A PRAGMATIC APPROACH FOR DETERMINING PRACTICAL QUANTITATION LEVELS (PQLs) FOR REGULATORY PURPOSES

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ABSTRACT

An approach for calculating the Practical Quantitation Level (PQL) is described that does not require changes in current laboratory practices. The Reliable Detection Level (RDL), when defined as twice the concentration of the Method Detection Limit (MDL), provides adequate protection against both false positive and false negative detection decisions. It can be shown that when analyte concentrations are at the RDL, the corresponding precision in the instrument response is adequate for analytical purposes. Therefore, the RDL (as determined by a single laboratory) is a reasonable lower limit of quantitation for that laboratory. To determine an interlaboratory Practical Quantitation Level (PQL) suitable for regulatory purposes, median interlaboratory MDLs were multiplied by a factor of 4 (as per suggested definition of the Reliable Quantitation Level (RQL)) or multiplied by a variable factor (usually 4-7, determined from actual laboratory performance data obtained from the survey). It was found that greater than 80 percent of the laboratories surveyed had RDLs less than or equal to the calculated PQL. This indicates that adequate quantitation was attainable at this level and the PQL should be suitable for regulatory purposes.

Need to mention somewhere
your survey of labs

INTRODUCTION

Recently, there has been considerable interest in the determination of the lowest quantifiable level that is suitable for regulatory purposes[1-8]. Since allowable concentration goals for a contaminant in a particular environmental compartment (soil, air, water, etc.) based on health-related risk assessments frequently are lower than levels that can be quantitated in a laboratory, the lowest quantifiable level frequently assumes the role of the regulatory limit for monitoring and compliance purposes.

Many different names have been attached to the lowest quantifiable level. Currently circulating terms include the Practical Quantitation Level (PQL, defined by the U.S. Environmental Protection Agency[9]), the Limit of Quantitation (LOQ, defined by the American Chemical Society[10]), the Reliable Quantitation Level (RQL, suggested for regulatory use[2]), the Minimum Level (ML, EPA Office of Wastewater Enforcement and Compliance[5]), the Compliance Monitoring Quantitation Level (CMQL)[11], the Quantitation Level (QL)[12], and the Method Quality Control Level (MQCL)[7]. While the rationale supporting these approaches may differ, the basis for each is shared, that is, the need to establish the lowest quantifiable level that is suitable for use as a regulatory level when evaluating compliance. To be useful in this role, the regulatory level should be adequately quantifiable by the majority of laboratories certified or registered for the particular compound and method of interest. At the same time, the regulatory level should be below the level achievable by poorly performing laboratories, in order to provide incentive for these laboratories to improve their detection and quantitation levels. The procedure to calculate the regulatory level therefore needs to take into account actual performance data from the laboratory community.

Three major approaches have been used for determining the lowest quantifiable level. First, interlaboratory studies may be conducted, in which a group of laboratories are challenged with low-level samples[9,13,14]. This approach is probably the most defendable, because direct measurements are made of the quantitative abilities of an actual laboratory "community". The lower limit of quantitation can then be set according to selected criteria of precision and accuracy. However, these studies are time-consuming and expensive, and one of the specific goals of this study was to investigate more rapid and cost-effective alternatives to interlaboratory studies. A second approach employs statistical techniques based on uncertainties in the calibration curve[6]. This approach is perhaps the most theoretically satisfying, because a quantitation level can be derived from the same calibration curve used to analyze environmental samples. Related approaches have been described for determining a limit of detection from calibration data[15,16]. However, such approaches would require some changes in current calibration practices. The final approach employs a multiplication factor, typically in the range of 3-10, applied to the detection limit[2,5,9,10]. This was the approach investigated in this study because it is widely used and does not require changes in current laboratory practices.

The starting point for determining a lower limit of quantitation using the multiplier approach is having a value for the detection limit. For environmental compliance monitoring in the United States under U.S. Environmental Protection Agency (U.S. EPA) regulations, a Method Detection Limit (MDL) is currently determined according to specific guidelines[17]. The MDL is not suitable as a regulatory level for the following reasons: 1) it varies from laboratory to laboratory[18], 2) precision of measurements at this level are generally poor[19], and 3) while the MDL provides adequate protection against false positive results, protection against false negatives is inadequate, since samples containing contaminants at a concentration near the MDL will not be reported as detected 50% of the time[16,18,20]. A proposed new parameter, the Reliable Detection Level (RDL), is twice the value of the MDL and is sufficiently above the MDL value so that samples at this concentration will be reliably reported as detectable, because it provides adequate protection against both false positives and false negatives[18]. (This parameter was originally proposed as a Detection Limit (DL) by Currie[20]). The RDL is therefore suitable as a regulatory level <u>if</u> adequate quantitation at this level is achievable. However, the RDL is derived from the MDL and will still vary between laboratories. Subsequently, each laboratory would report a different quantitation level for a particular method and compound. In order to determine a single regulatory level that most laboratories will be able to achieve, it is necessary to take performance variation in the laboratory community into account.

In this paper, we describe an approach for determining a lower limit of quantitation that most laboratories should be able to achieve, using readily available data from the laboratory community. First, the derivation of the precision of analytical measurements at the RDL will be examined, using two fundamental analytical relationships and the U. S. EPA-defined MDL. This precision will be shown to be adequate to justify including RDL on the calibration curve as a quantitative level. We then define the Practical

Quantitation Level (PQL), for purposes of this paper, as the level which is **greater than or equal to the RDLs for a majority of laboratories** in an appropriate laboratory community. This is similar to the definition of the RQL proposed by Keith[4]. Two different multipliers of the median interlaboratory MDL are then employed to determine a PQL: 1) a constant multiplier of 4, which corresponds to the suggested Reliable Quantitation Level (RQL), and 2) a variable multiplier which is determined from actual laboratory performance data gathered for the compound and method of interest.

THE MDL AND THE RDL: THEORETICAL CONSIDERATIONS

The MDL can be derived from two fundamental concepts of instrumental analysis: the calibration relationship and the minimum distinguishable signal. These two concepts can also be used to determine the precision of measurements made at the MDL. Throughout this discussion, it is assumed that a single laboratory is being considered.

The acceptable quantitation range for an analyte in solution is the concentration range for which there is a linear relationship between the instrument response and the concentration of the analyte within the constraints of a specified confidence level (usually 95%). This relationship defines the linear calibration curve[21]:

$$S=mC+S_{bl} \tag{1}$$

where S is the magnitude of the analytical signal, m is the slope of the calibration curve, C is the analyte concentration

and S_{bl} is the magnitude of the analytical signal for a blank sample.

The minimum distinguishable analytical signal has been described as

$$S_{min}=S_{bl}+ks \tag{2}$$

where S_{min} is the magnitude of the minimum detectable analytical signal, S_{bl} is again the magnitude of the analytical signal for a blank sample, s is the standard deviation of the blank signal in instrument response units, such as millivolts, and k is a multiple of the standard deviation of the blank signal[21].

If S in Equation (1) is set to S_{min} , C will correspondingly be equal to C_{min} , the sample concentration that gives the minimum distinguishable analytical signal. Both Equations (1) and (2) can then be solved for $S_{min} - S_{bl}$, and the equations can be combined to give

$$ks=mC_{min} \qquad (3)$$

This equation provides the basis for determining both the MDL and the precision of measurements at this concentration.

1. U.S EPA definition of the MDL.

Both sides of Equation (3) may be divided by m:

$$ks_C=C_{min}, \qquad (4)$$

where s_C is the standard deviation of the instrument response in <u>concentration units</u>. The U. S. Environmental Protection Agency defines the MDL as 3.14 times the standard deviation (in concentration units) of seven replicate measurements of a standard concentration (the spike level)[17]. An inherent assumption that is made when using unweighted least-squares calibration curves is that the standard deviation of the instrument response is constant at all concentrations, including blank samples, samples at the MDL, and samples at the MDL spiking level[15]. While this assumption is not necessarily true for the entire working range of the calibration curve, it is approximately correct at concentrations at the low end of the concentration range[16,18]. Therefore, the magnitude of s_C in equation (4) for the blank signal is also applicable at the MDL spike level. Substituting the multiplier of 3.14 for k in equation (4) above, C_{min} , which is the concentration which gives a minimum distinguishable signal, becomes the U.S. EPA-defined value for the MDL:

$$3.14 s_C = C_{min} \equiv MDL. \tag{5}$$

Equation (5) is identical to the MDL equation appearing in the EPA regulations, and it uses a value for s_C that is calculated from seven replicate determinations of the concentration at the given spike level.

2. Precision of Instrumental Measurements at the MDL

Equation (3) also provides the basis for determining the theoretical precision of instrumental measurements. According to the U.S. EPA approach, the slope (m) in Equation (3) is approximated by a response factor S/C , which is calculated from an average of seven replicate measurements at the MDL spike level. Note that this assumption ignores the magnitude of the blank signal, S_{bl}, shown in Equation (1). The assumption is made because S_{bl}, the y-intercept, cannot be determined from analysis at a single concentration point. Although theoretically invalid if the magnitude of S_{bl} is significant, in practice this quantity is generally small, since the calibration curve usually passes close to the origin. The response factor is assumed to be constant, including the concentration which gives a minimum distinguishable signal (S_{min}/C_{min}). Equation (3) can then be reexpressed as

$$ks=(S_{min}/C_{min})*C_{min} \tag{6}$$

or

$$ks=S_{min} \tag{7}$$

Rearrangement of Equation (7) indicates that the multiplier, k, is quantitively equal to the signal-to-noise ratio at the minimum distinguishable signal, S_{min}:

$$k=S_{min}/s\equiv S_{min}/N, \tag{8}$$

where N has been substituted for s.

The signal-to-noise ratio is also described as the inverse of the relative standard deviation (RSD) of the instrument response[21]:

$$S/N=1/RSD \tag{9}$$

If S is taken as S_{min}, Equations (8) and (9) can be combined:

$$k=1/RSD_{min} \tag{10}$$

where RSD_{min} is the relative standard deviation of the instrument response for the minimum distinguishable signal. The value of k is therefore inversely proportional to the relative standard deviation of the minimum distinguishable signal for a replicate set analysis. As discussed above, S_{min} is defined as the instrument signal at the MDL when k is set at 3.14. This value for k is selected because it is the student-t value for seven replicate measurements at the 99% confidence level, which ensures protection against false positive detection decisions. The inverse of this value, 0.318 or 31.8%, is the relative standard deviation of the instrument response at the MDL.

3. Precision of Instrumental Measurements at the RDL

The above derivations show that the multiplier, k, set to 3.14 by the U.S. EPA, determines both the value for the MDL and describes the precision of the instrument response at this level. As discussed in the introduction, the RDL is preferable as a concentration level to make a detection decision, since it also protects against false negative detection decisions. Since the RDL has been defined as twice the MDL[2], the multiplier, k, to obtain this value would be twice that used for the MDL, or 6.28. Since the absolute magnitude of the instrument noise is assumed to be constant at low levels, the relative standard deviation of the instrument response would be 1/6.28 or 0.159 (15.9%) at the RDL.

4. Precision of Reported Concentrations at the RDL

To translate the precision of the instrument response to a precision for a reported concentration at the RDL, a calibration curve must be used. A sample calibration curve for 1,1-dichloroethene using Method 502.2 is shown (Figure 1). The r-square value for this curve, 0.998, is typical from a good laboratory. Confidence limits at the 95% level are shown, which are routinely used as control limits. Prediction limits are also shown, which are discussed below. The relative standard deviation of the instrument response at the RDL (15.9%) represents one standard deviation of the instrument noise and can be multiplied by a factor of 2.45 (student's t multiplier for seven replicate measurements, two-tailed test) to give an estimate of ±39% as the uncertainty of the instrument signal at an equivalent confidence level (95%). The laboratory in this example reported an RDL of 1 μg/L. It can be shown through example that the precision of the instrument response at the RDL lies within the confines of the confidence interval for the calibration curve, and that the uncertainty in the predicted concentration due to instrument noise will be small relative to the concentration interval bounded by the confidence limits. As shown in the close-up of the low end of the calibration curve (Figures 2A-C) the instrument response at the RDL (1 μg/L) is 24,000 area units (trace d-e-f). The 95% confidence interval for the signal uncertainty at this level (±39%) corresponds to ±9,400 area units (Figure 2A, points g). When a 1 μg/L sample is analyzed, this translates to a reported concentration of 1.0 ± 0.3 μg/L (Figure 2A, point f ± points h) due to variation in **instrument response**. The estimated precision of a measurement of 24,000 area units based on the uncertainty of the **calibration curve** is described by the confidence interval (Figure 2B, interval e - i). This would lead to a reported concentration of 1.0 ± 1.2 μg/L (Figure 2B, point f ± point j). This concentration range is much larger than the range resulting from variations in the instrument response. Furthermore, although the confidence interval is commonly used in practice, it is theoretically valid only for the mean of replicate measurements[22]. For concentration predictions from individual measurements, it is theoretically more correct to use the prediction interval[22]. The estimated precision of a measurement of 24,000 area units based on the **prediction interval** can be described by concentration interval e - k (Figure 2C). This would lead to a reported concentration of 1.0 ± 2.7 μg/L (Figure 2C, point f ± point l).

It is clear that instrument precision at the RDL is much greater than that associated with the calibration curve in this region. As stated above, the calibration curve used in this example is typical and was being used by this laboratory to report concentrations down to its MDL (0.5 μg/L). Obviously, reporting concentrations at the RDL (1.0 μg/L) would pose no difficulty. Since the RDL, when defined as twice the EPA MDL, also offers adequate protection against both false negative and false positive detection decision errors, this parameter appears to be a justifiable quantitation level <u>for a single laboratory</u>.
As stated above, the PQL is defined for purposes of this paper as an interlaboratory parameter, specifically a quantitation level suitable for use by a <u>group</u> of laboratories. The RDL is not in itself sufficient to set as a regulatory level, since RDLs will vary from laboratory to laboratory. For this reason, it was necessary to investigate the variability of RDLs determined by different laboratories in order to determine a procedure for obtaining an adequate PQL.

CALCULATION OF PRACTICAL QUANTITATION LEVELS

1. Utilization of Laboratory Performance Data

Thirty-six environmentally important chemicals which were analytes in one or more of eight standard methods of the U.S. Environmental Protection Agency were studied (Table 1).

The methods chosen were either among the most frequently used EPA methods or were considered the current state-of-the-art methods technologically. These methods include water, drinking water and wastewater. The 200 series methods are used to determine individual metal analytes in water. The remaining methods determine multiple analytes. The three 500 series methods chosen are used for organic chemicals in drinking water and the two 600 series methods determine organic compounds in wastewater. The compounds studied were selected because they were either under current review by the New Jersey drinking water program or they were considered environmentally important due to use, mobility, or toxicity.

Thirty-six laboratories certified by the State of New Jersey and 15 member laboratories of the Association of California Testing Laboratories (ACTL) were surveyed for information routinely reported for quality assurance purposes.

Three types of relevant data were found to be easily obtainable from the various laboratories: the determined MDL value, the low point on the calibration curve, and the spike level used to determine the MDL. The spike levels and calibration curve low points were generally set by analysts, taking into consideration the MDL reported in the method of interest.

Data were rejected for this study if the MDL spike level was greater than 50 times the reported MDL for a particular laboratory or if the information provided on the calibration curve range was inconsistent with the cited method. U.S. EPA guidelines suggest that the spike level should be 1-5 times the reported MDL, and allows a ratio of up to ten[17], but for this study a ratio of up to 50 was allowed to minimize the number of rejected laboratories. Using the more conservative 1-10 range would have resulted in discarding many data points, for it was not uncommon for the ratio to be as high as 20.

2. Variability of Reliable Detection Levels

For a given chemical and method, distributions of the RDLs from the various laboratories were prepared in order to ascertain the variability of this parameter from laboratories certified for that method (Figures 3A-D). The MDLs reported by the laboratories were multiplied by a factor of 2 to obtain the RDLs. The RDL's were not normally distributed. Most were clustered within a well-defined range, while a few outliers were reported at significantly higher levels. In the previous section, it was demonstrated that an individual laboratory could adequately quantify a concentration at its own RDL. Therefore, a PQL that most laboratories could achieve would be at or near the upper end of the main RDL distribution, while excluding outliers that are above the bulk of the distribution. Several outliers are clearly visible in Figures 3A-D.

3. Calculation of PQLs from Laboratory Performance Data

While a PQL could be set by visual examination of RDL distributions such as those shown in Figures 3A-D, such a procedure would be subjective. A reproducible approach needed to be developed. As discussed in the introduction, a multiplier of an interlaboratory MDL was the approach selected for this study. (The multiplier could be divided by a factor of 2 and applied to the "interlaboratory RDL" instead, but since labs report the MDL, use of this parameter is more convenient).

The first step in this process was to select a representative interlaboratory MDL for the group of laboratories surveyed. For this study, the median of the individual MDL values from each laboratory for a given compound and method was used. The use of the non-parametric median value was chosen instead of the mean because it was desired to minimize the influence of outliers at the upper end of the MDL distributions. The values at the high end of the distributions represent poorly performing laboratories relative to most of the laboratories surveyed. This method of calculation of the central tendency of the MDL dataset was tested by several data rejection criteria. In each method used, the outlier was significant at the 10%, 5% and 1% levels. Once the outlier was rejected, the mean value was recalculated and compared to the median value prior to filtering the dataset. In every instance the mean value converged to the previously calculated median value. Visually, the advantages of median over the mean is illustrated in terms of the RDL distributions (Figures 3A-D) which look identical to the MDL distributions but are at twice the MDL concentrations. It was visually apparent that when the mean and median RDLs differed significantly, the median RDL better represented the central tendency of the bulk of the distribution.

Two multipliers were applied to the median interlaboratory MDL to calculate a PQL: 1) A multiplier of 4, suggested by Keith for calculating the Reliable Quantitation Level (RQL)[2], and 2) a variable multiplier, which was determined from the MDL spike level and calibration curve low point data supplied by the laboratories for this study. Specifically, this latter approach consisted of three steps for determining the PQL for each compound for a given method:

1. The ratio of the reported MDL spike level to the determined MDL was calculated for each laboratory (spike ratio). The <u>median</u> ratio was then calculated.
2. The ratio of the calibration curve low point to the determined MDL was calculated for each laboratory (calibration ratio). The <u>median</u> ratio was then calculated.
3. The lower of the two median ratios calculated in steps (1) and (2) was selected as the multiplier of the MDL to determine the PQL.

The variable multiplier approach described above is satisfying for two reasons. First, the approach is <u>practical</u>, in that the data needed for its determination is routinely reported by the laboratories (the MDL, the MDL spiking level, and the low point on the calibration curve). Second, the multiplier is based on actual laboratory performance data, rather than theoretical considerations. Individual calibration and MDL spike ratios for each laboratory represent multipliers that, if used for that single lab, would result in that lab's PQL being set at either it's MDL spike level or it's low point on the calibration curve. Adequate measurements of both of these levels must be made by the laboratory to routinely run the method in a quantitative mode. Therefore, the multiplier for a particular laboratory is <u>known</u> to give a quantitation level that is achievable. In step 3, the median MDL is multiplied by the lowest median ratio that is known to give a quantifiable level. This results in a median PQL that is <u>known</u> to be achievable by at least half of the laboratories. As will be illustrated in the next section, this PQL will in fact be found to be achievable by <u>most</u> of the laboratories. Note that this procedure results in a <u>method and chemical-specific</u> PQL.

Two additional useful features of this method may be described. First, the PQL value is derived from laboratory performance data, which means that it serves as a baseline for monitoring the improvement of analytical sensitivities with time. Second, this PQL is useful to the regulatory community in that it is indicative of the current analytical capabilities for a particular compound and method.

RESULTS AND DISCUSSION

Table 2 is an example of the data worksheet for trichloroethene, Method 524.2, showing the data collected from the laboratories and the calculation of the PQL using the floating multiplier approach. In this example, the median MDL, 0.22 μg/L, was slightly lower than the mean, 0.26. The median spike ratio, 5, was lower than the median calibration ratio 7. Thus, the median MDL was multiplied by 5 to result in a PQL of 1.1 μg/L for this compound.

As illustrated in Table 2, individual lab multipliers usually ranged from 3 to 20, although occasionally they exceeded these ranges. The median multiplier used for PQL calculation usually ranged from 4 to 7 (Table 1, Figure 4A). For Methods 502.2 and 524.2, the mode of the ratio distribution was 5 (Figure 4B,C). When only the wastewater methods were considered (600 series), the mode of the ratio was 6 (Figure 4D). This results from the somewhat higher spike levels and calibration curve low point values typically used in the 600 series methods, the higher levels being used in order to allow for matrix effects in these wastewater methods.

A comparison between the PQLs determined by the variable multiplier approach and the RQL determined using a multiplier of 4 are shown in Table 1. Since the variable multiplier was seldom less than 4, the PQL was seldom less than the fixed multiplier RQL. The exceptions were atrazine and simazine in Method 507, which had a variable multiplier of two, and 1,2,4-trichlorobenzene and dichloromethane in Method 524.2, where the multiplier was 3.

The final step in assessing the suitability of the calculated PQLs is to ascertain what percentage of the laboratories could adequately quantify at these levels. As discussed above, the variable multiplier approach results in a "median" PQL which by definition should be quantifiable by at least half of the laboratories, because the multiplier links the MDL to the calibration curve low point or to the MDL spiking level. However, both of these analytical levels are above the minimum quantifiable level, since they usually are somewhat greater than the RDL, which is a factor of only 2 times the MDL. Since the RDL represents a suitable minimum quantifiable level, the calculated PQL must be compared to the RDL distributions of the individual laboratories to determine what percentage of laboratories have RDLs less than or equal to the calculated PQLs. As illustrated in Figures 3A-D, the PQL typically fell at or near the upper end of the main RDL distribution and eliminated the outlier values from poorly performing laboratories. The percentage of laboratories that had RDLs that were less than or equal to the calculated PQLs for all methods and compounds were determined and are tabulated in Table 1. It can be seen that with only a few exceptions,

>80% of the laboratories were able to adequately quantify at the PQL based on their value for the RDL. There were a few additional laboratories that could not achieve the RQL when the fixed multiplier of 4 was used, but the differences between the two procedures were not large.

CONCLUSIONS

Analysis of quality assurance data from 51 California and certified New Jersey Laboratories has led to the development of a procedure for calculation of PQLs from existing data that yields a PQL that is quantifiable by a majority of the analytical laboratories participating in the study. The PQL, which is compound and method specific, most frequently is in the range of 4 to 6 times the median interlaboratory MDL. Based on this study, data from as few as five laboratories for a particular compound and method may provide meaningful results.

The data needed for the PQL calculation procedure described in this study is available without any changes in current laboratory analytical practicies. The procedure could either be used to calculate compound-specific multipliers to determine PQLs, or alternatively, the observed clustering of multiplier values in the range of 4 to 7 could be used to justify selection of a constant multiplier in this range.

This procedure should be applicable to any standard method and chemical for which adequate data is available. It provides a basis for judging the current state-of-the-art quantitative ability of the laboratory community and a scientific basis for regulations which require an actual reportable concentration value for use as standards.

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DISCLAIMER

The contents of this publication do not represent the policy of the New Jersey Department of Environmental Protection.

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Table 1. PQLs and Laboratory Achievability For Methods and Compounds Studied

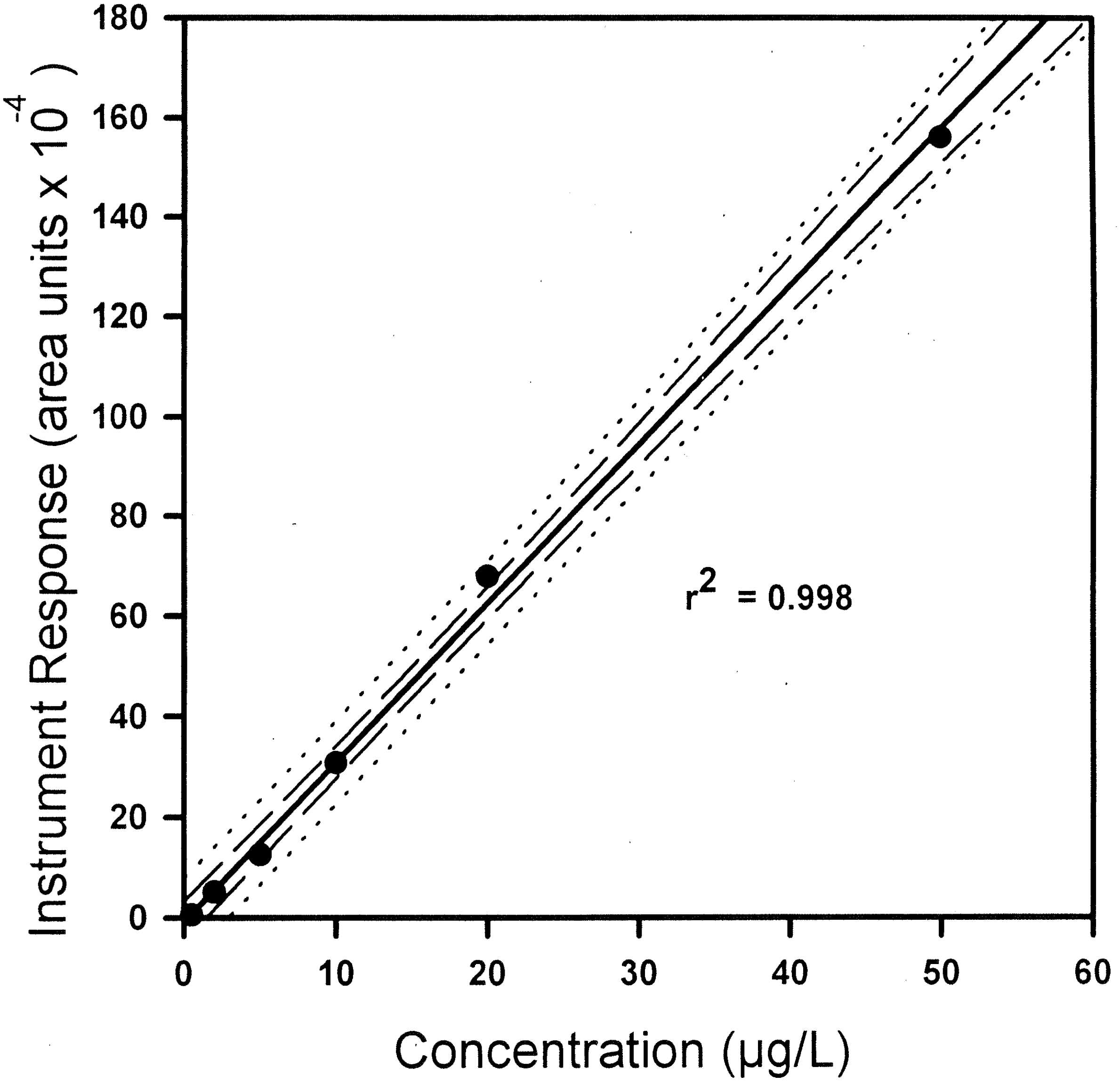
Method	Compound	# of labs	Median MDL (µg/L)	Median Spike Spike Level (µg/L)	Median Calibration Low Point (µg/L)	Lowest ratio	PQL (µg/L)	EPA RQL (µg/L)	% labs able to quantify	
									at PQL	at EPA RQL
220.2	Copper	15	1.00	5	5	4	4	4	93	93
239.2	Lead	39	1.30	6	5	4	5.2	5.2	87	87
213.2	Cadmium	28	0.18	1	1	4	0.7	0.7	79	79
502.2	1,1,1-Trichloroethane	11	0.22	1	1	6	1.3	0.88	100	91
	1,1-dichloroethene	12	0.18	1	1	5	0.88	0.7	92	75
	1,2,4-trichlorobenzene	12	0.21	1	1	6	1.2	0.82	92	83
	1,2-dichloroethane	11	0.15	1	1	7	1	0.6	100	82
	cis-1,2-dichloroethene	12	0.19	1	1	7	1.3	0.76	92	83
	1,2-dichlorobenzene	11	0.16	1	1	5	0.87	0.64	91	91
	1,3-dichlorobenzene	11	0.17	1	1	7	1.2	0.68	100	91
	1,4-dichlorobenzene	11	0.15	1	1	6	0.94	0.6	100	82
	Benzene	12	0.28	1	1	6	1.6	1.1	92	92
	Chlorobenzene	12	0.21	1	1	6	1.3	0.84	100	92
	Ethyl benzene	12	0.23	1	1	5	1.2	0.92	100	100
	Dichloromethane	11	0.50	1	1	4	1.8	2	91	91
	Styrene	12	0.28	1	1	5	1.5	1.1	92	83
	trans-1,2-dichloroethene	12	0.22	1	1	6	1.2	0.86	92	92
	Tetrachloroethene	12	0.28	1	1	5	1.3	1.1	92	92
	Toluene	12	0.20	1	1	8	1.6	0.8	100	92
	Vinyl chloride	10	0.27	1.5	1.5	4	1.2	1.1	90	80
	Xylenes	12	0.29	1	1	5	1.4	1.1	92	92
	Naphthalene	12	0.28	1	1	5	1.5	1.1	92	83
	1,1,2,2-tetrachloroethane	11	0.20	1	1	5	1	0.8	100	91
	1,1,2-trichloroethane	11	0.17	1	1	9	1.5	0.68	100	91
	1.1-dichloroethane	11	0.17	1	1	7	1.2	0.68	100	91
524.2	1,1,2-trichloroethane	19	0.25	1	2	4	1	1	84	84
	1,1,2,2-tetrachloroethane	20	0.31	1	2	4	1.2	1.2	85	85
	1,2-dichloropropane	21	0.24	1	2	6	1.4	1	95	90
	Carbon tetrachloride	21	0.20	1	2	5	1	0.8	95	90
	Trichloroethene	22	0.22	1	2	5	1.1	0.9	95	86
	Chloroform	20	0.22	1	2	5	1.1	0.9	90	90
	1,1,1-Trichloroethane	12	0.19	1	2	7	1.4	0.74	92	92
	1,1-dichloroethene	12	0.31	1	2	5	1.6	1.2	100	92
	1,2,4-trichlorobenzene	12	0.31	1	2	3	1	1.2	83	92
	1,2-dichloroethane	12	0.25	1	2	4	1	1	92	92
	cis-1,2-dichloroethene	12	0.20	1	2	5	1.1	0.8	83	83
	1,2-dichlorobenzene	12	0.23	1	2	4	0.96	0.91	83	83
	1,3-dichlorobenzene	12	0.18	1	2	8	1.4	0.72	92	92
	1,4-dichlorobenzene	12	0.19	1	2	5	1	0.76	92	92
	Benzene	12	0.22	1	2	5	1.1	0.86	83	83
	Chlorobenzene	12	0.17	1	2	8	1.3	0.68	92	92
	Ethyl benzene	12	0.16	1	2	8	1.2	0.64	92	92
	Dichloromethane	12	0.41	1	2	3	1.3	1.6	92	92
	Styrene	12	0.16	1	2	7	1.1	0.64	92	92
	trans-1,2-dichloroethene	12	0.17	1	2	5	0.79	0.67	75	67
	Tetrachloroethene	12	0.21	1	2	6	1.2	0.84	92	83
	Toluene	12	0.15	1	2	8	1.3	0.6	92	83
	Vinyl chloride	12	0.37	1	2	4	1.6	1.5	92	92
	Xylenes	11	0.31	2	2	6	1.8	1.2	91	91
	Naphthalene	11	0.42	1	2	4	1.5	1.7	73	73
	1,1,2-trichloroethane	11	0.25	1	2	4	1.1	1	91	91
	1,1-dichloroethane	11	0.18	1	2	6	1.1	0.72	82	82
624	Trichloroethene	38	0.89	5	20	6	5.4	3.6	97	82
	1,1,1-Trichloroethane	39	0.83	5	20	6	5	3.3	87	79
	Chloroform	38	0.74	5	20	8	5.9	3	95	87
	Carbon Tetrachloride	38	0.73	5	20	7	5.1	2.9	95	82
	Tetrachloroethene	40	0.90	5	20	6	5.4	3.6	93	83
	Dichlorobenzenes	31	1.00	5	20	5	5	4	84	77
625	di(2-ethylhexyl)phthalate	39	2.70	10	20	5	14	11	90	87
	benzo(a)pyrene	40	1.50	10	20	8	12	6	95	83
	benzo(a)anthracene	38	1.10	10	20	10	11	4.4	97	63
	2,4-dichlorophenol	33	1.30	10	20	6	8	5.2	79	73
	Pentachlorophenol	37	3.10	20	20	5	16	12	78	68
	2,4,6-trichlorophenol	39	1.80	20	20	6	11	7.2	79	74
507	Atrazine	5	0.24	2.3	0.8	2	0.5	1	80	80
	Simazine	5	0.29	2.3	0.95	2	0.6	1.2	60	80

Table 2. Data Sheet for Trichloroethene, Method 524.2

Lab Code	MDL (ug/L)	MDL Spike level (ug/L)	Calib low Point (ug/L)	MDL Spike level/MDL	Calib low point/MDL
C010	0.04	0.1	0.5	3	13
77434	0.07	1	4	14	57
18725	0.09	1	2	11	22
C003	0.1	0.5	2	5	20
07059	0.1	1	2	10	20
20044	0.12	0.4	0.5	3	4
74603	0.16	1	1	6	6
55735	0.16	1	2	6	13
C005	0.19	1	0.5	5	3
77360	0.2	2	2	10	10
61667	0.2	0.5	2	3	10
C002	0.23	1	2	4	9
16107	0.24	1	0.3	4	1
73331	0.24	2	0.5	8	2
C001	0.29	1	1	3	3
01289	0.4	2	2	5	5
49529	0.4	1	1	3	3
C008	0.41	2	5	5	12
C009	0.43	2	2	5	5
C007	0.46	2	5	4	11
77166	0.49	2	2	4	4
73469	0.8	4	4	5	5
MEAN	0.26	1	2	6	11
MEDIAN	0.22	1	2	5	7
MAXIMUM	0.8	4	5	14	57
MINIMUM	0.04	0.1	0.3	2.5	1
STANDARD DEVIATION	0.18	0.8	1.4	3	12

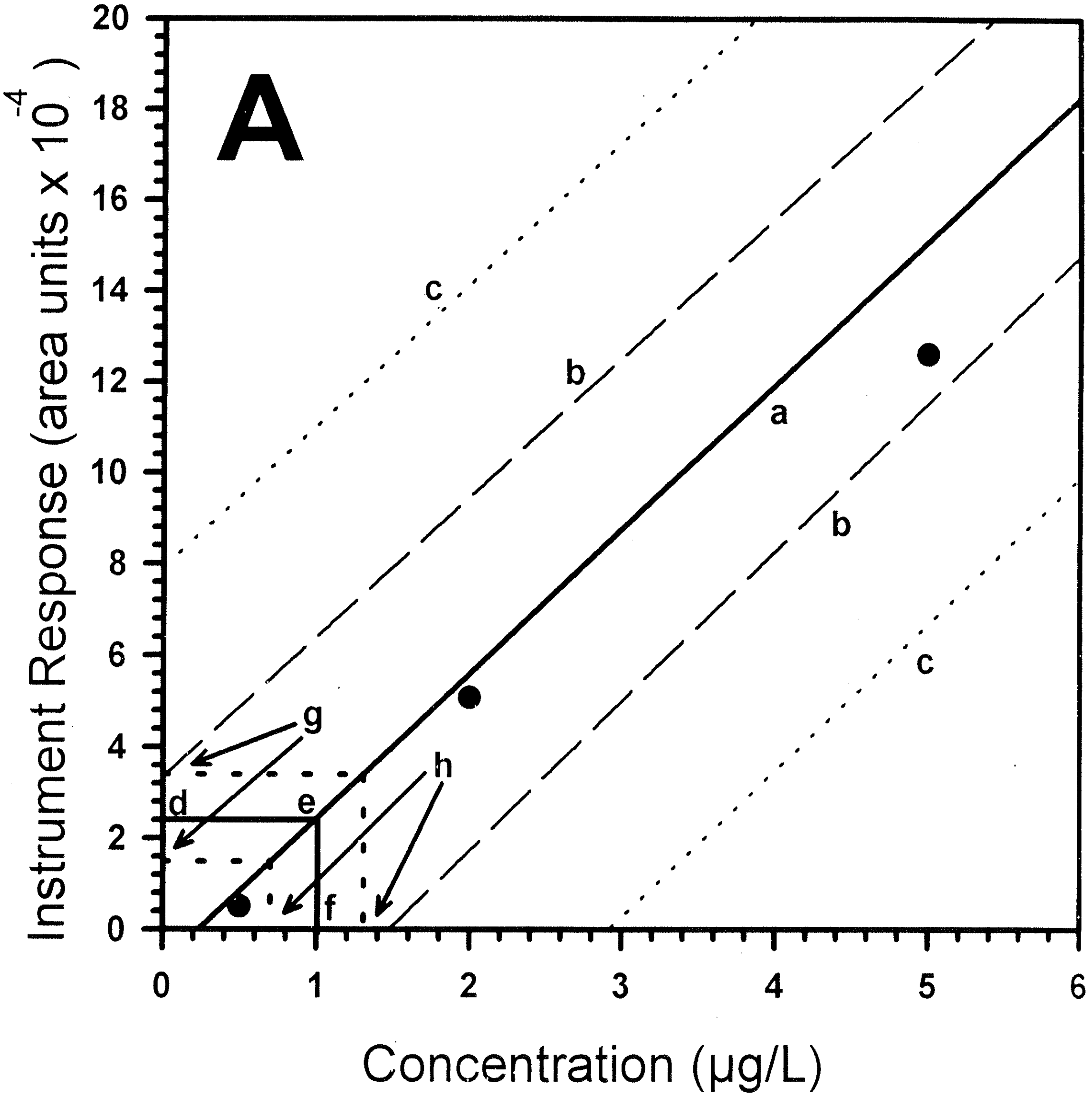
Lowest ratio	5
PQL	1.1 µg/L
RQL	0.88 µg/L

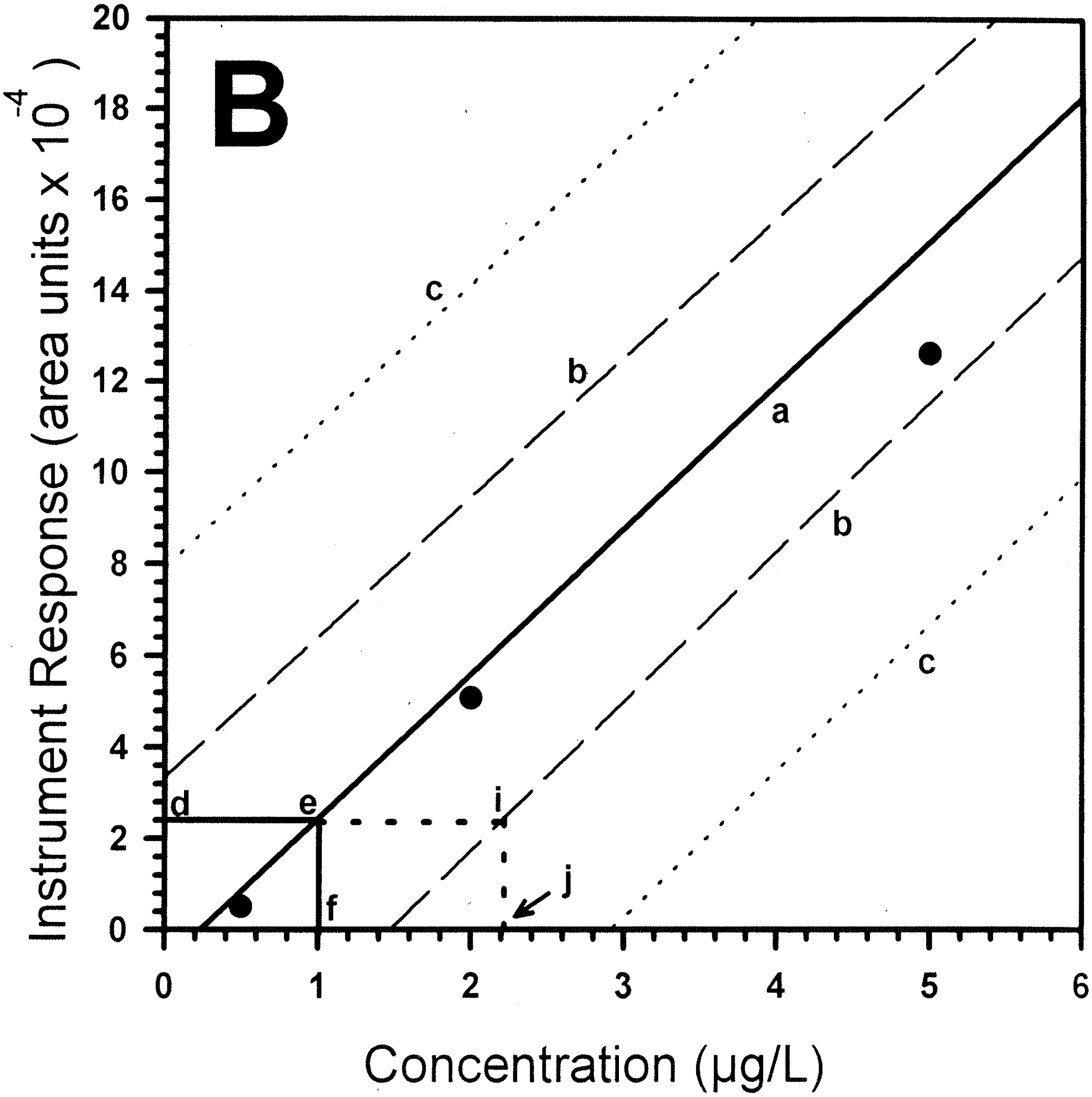
Figure 1. Sample calibration curve for 1,1-dichloroethene **using Method 502.2.** 95% confidence intervals are shown as **dashed lines; 95%** prediction intervals are shown as dotted lines.



180
160
140
120
100
80
60
40
20
0
Instrument Response (area units x 10^{-4})
0
10
20
30
40
50
60
Concentration (µg/L)
$r^2 = 0.998$

Figure 2. Close-up of Figure 1, showing uncertainties in predicted concentrations for a sample containing 1,1-dichloroethene at the RDL (1 µg/L). All figures: a, calibration curve; b, 95% confidence interval; c, 95% prediction interval; d, mean value of instrument reading; e, point on calibration curve corresponding to mean instrument reading; f, true concentration of theoretical sample. Figure 2A: uncertainty in predicted concentration due to instrument response variability. Points g: upper and lower limits (95% confidence level) for instrument response variability. Points h: upper and lower limits of estimated concentration based on instrument variability. Figure 2B: uncertainty in predicted concentration due to confidence interval of calibration curve. Trace e-i, confidence interval for instrument reading of d; j, upper limit of estimated concentration based on confidence interval; Figure 2C: uncertainty in predicted concentration due to prediction interval of calibration curve. Trace e-k, prediction interval for instrument reading of d; l, upper limit of estimated concentration based on prediction interval.


A
Instrument Response (area units x 10^-4)
Concentration (µg/L)
0
2
4
6
8
10
12
14
16
18
20
0
1
2
3
4
5
6
a
b
b
c
c
d
e
f
g
h


B
Instrument Response (area units x 10^{-4})
Concentration (µg/L)
0
2
4
6
8
10
12
14
16
18
20
0
1
2
3
4
5
6
a
b
b
c
c
d
e
f
i
j

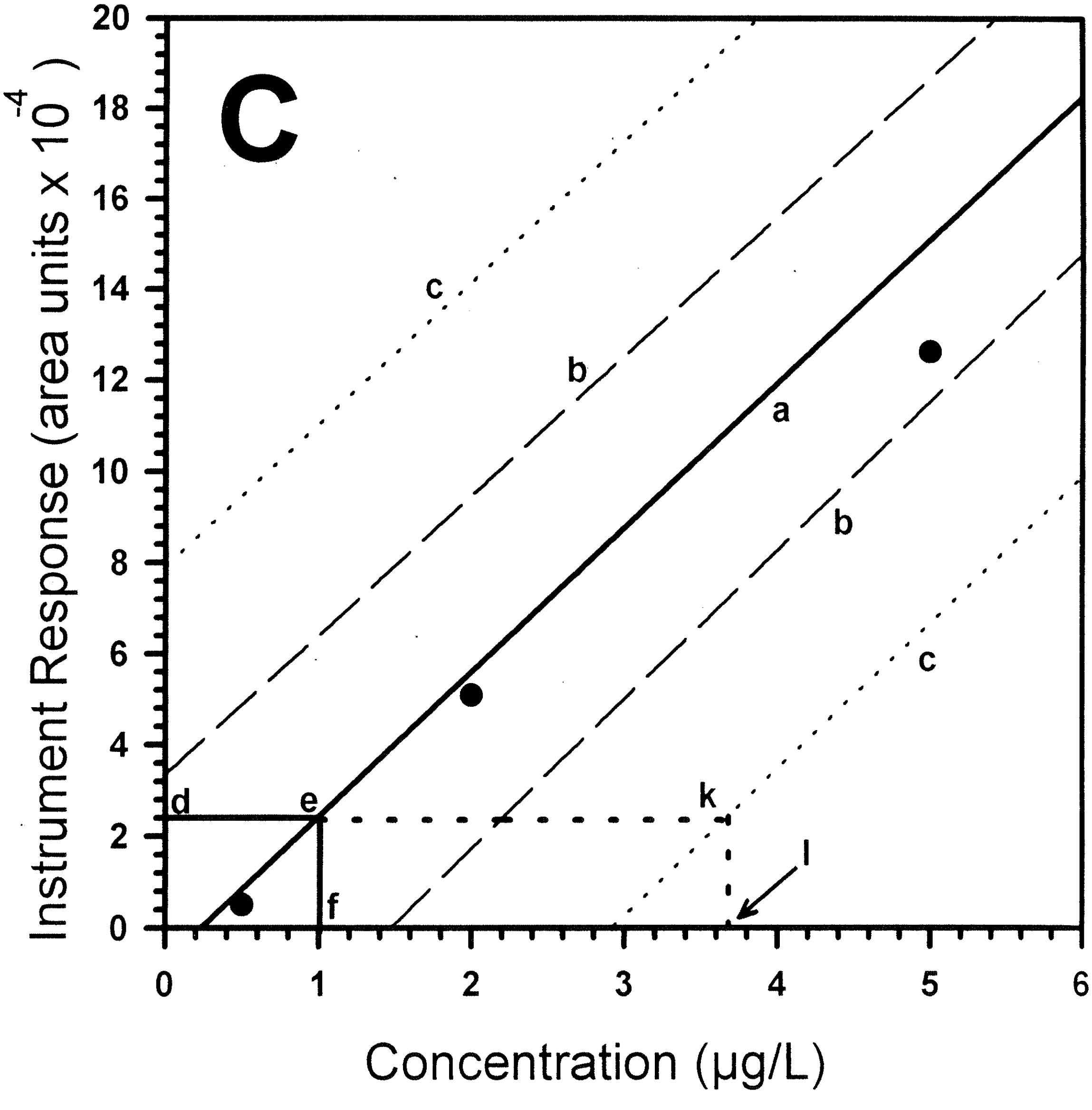
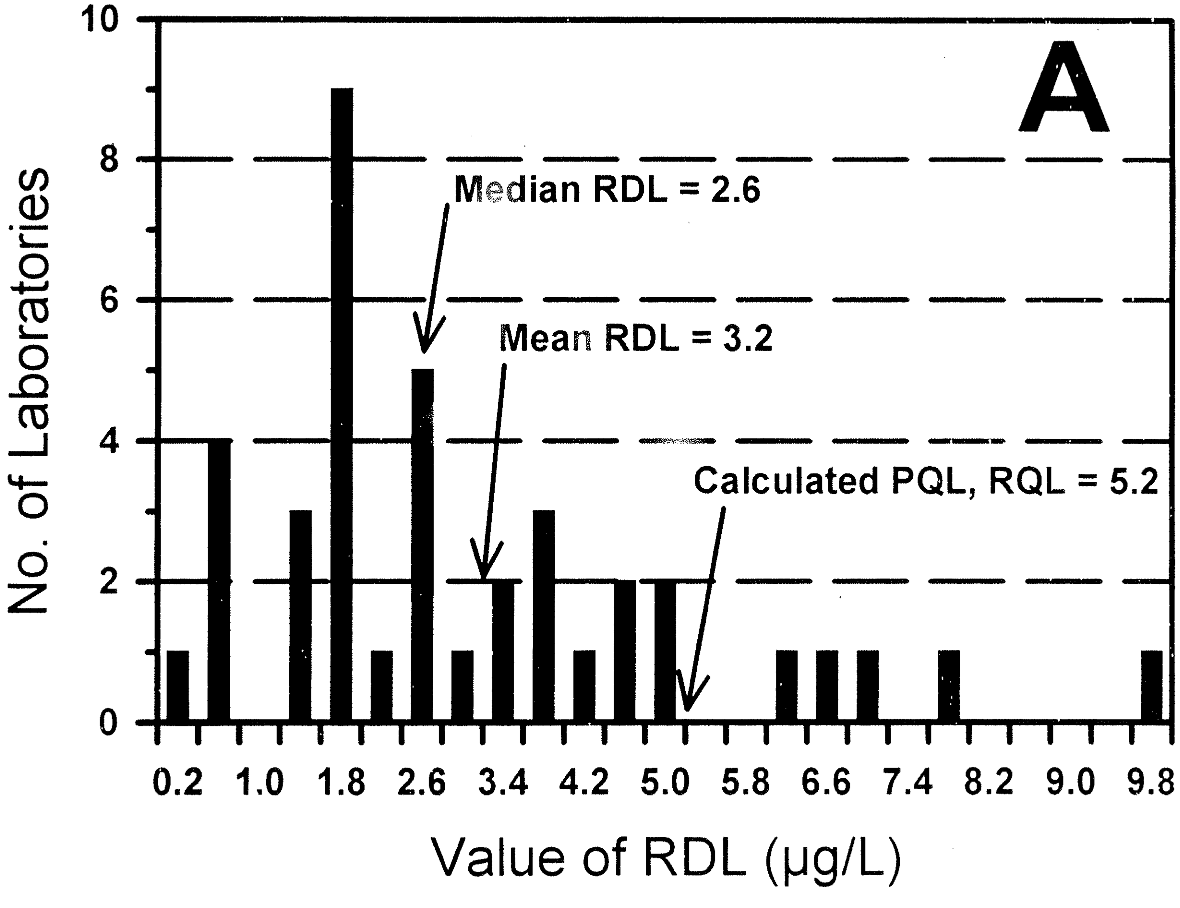
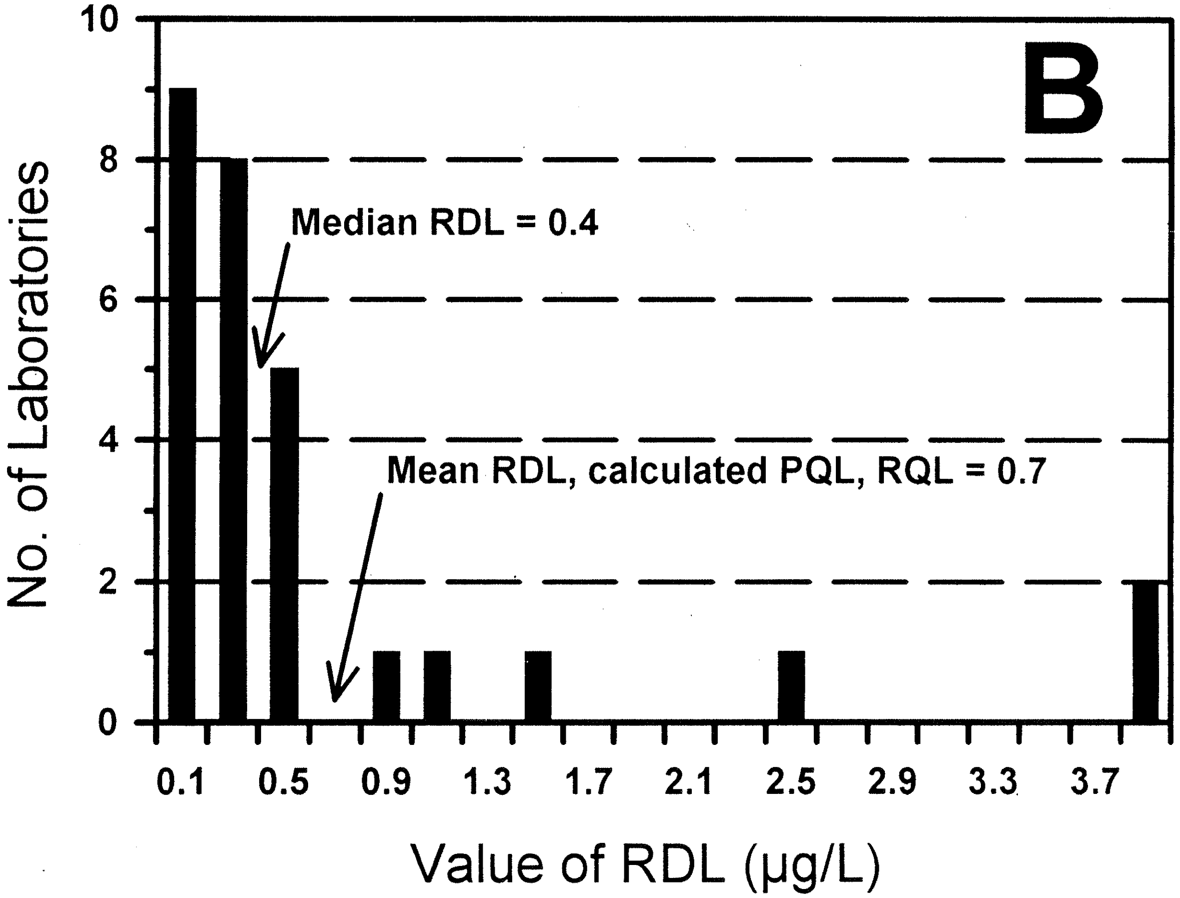
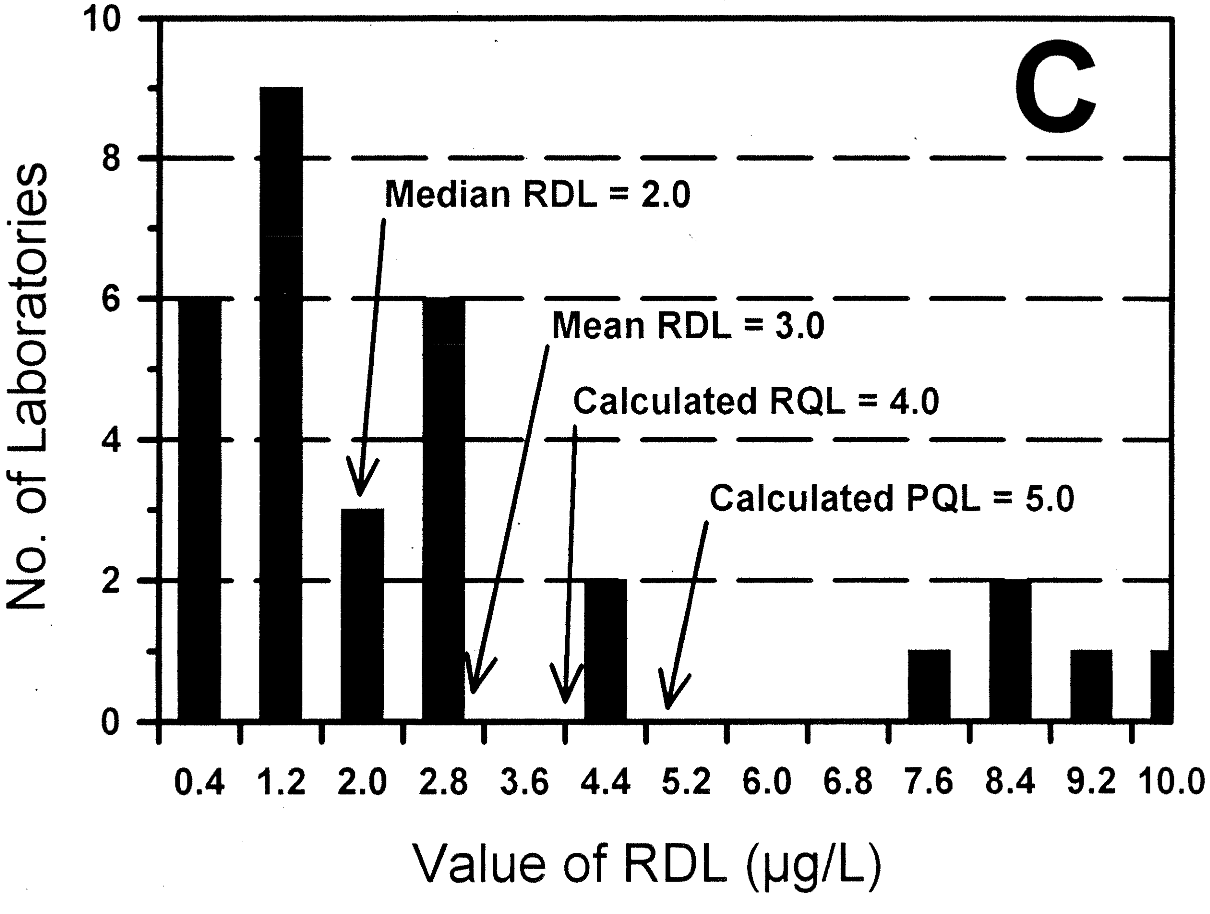

C
Instrument Response (area units x 10^{-4})
Concentration (µg/L)
0
2
4
6
8
10
12
14
16
18
20
0
1
2
3
4
5
6
a
b
b
c
c
d
e
f
k
l

Figure 3. Distribution of RDLs for selected contaminants and methods. Also shown are median RDLs, mean RDLs, calculated PQL (floating multiplier approach) and calculated RQL (Keith 1992b). A: lead, Method 239.2 (number of labs = 39); B: cadmium, Method 213.2 (number of labs = 28); C: dichlorobenzene, Method 624 (number of labs = 31); D: naphthalene, Method 524.2 (number of labs = 11).


A
Median RDL = 2.6
Mean RDL = 3.2
Calculated PQL, RQL = 5.2
No. of Laboratories
0
2
4
6
8
10
0.2
1.0
1.8
2.6
3.4
4.2
5.0
5.8
6.6
7.4
8.2
9.0
9.8
Value of RDL (µg/L)


B
No. of Laboratories
0
2
4
6
8
10
Median RDL = 0.4
Mean RDL, calculated PQL, RQL = 0.7
0.1
0.5
0.9
1.3
1.7
2.1
2.5
2.9
3.3
3.7
Value of RDL (µg/L)


C
Median RDL = 2.0
Mean RDL = 3.0
Calculated RQL = 4.0
Calculated PQL = 5.0
No. of Laboratories
0
2
4
6
8
10
0.4
1.2
2.0
2.8
3.6
4.4
5.2
6.0
6.8
7.6
8.4
9.2
10.0
Value of RDL (µg/L)

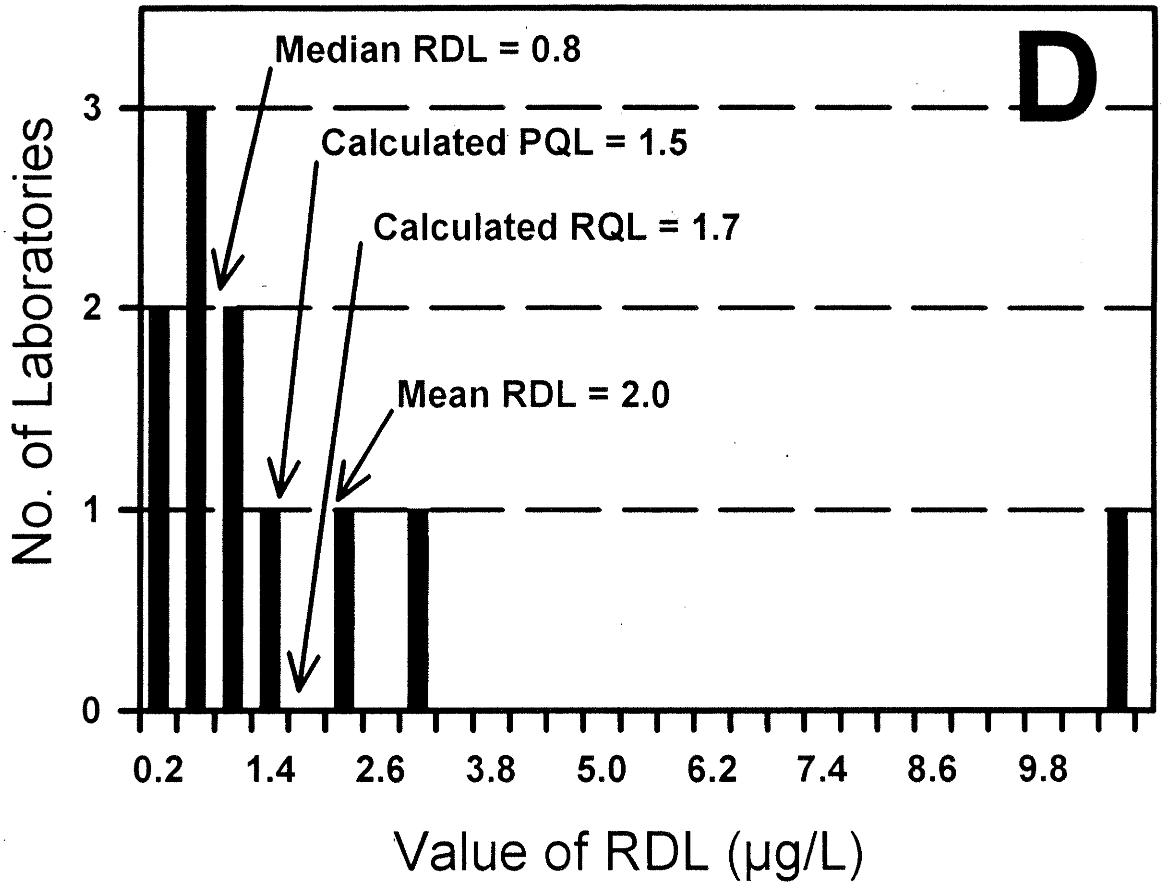
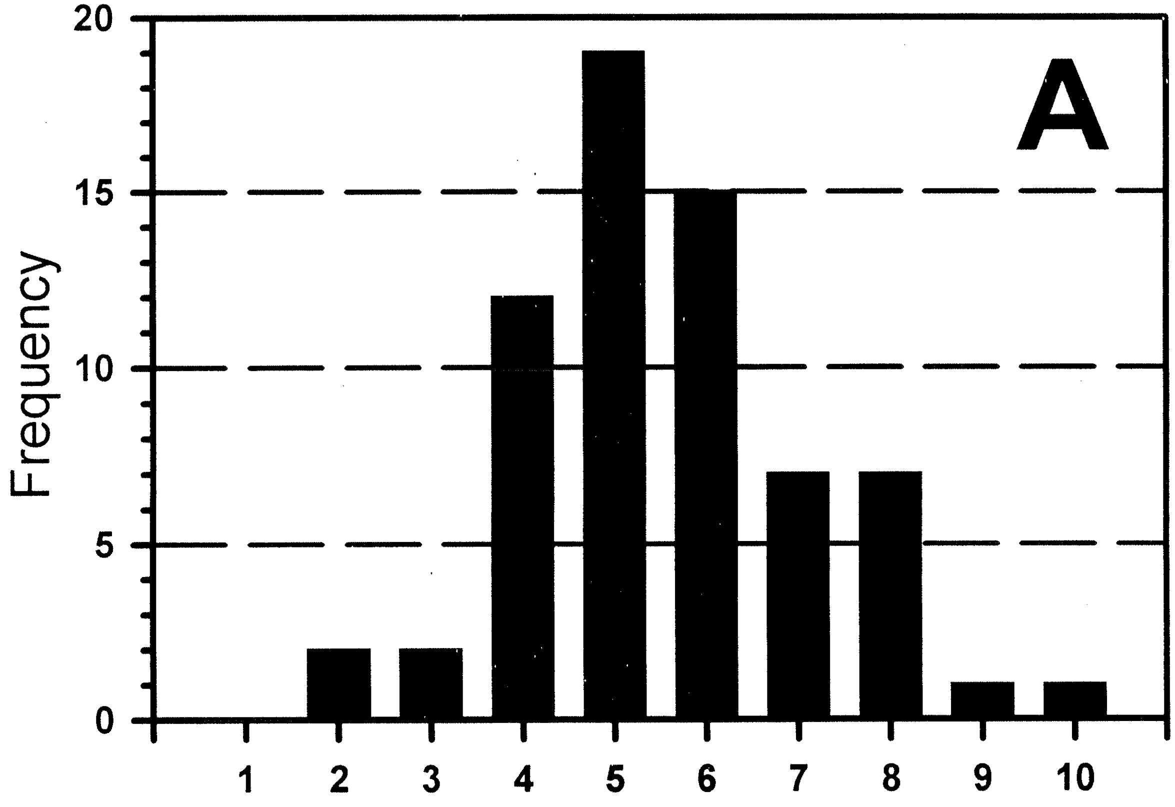
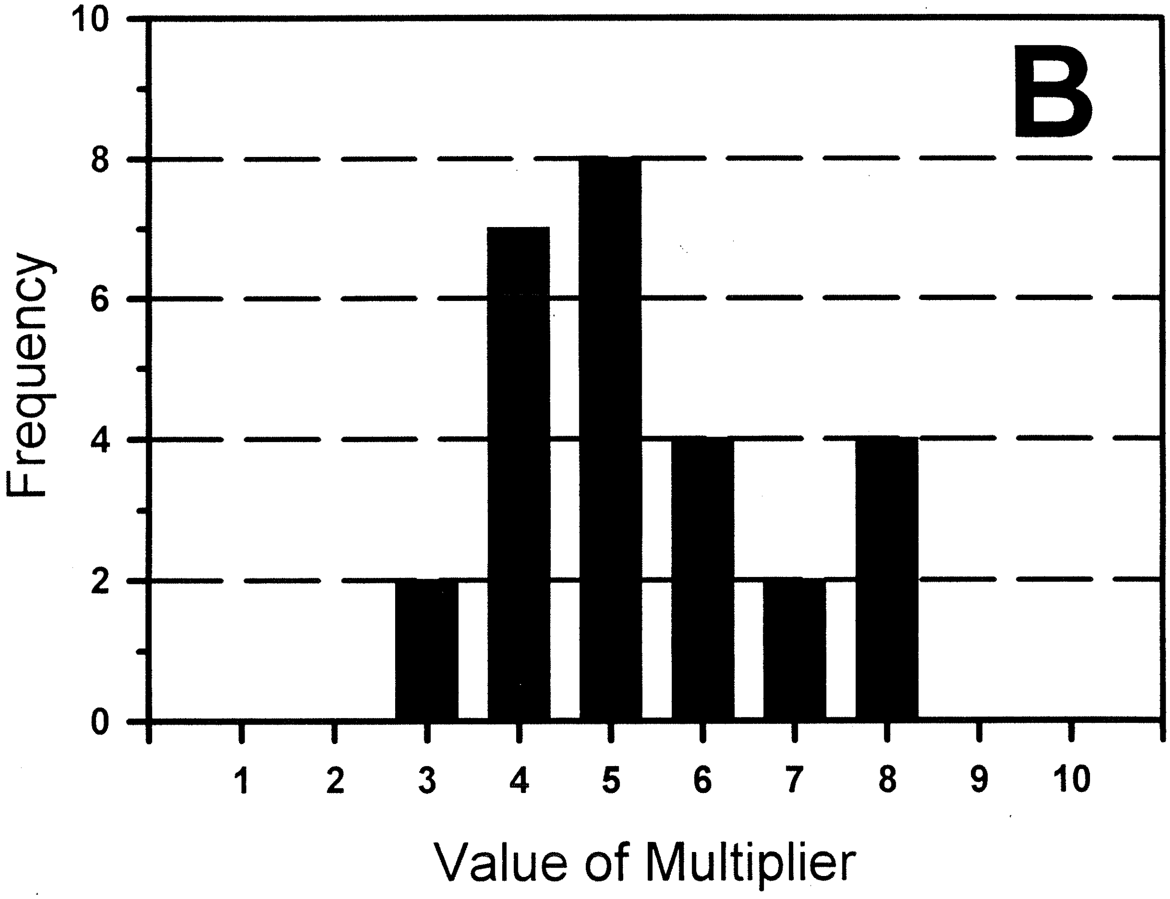
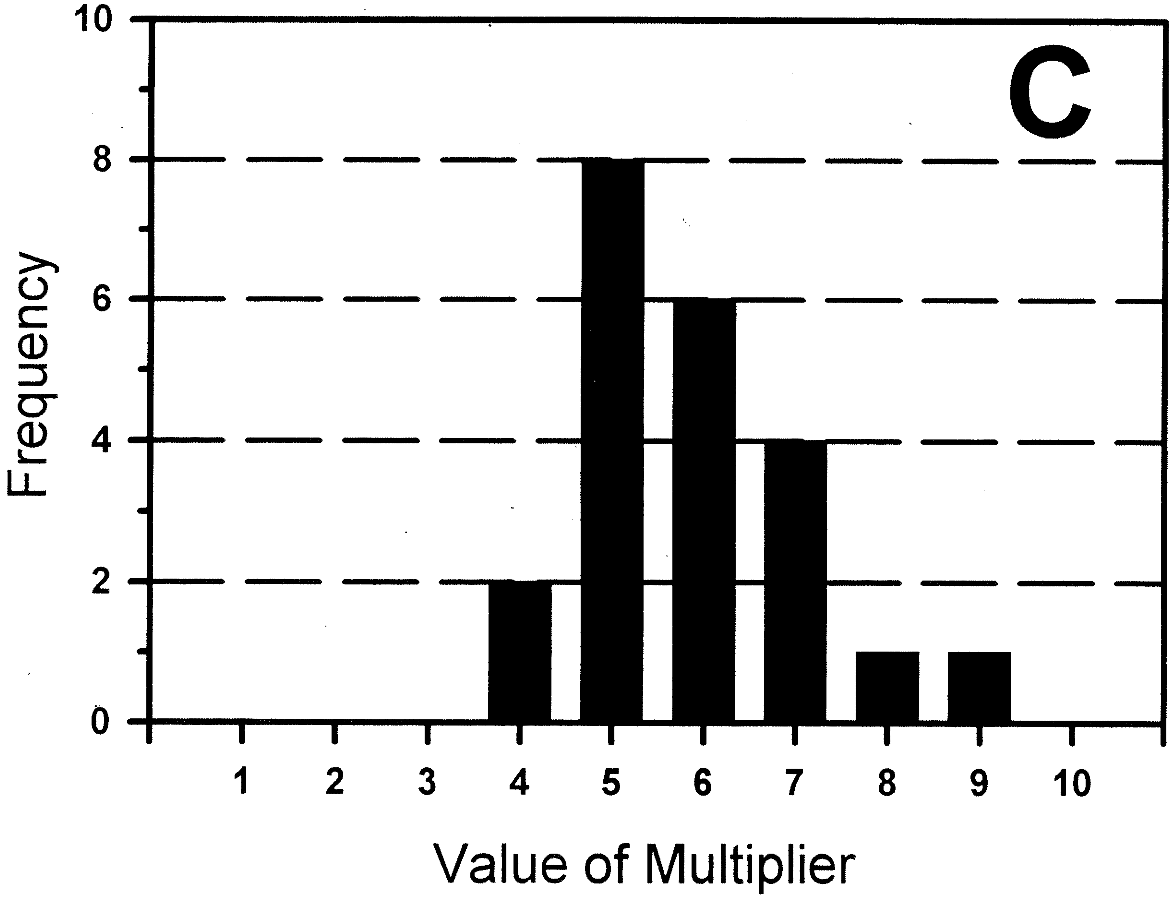
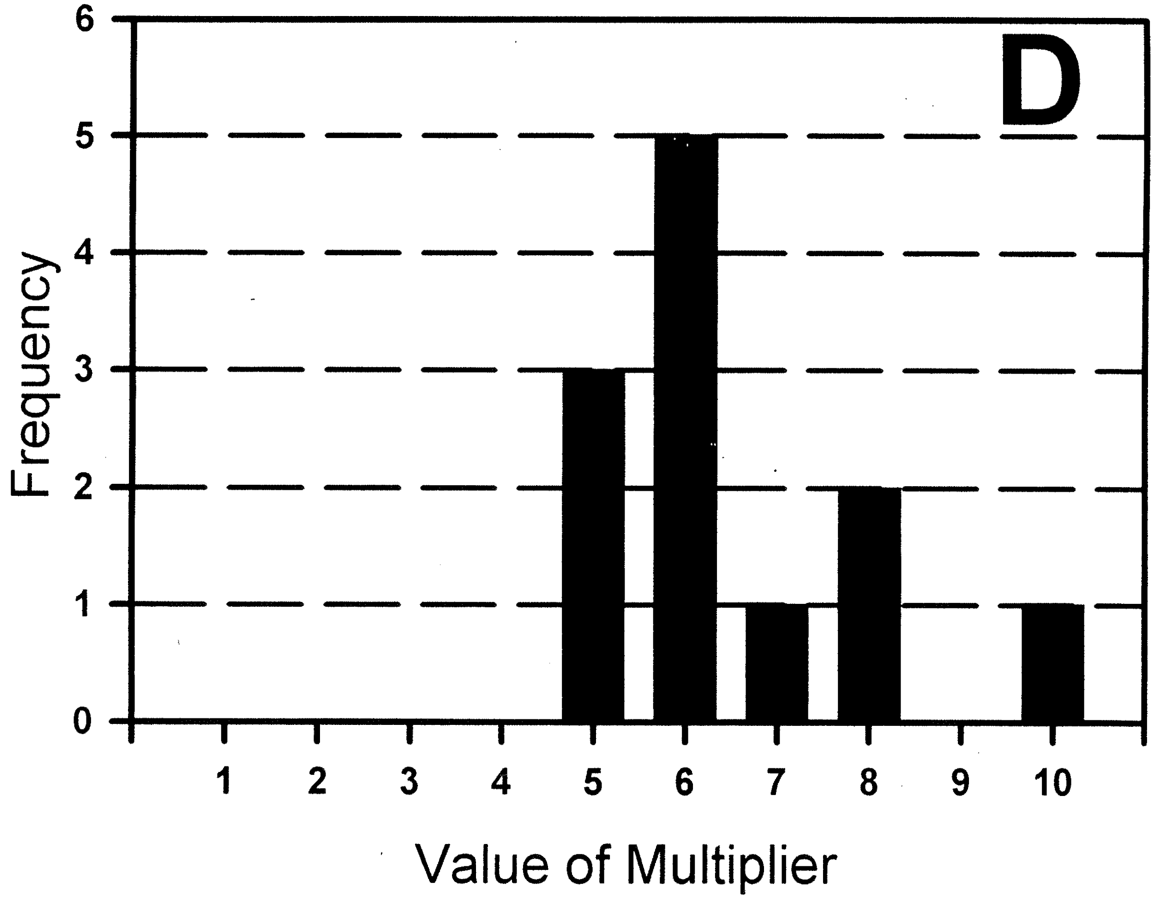

D
Median RDL = 0.8
Calculated PQL = 1.5
Calculated RQL = 1.7
Mean RDL = 2.0
No. of Laboratories
0
1
2
3
0.2
1.4
2.6
3.8
5.0
6.2
7.4
8.6
9.8
Value of RDL (µg/L)

Figure 4. Distribution of multiplier for calculation of PQL. A: all methods, B: Method 524.2, C: Method 502.2, D: Methods 624 and 625 combined.


A
Frequency
0
5
10
15
20
1
2
3
4
5
6
7
8
9
10
Value of Multiplier


B
Frequency
0
2
4
6
8
10
1
2
3
4
5
6
7
8
9
10
Value of Multiplier


C
Frequency
0
2
4
6
8
10
1
2
3
4
5
6
7
8
9
10
Value of Multiplier


D
Frequency
0
1
2
3
4
5
6
1
2
3
4
5
6
7
8
9
10
Value of Multiplier