liquid in the tank was calculated to be between 99,300 and 100,400 liters. The calculated concentration of ammonia was between 2.49 mg/L and 2.52 mg/L. The synthetic water was analyzed for all of the added

constituents, ammonia and the five study metals. The metals analysis was done by graphite furnace atomic absorption, GFAA, for all metals except selenium. Selenium was determined by hydride generation. No metals were detected in any of the samples run. The synthetic water was prepared on April 19, 1992.

Preparation of the mixed metal standards

The four standard solutions were prepared in four new 20 liter LPE carboys, with lids. The new carboys was rinsed with tap water and filled with deionized water. The carboys sat for a total of 9 days, filled with deionized water. The carboys emptied and refilled with deionized water every 3 days during the 9 day period to clean and condition the new containers. Eight liters of the synthetic water were transferred from the tank into each carboy, with the 4 liter graduated cylinder. Commercial metals standards were weighed to 0.1 mg for each metal and added to a 4 liter graduated cylinder. The solutions was brought to volume and the contents of the cylinder transferred to the carboy. The graduated cylinder was filled to volume two more times and the contents added to the carboy. The nominal volume added to the carboy was between 19,916 to 20,084 milliliters. The calculated concentration of the prepared solutions was within 0.05 and 0.1 $\mu\text{g/l}$ of the nominal value. Table 1 gives the nominal value for each solution. The standard solutions were prepared on April 21, 1992.

Table II

	Cadmium	Copper	Lead	Silver	Selenium	Ammonia
A	Blank*	Blank	Blank	Blank	Blank	2.5 mg/L
B	Blank	16.0 $\mu\text{g/l}$	10.0 $\mu\text{g/L}$	8.0 $\mu\text{g/L}$	10.0 $\mu\text{g/L}$	2.5 mg/L
C	1.6 $\mu\text{g/L}$	20.0 $\mu\text{g/L}$	12.0 $\mu\text{g/L}$	10.0 $\mu\text{g/L}$	12.0 $\mu\text{g/L}$	2.5 mg/L
D	2.0 $\mu\text{g/L}$	24.0 $\mu\text{g/L}$	Blank	12.0 $\mu\text{g/L}$	Blank	2.5 mg/L
E	2.4 $\mu\text{g/L}$	Blank	8.0 $\mu\text{g/L}$	Blank	8.0 $\mu\text{g/L}$	2.5 mg/L

*The concentration of all blank constituents is the same as the synthetic water. There was nothing detected when samples were run in triplicate by GFAA. Selenium was run by hydride generation.

Dispensing the samples

The coolers and empty sample bottles were picked up by courier from each of the laboratories and shipped to the sample preparation laboratory. The coolers remained in the custody of the sample preparation laboratory until samples were dispensed. The coolers were opened the trip blanks removed, labeled and placed in the sample holding refrigerator at 4 degrees C. All of the empty bottles were removed from the coolers, separated into the appropriate preservation groups, by laboratory, and labeled. Most of the laboratories used

prelabeled containers. The samples were given a sample designation of SB-SBx, where B was the carboy number and the x was the shipment number. 24 nitric acid preserved bottles for metals, 3 from each lab, were filled from carboy B. Bottles were taken in random order. 24 sulfuric acid preserved bottles for ammonia, 3 from each lab, were filled from carboy B. The procedure was repeated for carboys C, D and E. Samples were placed in the sample holding refrigerator at 4 degrees C. Bottles taken at random from the empty bottles provided from each laboratory were used for field blanks. The remaining synthetic water in the 100 Liter container was dispensed into the sulfuric acid preserved bottles and the bottles were labeled with the sample designation SB-BFx.

Sample shipment

Samples with the same batch number were transferred from the sample holding refrigerator to the coolers supplied by the analytical laboratories, frozen blue ice was added and the coolers were shipped to the sample delivery courier by overnight air express. The courier delivered the samples the following day to the analytical laboratories. Samples were shipped on April 27, May 4, and May 6. Samples were in transit approximately 24 hours longer than normal delivery times for local samples. However, all samples were acid preserved as the primary preservation technique.

III. Data handling

The initial results from the laboratories were reviewed to duplicate a careful examination of the data by a client with a knowledgeable technical staff. Data was examined to determine if the detection limit was appropriate for the specified method, if trip blanks and field blanks were free from contamination, and if data was reported to the correct number of significant figures. The agreement between field duplicates was checked. The QA/QC data supplied with the raw data was reviewed. Letters were sent to each of the participating laboratories asking them to verify that the correct method had been run, that the data had not been rounded off before it was reported and to recheck specified samples based on contamination of field blanks or poor agreement between field duplicates. The objective was to provide an opportunity for the correction of errors that a normal level of review would identify. The laboratory was not notified of sample results that did not fall into the expected concentration range since in normal practice, neither the commercial laboratory nor client staff would have accurate concentration information about the sample. Three of the laboratories made major revisions to the data and the final data set. The most common errors corrected were using the wrong method, reporting the numbers to the wrong number of significant figures and data transcription errors. The copper data from one laboratory was rejected because of apparent copper contamination of field blanks and trip blanks. The ammonia data from one laboratory was rejected because of blank contamination and a level of precision that was not typical of the performance of the other seven laboratories. All of the obvious, correctable errors have been removed from the data set that was used for the statistical analysis.

The corrected data set eliminated a number of outlying values that made large changes in some of the statistical calculations. The decision to err on the side of over correction was an

Table III

Chemical Spikes	Freq. Error Exceeds 20%	@ Confidence Limits:			Range Lo-Hi	N	Avg. Error: Mean/Median		Std Coef. Dev. Var.	
		75% CL	95% CL	99%CL						
Cadmium 1.6 - 2.4 µg/l.	p=70% a=69%	<172%	<273%	<351%	0-587%	77	83%	50%	115 %	138%
Copper 16 - 24 µg/l.	p=32% a=14%	<25%	<38%	<48%	0-100%	71	13%	10%	15%	117%
Lead 8-12 µg/l.	p=61% a=38%	<65%	<103%	<132%	0-217%	77	32%	13%	43%	135%
Selenium 8 - 12 µg/l.	p=73% a=69%	<60%	<86%	<106%	0-112%	77	38%	31%	29%	76%
Silver 8 - 12 µg/l.	p=63% a=54%	<105%	<172%	<224%	0-450%	79	45%	23%	77%	171%
Ammonia 2.5 mg/l.	p=52% a=37%	<33%	<47%	<58%	0-52%	106	21%	16%	16%	76%

*Note: The percent of time analytical error exceeds plus or minus 20%; p= predicted error based on mean and standard deviation, a=actual percent of cases exceeding 20% error within study population. All data reported here is considered preliminary and draft.

attempt to separate laboratory performance issues from the performance of the analytical method. Laboratory performance issues would have been compliance issues if these samples had been real samples, submitted for compliance monitoring. Normal NPDES reporting deadlines would not have allowed time for the laboratories to reevaluate data and correct mistakes. The triplicate values for every sample provided an opportunity to spot variability that is usually not available. Many of the values that were obviously in error in the study were confirmed by the laboratories and would have been required to be reported as violations by the permittee.

RESULTS

Cadmium

Labs located in Southern California claim 2 $\mu\text{g/L}$ is the practical quantitation level (PQL). Table 3 shows that, under real world conditions, most of those labs cannot accurately and reliably quantify the level of Cadmium within 20% of the known quantity (see Table 3).

An artificial effluent matrix spiked to levels between 1.6 and 2.4 $\mu\text{g/L}$ have an average error of 83%. The median error is 50%. Reported values ranged as high as 587% of the spiked concentrations.

California state law requires that laboratory analyses be within 20% of the known value 75% of the time. In this study, the laboratories actually exceeded the 20% error limit 69% of the time.

Based on 77 spiked Cadmium samples, with a mean error of 83% and a standard deviation of 115%, the labs are only capable of being within 172% of the actual value 75% of the time. 95% of the time the error is less than 273% and 99% of the time the error is less than 351%. This model estimates that laboratory analysis of Cadmium near the PQL will only be within 20% of the true value 30% of the time.

Copper

Labs located in Southern California claim 20 $\mu\text{g/L}$ is the practical quantitation level (PQL). Table 3 shows that, under real world conditions, most of those labs cannot reliably quantify the level of Copper within 20% of the known quantity (see Table 3).

An artificial effluent matrix spiked to levels between 16 and 24 $\mu\text{g/L}$ have an average error of 13%. The median error is 10%. Reported values ranged as high as 100% of the spiked concentrations.

California state law requires that laboratory analyses be within 20% of the known value 75% of the time. In this study, the laboratories actually exceeded the 20% error limit 14% of the time.

However, based on 71 spiked Copper samples with a mean error of 13% and a standard deviation of 15%, the labs are only capable of being within 25% of the actual value 75% of the time. 95% of the time the error is less than 38% and 99% of the time the error is less than 48%. This model estimates that laboratory analysis of Copper near the PQL will only be within 20% of the true value 68% of the time.

Lead

Labs located in Southern California claim 10 µg/L is the practical quantitation level (PQL). Table 3 shows that, under real world conditions, most of those labs cannot accurately and reliably quantify the level of Lead within 20% of the known quantity (see Table 3).

An artificial effluent matrix spiked to levels between 8 and 12 µg/L have an average error of 45%. The median error is 23%. Reported values ranged as high as 450% of the spiked concentrations.

California state law requires that laboratory analyses be within 20% of the known value 75% of the time. In this study, the laboratories actually exceeded the 20% error limit 38% of the time.

Based on 77 spiked Lead samples, with a mean error of 32% and a standard deviation of 43%, the labs are only capable of being within 65% of the actual value 75% of the time. 95% of the time the error is less than 103% and 99% of the time the error is less than 132%. This model estimates that laboratory analysis of Lead near the PQL will only be within 20% of the true value 39% of the time.

Selenium

Labs located in Southern California claim 10 µg/L is the practical quantitation level (PQL). Table 3 shows that, under real world conditions, most of those labs cannot accurately and reliably quantify the level of Selenium within 20% of the known quantity (see Table 3).

An artificial effluent matrix spiked to levels between 8 and 12 µg/L have an average error of 38%. The median error is 31%. Reported values ranged as high as 450% of the spiked concentrations.

California state law requires that laboratory analyses be within 20% of the known value 75% of the time. In this study, the laboratories actually exceeded the 20% error limit 69% of the time.

Based on 77 spiked Selenium samples, with a mean error of 38% and a standard deviation of 29%, the labs are only capable of being within 60% of the actual value 75% of the time. 95% of the time the error is less than 86% and 99% of the time the error is less than 106%. This model estimates that laboratory analysis of Selenium near the PQL will only be within 20% of the true value 37% of the time.

Silver

Labs located in Southern California claim 10 µg/L is the practical quantitation level (PQL). Table 3 shows that, under real world conditions, most of those labs cannot accurately and reliably quantify the level of Silver within 20% of the known quantity (see Table 3).

An artificial effluent matrix spiked to levels between 8 and 12 ug/L have an average error of 45%. The median error is 23%. Reported values ranged as high as 450% of the spiked concentrations.

California state law requires that laboratory analyses be within 20% of the known value 75% of the time. In this study, the laboratories actually exceeded the 20% error limit 54% of the time.

Based on 79 spiked Silver samples, with a mean error of 45% and a standard deviation of 77%, the labs are only capable of being within 105% of the actual value 75% of the time. 95% of the time the error is less than 172% and 99% of the time the error is less than 224%. This model estimates that laboratory analysis of Silver near the PQL will only be within 20% of the true value 37% of the time.

Ammonia

Labs located in Southern California claim .1 mg/L is the practical quantitation level (PQL) for ammonia. Table 3 shows that, under real world conditions, most of those labs cannot reliably quantify the level of Ammonia within 20% a the known quantity of 2.5 mg/L (see Table 3).

An artificial effluent matrix spiked to a level of 2.5 mg/L had an average error of 21%. The median error is 16%. Reported values ranged as high as 52% of the spiked concentrations.

California state law requires that laboratory analyses be within 20% of the known value 75% of the time. In this study, the laboratories actually exceeded the 20% error limit 37% of the time.

Based on 106 spiked Ammonia samples, with a mean error of 21% and a standard deviation of 16%, the labs are only capable of being within 33% of the actual value 75% of the time. 95% of the time the error is less than 47% and 99% of the time the error is less than 58%. This model estimates that laboratory analysis of Ammonia at level near 2.5 mg/L will only be within 20% of the true value 48% of the time.

DISCUSSION

Individual laboratory performance issues made it difficult to evaluate the performance of the analytical method and the influence of sample matrix. All of the laboratories had problems with one or more methods. There was always at least one laboratory that performed well on multiple samples for each method. There was no way to predict which laboratories would do well with any given method. There is no guarantee that the pattern of performance on a given method will be consistently repeated in subsequent studies.

The standard deviation for all samples was greater than expected, even for methods where the average performance was acceptable. This study indicates that the probability of making an incorrect measurement on any single sample is significant. Compliance determinations based on single samples in these concentration ranges will be made incorrectly due to normal analytical variability. Basing compliance determinations on averages will significantly reduce the number of violations that are due to analytical variability.

The analytical variability at the PQL level was greater than expected. This study indicates that it may be impossible to separate the variability of measurements with the variability of the concentration of a substance in an effluent. Interpreting the analytical variability in this study as effluent variability could have led to serious and erroneous conclusions. This data set was more tightly controlled both with respect to methods used and the elapsed time from beginning to end of the study, than programs like the 304 L process, which relied on data sets from different agencies, using different methods, over periods of several years, at levels that were at or below the PQL. The statistical methods used in the 304 L process placed great importance on the detection of a single value above the PQL through the use of substitution techniques for all non detected values.

The laboratories were consistently able to detect the substances when they were present and in not detecting the substances when they were absent. The selenium data indicates that the ability of the laboratories to detect the presence or absence of selenium in the 0 to 8 $\mu\text{g/L}$ range is excellent, while they were unable to quantify reliably at 10 $\mu\text{g/L}$. All of the zero concentrations in the study were determined in the presence of the other four analytes. Zinc was present in all samples at approximately 50 $\mu\text{g/L}$. The matrix contained common cations and anions in the 300 to 500 milligram per liter range. The ability of the methods to reliably determine presence or absence of a compound under difficult analytical conditions was demonstrated. The difference in the ability of the same laboratories to accurately quantify the same elements at a level 5 to 10 times the MDL in the same matrix was also demonstrated.

A number of serious errors were not identified by laboratory QA-QC systems. Results were reported using the wrong methods, in spite of written instructions to the laboratories. Reporting conventions, including significant figures and rounding were inconsistent. Internal QA-QC procedures were not able to explain analytical results that clearly were inaccurate or to identify possible contamination when travel blanks had measureable concentrations of an analyte. Probably error sources such as data transcription, improper sample sequencing, or

improper dilution factor calculations were not identifiable. All of these errors could lead to a finding of non compliance, since there was no analytical grounds to reject these results.

The study was able to identify problems with analytical methods because of the large number of replicates and the known value of the samples. Many of the analytical problems would not have been identified even with a well designed study, especially if a high degree of effluent variability was suspected. The study indicates large differences in laboratory performance between methods and between certified laboratories, using approved methods. As significant as these differences were to compliance determinations and statistical evaluation, there is no evidence that a discharger or a regulatory body could identify the laboratories with method problems, either through physical audits, review of internal QA-QC, or the level of external quality control usually found in effluent monitoring.

ACKNOWLEDGEMENTS

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REFERENCES

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CADMIUM

	SPIKE B	SPIKE C	SPIKE D	SPIKE E	FIELD BLANK	TRAVEL BLANK
KNOWN VALUES	ND µg/L	1.6 µg/L	2.0 µg/L	2.4 µg/L	ND µg/L	ND µg/L
LAB #1						
Sample 1	ND	ND	ND	ND	ND	ND
Sample 2	ND	ND	ND	ND	ND	ND
Sample 3	ND	ND	ND	ND	ND	ND
LAB #2						
Sample 1	ND	1.7	1.7	2	ND	ND
Sample 2	ND	3	4	4	NA	.3
Sample 3	ND	2	3	4	NA	NA
LAB #3						
Sample 1	ND	2	3	3	ND	ND
Sample 2	ND	2	2	3	ND	NA
Sample 3	ND	2	3	3	ND	ND
LAB #4						
Sample 1	ND	3	3	3.4	ND	NA
Sample 2	ND	2.4	3	3.4	ND	NA
Sample 3	ND	2.4	3.2	3.6	NA	ND
LAB #5						
Sample 1	ND	3	3	4	ND	ND
Sample 2	0.4	8	9	12	ND	NA
Sample 3	ND	8	10	11	NA	ND
LAB #6						
Sample 1	ND	1.5	1.9	2.3	ND	ND
Sample 2	ND	1.5	1.9	2.1	ND	NA
Sample 3	ND	1.4	1.7	2.1	ND	NA
LAB #7						
Sample 1	ND	2.9	3.2	4	ND	ND
Sample 2	ND	ND	3.3	4.1	ND	ND
Sample 3	ND	2.8	3.4	4.1	NA	ND
LAB #8						
Sample 1	ND	1.69	2.3	2.4	ND	NA
Sample 2	.08	1.51	2.04	2.24	ND	NA
Sample 3	.07	1.4	1.81	2.18	NA	NA

COPPER

	SPIKE B	SPIKE C	SPIKE D	SPIKE E	FIELD BLANK	TRAVEL BLANK	
KNOWN VALUES	16 µg/L	20 µg/L	24 µg/L	ND µg/L	ND µg/L	ND µg/L	
LAB #1	Sample 1	190	70	60	30	70	40
	Sample 2	20	20	20	ND	6	10
	Sample 3	ND	ND	ND	ND	ND	ND
LAB #2	Sample 1	18	25.5	23.5	ND	ND	ND
	Sample 2	18	18.5	26	ND	NA	ND
	Sample 3	16	18	11	ND	NA	NA
LAB #3	Sample 1	16	21	26	ND	ND	ND
	Sample 2	17	20	25	3	ND	NA
	Sample 3	18	21	26	2	3	3
LAB #4	Sample 1	15	15	19	ND	ND	NA
	Sample 2	15	18	22	ND	ND	NA
	Sample 3	14	17	20	ND	NA	ND
LAB #5	Sample 1	18	20	24	ND	ND	ND
	Sample 2	15	19	20	ND	ND	NA
	Sample 3	16	19	23	ND	NA	ND
LAB #6	Sample 1	16	29	24	ND	ND	ND
	Sample 2	13	18	21	ND	ND	NA
	Sample 3	13	18	20	ND	ND	NA
LAB #7	Sample 1	19	11	27	ND	ND	ND
	Sample 2	19	22	28	ND	ND	ND
	Sample 3	19	24	27	ND	NA	ND
LAB #8	Sample 1	20	20	20	ND	ND	NA
	Sample 2	19	18	25	ND	ND	NA
	Sample 3	17	21	33	ND	NA	NA

LEAD

	SPIKE B	SPIKE C	SPIKE D	SPIKE E	FIELD BLANK	TRAVEL BLANK
KNOWN VALUES	10 µg/L	12 µg/L	ND µg/L	8 µg/L	ND µg/L	ND µg/L
LAB #1 Sample 1	3	4	ND	3	ND	ND
Sample 2	3	4	ND	2	ND	ND
Sample 3	2	3	ND	2	ND	ND
LAB #2 Sample 1	8	10	ND	10	ND	ND
Sample 2	9	9	ND	4	NA	ND
Sample 3	9	13	ND	8	NA	NA
LAB #3 Sample 1	12	13	ND	9	ND	ND
Sample 2	10	29	ND	9	ND	NA
Sample 3	12	19	6	11	ND	ND
LAB #4 Sample 1	11	11	ND	5.6	ND	NA
Sample 2	9.8	12	ND	8.2	ND	NA
Sample 3	10	12	ND	7.8	NA	ND
LAB #5 Sample 1	12	13	ND	9	ND	ND
Sample 2	9	11	ND	8	ND	NA
Sample 3	9	11	ND	7	NA	ND
LAB #6 Sample 1	9	11	ND	7	ND	ND
Sample 2	8	11	ND	7	ND	NA
Sample 3	9	10	ND	7	ND	NA
LAB #7 Sample 1	9	23	ND	7.1	ND	ND
Sample 2	9.3	11	ND	7	8	ND
Sample 3	9.3	11	ND	7.2	NA	ND
LAB #8 Sample 1	9.09	11.6	ND	6.93	ND	NA
Sample 2	31	38	ND	ND	ND	NA
Sample 3	16	15	ND	ND	NA	NA

SILVER

		SPIKE B	SPIKE C	SPIKE D	SPIKE E	FIELD SPIKE	TRAVEL BLANK
	KNOWN VALUES	8 µg/L	10 µg/L	12 µg/L	ND µg/L	ND µg/L	ND µg/L
LAB #1	Sample 1	7	9	10	ND	ND	ND
	Sample 2	7	9	11	1	ND	ND
	Sample 3	10	14	16	1	ND	ND
LAB #2	Sample 1	7.5	5.5	5.0	2	ND	ND
	Sample 2	7	5.0	5.0	ND	NA	ND
	Sample 3	6.5	5.0	7.0	4	NA	NA
LAB #3	Sample 1	6	8	10	ND	ND	ND
	Sample 2	6	7	9	ND	ND	NA
	Sample 3	ND	11	10	ND	ND	ND
LAB #4	Sample 1	10	11	9.2	ND	ND	NA
	Sample 2	6.1	12	12	ND	ND	NA
	Sample 3	6.7	10	ND	ND	NA	ND
LAB #5	Sample 1	24	16	16	ND	ND	ND
	Sample 2	25	55	44	ND	ND	NA
	Sample 3	7	47	39	ND	NA	ND
LAB #6	Sample 1	7	9	10	ND	ND	ND
	Sample 2	6	8	10	ND	ND	NA
	Sample 3	6	9	10	ND	ND	NA
LAB #7	Sample 1	10	13	14	ND	ND	ND
	Sample 2	7.4	13	14	ND	ND	ND
	Sample 3	9.1	13	16	ND	NA	ND
LAB #8	Sample 1	6.56	8.08	11.1	ND	ND	NA
	Sample 2	6.57	8.9	10.8	ND	ND	NA
	Sample 3	6.0	9.0	8.39	ND	NA	NA

SELENIUM

	SPIKE B	SPIKE C	SPIKE D	SPIKE E	FIELD BLANK	TRAVEL BLANK
KNOWN VALUES	10 µg/L	12 µg/L	ND µg/L	8 µg/L	ND µg/L	ND µg/L
LAB #1 Sample 1	6	8	ND	5	ND	ND
Sample 2	7	8	ND	5	ND	ND
Sample 3	5	ND	ND	5	ND	ND
LAB #2 Sample 1	3.7	2.5	ND	3	ND	ND
Sample 2	3	4	ND	ND	NA	ND
Sample 3	ND	ND	ND	ND	NA	NA
LAB #3 Sample 1	12	13	ND	9	ND	ND
Sample 2	10	12	ND	9	ND	NA
Sample 3	10	10	5	17	ND	ND
LAB #4 Sample 1	5.3	8.9	ND	5.9	ND	NA
Sample 2	6.9	8.4	ND	6.1	ND	NA
Sample 3	6.5	9.0	ND	6.5	NA	ND
LAB #5 Sample 1	3	4	ND	ND	ND	ND
Sample 2	5	6	ND	3	ND	NA
Sample 3	5	9	ND	7	NA	ND
LAB #6 Sample 1	10	12	ND	6	ND	ND
Sample 2	9	11	ND	6	ND	NA
Sample 3	6	9	ND	5	ND	NA
LAB #7 Sample 1	15	14	ND	9.3	ND	ND
Sample 2	11	13	ND	9	ND	ND
Sample 3	11	13	ND	9.7	NA	ND
LAB #8 Sample 1	9.6	10	ND	5.5	ND	NA
Sample 2	5.2	11	ND	4.3	ND	NA
Sample 3	8.05	9.74	ND	ND	NA	NA

AMMONIA

	SPIKE B	SPIKE C	SPIKE D	SPIKE E	FIELD BLANK	TRAVEL BLANK
KNOWN VALUES	2.5 mg/L	2.5 mg/L	2.5 mg/L	2.5 mg/L	2.5 mg/L	ND mg/L
Sample 1	2.5	2.9	3.1	2.5	2.2	1.0
Sample 2	2.8	2.5	2.5	2.7	2.1	2.8
Sample 3	1.75	2.58	2.35	1.74	NA	ND
Sample 1	2.3	2.3	2.3	2.3	NA	ND
Sample 2	2.7	2.7	2.9	2.6	NA	ND
Sample 3	3.0	2.8	2.8	2.8	NA	NA
Sample 1	1.7	1.3	1.2	1.6	2.7	0.7
Sample 2	1.8	1.4	1.3	1.9	1.8	NA
Sample 3	1.3	1.6	1.6	2.2	NA	0.6
Sample 1	2.6	2.9	2.8	2.6	2.6	.1
Sample 2	2.8	2.7	2.7	2.5	2.3	ND
Sample 3	2.5	2.6	2.6	2.5	NA	NA
Sample 1	2	ND	3.3	3.1	3.1	2.5
Sample 2	3.6	3.4	3.4	3.2	2.8	NA
Sample 3	3.0	3.3	3.6	3.2	NA	NA
Sample 1	1.2	1.4	1.3	1.4	1.6	ND
Sample 2	1.3	1.2	1.4	1.5	1.4	NA
Sample 3	1.5	1.5	1.5	1.7	1.7	NA
Sample 1	13.6	7.2	5.0	7.2	1.1	ND
Sample 2	15.2	16.8	3.8	8	.7	ND
Sample 3	14	10.3	4.2	7.6	NA	ND
Sample 1	3.24	3.13	3.26	2.98	2.68	NA
Sample 2	2.72	2.86	3.02	2.76	2.52	NA
Sample 3	2.85	3.04	3.04	2.85	2.34	NA

APPENDIX D

LITERATURE SEARCH REVIEW
(PHASE I OF PROJECT)

LITERATURE SEARCH/SUMMARY OF PQL APPROACHES

Our literature search was performed in three ways. We initially performed several searches on different databases, including both scientific literature and the Federal Register using the DIALOG system with a variety of key words such as Practical Quantitation Limit, Detection Limit, Uncertainty, and Regulations in various combinations. This search turned up very little. We searched both the chemical literature and several legal databases. As you are already aware, there is little published in the open literature in this area, with most work being done by private industry or EPA, with publications in the grey literature. Our DIALOG search confirmed this, with less than half a dozen papers located in this manner. None of these articles are in the open literature. The literature search was terminated in April of 1992. Since that time additional work has been done by several groups, notably ASTM and EPA. Relevant articles through the original date are summarized below.

The second approach was to post a notice on the EPA Quality Assurance Bulletin Board System (BBS) in Cincinnati, which is accessed by a variety of laboratories and regulators, to determine whether any users were familiar with any unknown literature. Access to the Bulletin Board is available 24 hours a day (access number 513-569-7610). This proved even less fruitful than the DIALOG search, eliciting no responses to a posted mail message. It may still be fruitful for NJDEP to access this BBS for other searches pertaining to standard setting.

Our most successful approach was direct contact with colleagues and regulators. Several groups are actively working in this area in anticipation of regulatory changes at the Federal level. These include ASTM, ACS, Chemical Waste Management, EPRI, and EPA. We contacted several state regulators, industrial clients and consultants, and senior staff of the Office and Ground and Drinking Water at EPA to gain access to unpublished literature, including the upcoming Federal Register Notice pertaining to PQLs. In particular, because of our work in this field, we were asked to participate in the development of the Federal Register Notice. Because this notice is still in Draft Form, we are unable to cite it directly. However, because the nature of the information was presented recently at a public forum (April 1992 ACS Meeting) we can provide a synopsis of the key aspects of the Notice as they may impact NJDEP for Standard Setting. In addition, our direct contacts have uncovered several other relevant articles and presentations.

We are aware that some of the articles/presentations noted below are already available to NJDEP, because they are in the citation list for the new Proposed Surface and Ground Water Regulations for the State. Any of our articles which are also noted in there are not discussed in any detail. Copies of cited articles are available from us on request unless otherwise noted.

ABBREVIATIONS

Several abbreviations are used routinely in this summary and are defined here.

IDL - Instrument Detection Limit

LOD - Limit of Detection

MDL- Method Detection Limit (or Level)

ND - Non Detected PQL - Practical Quantitation Limit

RDL - Reliable Detection Level

MRL - Minimum Reporting Level

LOQ - Level of Quantitation, typically set at 10 sigma.

RQL - Reliable Quantitation Level

CMDL - Compliance Monitoring Detection Level

CMQL - Compliance Monitoring Quantitation Level

PE - Performance Evaluation

DQO- Data Quality Objectives

SDWA - Safe Drinking Water Act

MCLG - Maximum Contaminant Limit Goal

Alpha Error - false positive error rate (risk of saying something is present when it's absent).

Beta Error - false negative error rate (risk of saying something is absent when it's present).

APPROACHES TO DETERMINING QUANTITATION LIMITS

There are three major approaches to quantitation limits discussed in the literature. These include: conventional calculation of PQLs from performance data or multipliers of the MDL using the 40CFR136 definition of MDLs (original approach); determining PQLs based on uncertainty in calibration curves (alternative number 1); and finally multiples of the MDL where MDLs are defined in various manners but are generally more rugged than the original 40CFR136 definition (alternative number 2). EPA is proposing to abandon the PQL terminology and replace it with RQL, which is fundamentally similar in intent, but uses more rugged and consistent approaches. Each of the articles below addresses one of these approaches. A consensus is not yet available as to the best approach.

ABSTRACTS/SUMMARIES OF LITERATURE

Abstracts of relevant articles and presentations follow.

Newman, M. and Pinder, J. 1987. "Coping with Uncertainty: Limits of Detection, Limits of Quantitation, and Nested Sources of Error." WQTC Portland Oregon 1986 p 509. Discusses issues of censored data (non detects) and proposes several approaches to dealing with estimating means and variances for censored data sets. Relevant to the issue of making decisions on data which is below any proposed PQL.

Kempic, J., 1988. Memorandum: "Calculation of PQL for Lead and Copper." 22 Sept 1988. NTIS Document PB90-271966/XAB. Memo discussing the PQL calculation for lead and copper from results of PE studies. The same information was presented in a paper at the 12th Annual EPA Conference on Analysis of Pollutants (May 10-11, 1989). *Abstract only available*

Currie, L. Ed. 1988 "Detection in analytical chemistry". ACS Symposium Series 361. pp 335. A significant symposium volume which lays out the theory of hypothesis testing, focusing in particular on false negative/false positive issues. See in particular the introductory paper by Currie. "Detection: Overview of Historical, Societal, and Technical issues." Focuses on detection issues rather than quantitation issues.

Kempic, J. 1989. "Use of Water Supply Performance Evaluation Data to Calculate Laboratory Certification Criteria and Practical Quantitation Limits for Inorganic Contaminants". Presented at 12th Annual EPA Conference on Analysis of Pollutants (May 10-11, 1989). NTIS Document PB90-271933/XAB. Discussion of protocols used by EPA to calculate PQLs for inorganic contaminants for the SDWA. Generation of regression equations for Precision and Accuracy using EPA and State lab data. Calculation of 95% confidence limits from % recovery and RSD at the MCLG. Set certification criteria based on the 95% confidence limits ($2 \times \text{SD}/\text{True value}$). Determine PQL as the lowest level where 75% of State/EPA labs can still achieve the specified %RSD. As an example, Copper 95% confidence limits at the MCLG (1300 ppb) are 91-107% (approximately $\pm 10\%$) and 75% of the State/EPA labs could achieve $\pm 10\%$ down to just above 50 ppb in WS20-22. For lead, with an MCLG of zero, PQLs were initially estimated as 5 x the MDL of 1 ppb and subsequently verified in WS22 using the same criterion of 75% of State/EPA labs meeting the 95% acceptance criteria (in this case $\pm 30\%$).

Koorse, S. 1989. "False Positives, Detection Limits, and Other Laboratory Imperfections: The Regulatory Implications" Environmental Law Reporter. p 10211. This widely cited article discusses MDL, PQL concepts from a legal standpoint and suggests that MDLs are not an appropriate regulatory standard because they do not represent real world variability. Provides guidance to permittees on what to look for in laboratory reports to provide meaningful data for permit compliance.

Rosengrant, L, Craig, R. 1990. "Final Response to BDAT Related Comments Document: Halogenated Wastes. Volume 1-N" and "General BDATA Issues. Volume 1-A-2" EPA/530/SW-90/061B and 061P. NTIS PB90-234634/XAB and PB90-234493/XAB. EPA response to comments on BDAT treatment regulations relating to land disposal restrictions. Some of the comments deal with PQL concepts applied to land disposal. No details of the nature of comments available, but various industry viewpoints are addressed. Standard EPAOSW approach to PQLs. *Abstract only available.*

Grant, C. et al. 1991. "Experimental comparison of EPA and USATHAMA detection and quantitation capability estimators". American Laboratory February 1991 p 15. Compares MDL and quantitation limit calculations using the traditional EPA approach and US Army Toxic and Hazardous Materials Agency (USATHAMA), in which limits are determined from confidence bands on a regression analysis, using two example data sets (copper by Graphite furnace Atomic Absorption) and dinitrobenzene by HPLC). Recommends setting alpha and beta errors to meet DQOs. The USATHAMA approach pools data over several days, providing a more rugged estimate of the reporting limit (CRL). The calculation procedures also minimize both the alpha and beta errors. Demonstrates that when variance increases with concentration, the CRL is substantially above the calculated MDL. For methods which do not show much variation in precision at a variety of low concentrations, MDL and CRL estimates are similar. Demonstrates the need to choose accurate spike levels for assessing reporting limits. Similar conclusions to Hertz et al (1992). Does not directly address the concept of the PQL.

Gibbons, R. et al. 1991. "Detection Limits for linear calibration curves with increasing variance and multiple future detection decisions". Waste Testing and Quality Assurance: Third Volume, ASTM STP 1075, D. Friedman, ed. ASTM Philadelphia. p 377. Expands on earlier work of Clayton to define the detection limit based on calibration curve data and the variation in precision with concentration. The definition uses a regression equation of concentration versus response and minimizes both false negative and false positive errors. Results can be extrapolated from single lab data over time. Gibbons views are also represented by Grams and other industrial users and manufacturers.

Keith, L. 1991. "Report Results Right! Part 1". ChemTech p 352. Defines LOD, MDL, IDL, and RDL in accordance with proposed ACS definitions. Sets forth the concepts of acceptable alpha and beta errors based on desired confidence levels. Provides the definitions only. Guidelines for using the definitions are given in Part 2.

Keith, L. 1991. "Report Results Right! Part 2." ChemTech p 486. Recommends reporting data based on the data user interpreting the data, with either "liberal" or "conservative" guidelines depending on DQOs and the sophistication of the data user. Strongly recommends that each lab determine its own MDL. Examples of reporting approaches are listed here:

Result	Liberal	Conservative
"zero"	ND (RDL=x)	ND (RDL=x)
<MDL	value* (MDL=y)	less than y (MDL=y)
>MDL but <RQL	value** (LOQ=z)	value**(LOQ=z)
>RQL	value	value

where * and ** are flags for data below the MDL and LOQ respectively. Also recommends that symbols such as "<" NOT be used because of possible loss in electronic data transfer.

Hertz, C. et al. 1992. "Verification of Method Detection Limits for Organic Compounds in Drinking Water." WQTC Orlando, Florida November 1991. Presents single lab data comparing precision to concentration relative to the lab determined MDL, and then sets a Minimum Reporting Level based on Data Quality Objectives for Precision and Accuracy. Demonstrates that a single multiplier of the 40CFR determined MDL is not applicable for quantitation, but instead shows that minimum reporting levels may be substantially greater than the MDL or less than the MDL, as a function of the compound tested. This article raises questions on whether a single multiplier of the MDL is appropriate for environmental samples. Because Hertz used to work at NJDEP, we feel you are familiar with this work. It is a significant paper in that it calls into question the proposed NJDEP simple MDL multiplier approach.

Keith, L and D. Lewis. 1992. "Revised Concepts for Reporting Data Near Method Detection Levels". Presented at ACS April 1992 Meeting. Presents the proposed ACS Committee on Environmental Improvement (CEI) definitions for MDL, RDL, and RQL, which are also incorporated into the proposed EPA Federal Register Notice. Focuses on the use of the term "Level" rather than "Limit" since increased numbers of

measurements may reduce the measurable level, whereas limit implies a fixed point. Recommends inclusion of blanks and the use of representative matrices in calculating MDLs. and defining a reliable level of detection (RDL) as the point where alpha and beta error are both low, eg. twice the MDL. Recommends setting a quantitation level (RQL), which is twice the RDL determined in a single lab. The RQL value is considered arbitrary but consistent and is quite comparable to the original ACS concept of a level of quantitation equal to 10 sigma, when MDL is set at 3 sigma. The RQL would be equivalent to 12 sigma (4 times the MDL). Recommends having the users decide whether they wish to have labs report data at or below the MDL. The key part of the recommendation (with respect to Quantitation levels) is that MDLs be determined on representative matrices and under more representative conditions. *Because the MDL measured in a lab using this approach would typically be slightly higher than values determined under the old EPA approach (40 CFR 136), the expected quantitation levels should be reasonably close to PQLs estimated as 5 to 10 times the old MDL.*

Maddalone, R. et al., 1992. "Proposed Definitions for Compliance Monitoring Detection and Quantitation levels". Presented at ACS Committee on Environmental Improvement April 1992. Defines two new terms - CMDL and CMQL. Compares proposed EPA definitions of MDL, RDL, and RQL to calculations based on interlaboratory precision (CMDL and CMQL). Argues that pooled single operator precision from multiple labs yields an underestimate of the detection level compared to overall interlab precision and shows demonstration data from EPA Method Validation studies and Electric Power Research Institute (EPRI) studies demonstrating the difference in results. Does not address the fact that overall interlab precision does not correct for laboratories which have a systematic bias, thereby leading to increased estimates of variance. The proposed CMDL is theoretically equivalent to the MDL (alpha error = 1%) and the CMQL is theoretically equivalent to the RDL (beta error = 1%). This is an EPRI funded proposal and approach.

Gibbons, R. et al, 1992. "Practical Quantitation Limits." Chemometrics and Intelligent Laboratory Systems, 12:225. Recently published journal article suggesting an alternative approach to PQL calculations. Expands on the work of Clayton and Hubaux and Vos, using confidence limits to calculate MDLs and thus PQLs. With this method, the PQL can be estimated directly from calibration data over time in a single lab. The PQL is defined as the concentration for which the instrument response signal is $100/\alpha$ times the standard deviation of the response. This approach also allows one to calculate 95% confidence limits for the PQL. $100/\alpha$ is equal to the %RSD. Using a 10% RSD value yields PQLs for 10 volatile organics which are similar to the EPA published PQLs for the same compounds. Because a 10% RSD is equivalent to plus or minus 30% for 99% confidence limits, the resulting numbers should be more or less equal to EPA's results for VOAs, where the PQL was defined as +/-40% of true values.

OTHER RELATED ACTIVITIES:

ASTM has developed a task group under the auspices of Committee D-19 working on Detection and Quantitation concepts. The committee is chaired by Nancy Grams of Waste Management, Inc. This group now includes a number of other interested parties (including myself) who were in attendance at the recent ACS meeting in San Francisco and represents opinions of both regulators and the regulated community. A workshop following the ACS meeting focused on defining detection and quantitation and reporting and calculation of "DLs and QLs". No consensus has been reached in this group as yet. The ASTM group is not totally in accord with EPA's approach, leaning more towards the Gibbons et al. approach, but that is in part due to the interest in ASTM in developing definitions which may be site specific to take into account matrix effects. Since ASTM represents a set of diverse viewpoints it is unclear how quickly consensus will be achieved on the approach. The committee is extremely active and may well develop a "practice" document within the next 6-9 months. ASTM is concerned that EPA not promulgate a replacement to the PQL without insuring that it is reliable. For additional information, contact Nancy Grams at 708-208-3117.

EPA is proceeding with the draft Federal Register Notice (FRN) on replacing the PQL concept with the three new terms and definitions referred to earlier. The terms and definitions have been summarized in several public forums (WQTC 1991, ACS 1992, WQTC 1992) and we can therefore provide the basic concepts, **although the FRN itself is still in draft form and therefore not directly citable.** The latest proposed publication date is in the spring of 1993. EPA is proposing to replace the PQL term with the terms MDL (for Method Detection Level), RDL (for reliable Detection Level), and RQL (for Reliable Quantitation Level). The MDL definition is unchanged from earlier concepts and represents the level where the statistical likelihood of a false positive is <1%. The principle change in the MDL definition itself is a commitment by EPA to emphasize interlaboratory determinations and a recognition that MDLs within a single laboratory should not be overly optimistic for real-world measurements (eg. they must be conducted over time and also in a representative matrix). The RDL is defined as the point where the likelihood of a false negative is equal to the false positive probability and is essentially equal to twice the MDL. Interlaboratory performance studies can quantify this level. EPA is not directly addressing the issue of whether results should be reported to the MDL or only to the RDL, but the RDL is in general the recommended lowest level for qualitative decisions based on individual measurements. The RQL is proposed to replace the PQL concept and is defined as twice the RDL (equivalent to 12 sigma if the MDL is defined as 3 sigma). This recognizes that RDL estimates produced at different times by different operators for different representative matrices

will not often exceed the RQL. For rugged determinations of MDLs (eg NOT single lab, single operator) the RQL will probably be relatively close to the PQL under current definitions. The method for determining interlab MDLs is not yet fixed and options include calculations from validation studies with multiple labs (expensive), calculation from Youden Pair equivalent data in PE studies (relatively less expensive), or medians or means from multiple intralab determinations of MDLs (comparatively cheap). The PQL has historically been considered as somewhat arbitrary and capricious in its application (eg. when is a multiplier of 5 x MDL vs 10 x MDL used?) whereas the MDL/RDL/RQL definitions have a more firm statistical basis. The FRN is expected to be issued in June or July of this year and will generate extensive comment. EPA is unlikely to resolve this issue before the fall of 1992. The principal impetus for resolving it is in conjunction with the Phase V Drinking Water Regulations, but if reaction is favorable, the concepts may well be applied to other matrices, although perhaps with different confidence limits, depending upon Data Quality Objectives (DQOs). The FRN is designed as a request for comments and NJDEP may want to comment.

Listed below are several additional examples of "Reporting limits" which exist in the literature for promulgated methods. Neither of these proposals is well defined and are probably not worth considering for experimental verification of Quantitation limits.

California Air Resources Board (CARB). Reporting limit (RL). Lowest level which can be reliably quantitated with specified limits of precision and accuracy during routine analysis. Also defined as 5 times the LOQ.

EPA Technical Support Division (TSD). Minimum Level (ML). Lowest point at which the calibration curve determined in reagent water gives recognizable data and acceptable calibration points. May be significantly above the MDL because precision requirements are tighter. Specifically cited as distinct from the PQL, which is noted as arbitrary. EPA Office of Ground and Drinking Water is not familiar with this proposal, but it may be superseded by the new Federal Register Notice.

