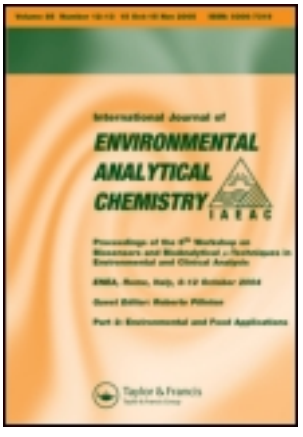

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/geac20

An interlaboratory study of quantitation procedures for the analysis of water and wastewater for organo-chlorine pesticides by gas chromatography-electron capture detector

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Available online: 11 Jul 2011

To cite this article: David Eugene Kimbrough (2011): An interlaboratory study of quantitation procedures for the analysis of water and wastewater for organo-chlorine pesticides by gas chromatography-electron capture detector, International Journal of Environmental Analytical Chemistry, 91:10, 945-959

To link to this article: http://dx.doi.org/10.1080/03067310903509294

Intern. J. Environ. Anal. Chem.
Vol. 91, No. 10, 20 August 2011, 945–959

Taylor & Francis
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An interlaboratory study of quantitation procedures for the analysis of water and wastewater for organo-chlorine pesticides by gas chromatography–electron capture detector

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(*Received 4 May 2009; final version received 27 October 2009*)

An interlaboratory study was conducted to assess two widely used procedures for estimating quantitation levels. Six laboratories participated in the analysis of artificially prepared water samples for organo-chlorine compounds by liquid-liquid extraction followed by gas chromatography–electron capture detector using USEPA Method 608. The study consisted of three phases, including six months of results from analyte free samples, the replicate analysis of fortified samples at a single concentration by the laboratory, and finally the analysis of blind fortified samples prepared by a third party. Estimated detection and quantitation limits (Currie's L_C and L_Q and USEPA's MDL and ML) were determined for each laboratory-method-analyte combination and then compared to the observed detection and quantitation limits. The overwhelming majority of analyte free samples had a reported value of zero. As a result, observed quantitation and detection limits were frequently zero. When they were not zero, the observed quantitation limits were sometimes less than the observed detection limits and when they were not, there was no observed fixed ratio between the quantitation and detection limits. The variability between days of analysis and the use of noise reducing techniques proved to be a significant source of the observed non-normal distribution of results from distilled water samples with a concentration of zero. Conventional procedures and their underlying analytical and statistical assumptions did not provide useful predictions of laboratory quantitation based upon the results of this study. Rather than one time statistical determinations, ongoing verification of quantitation limits may be a better approach.

Keywords: quantitation limit; organo-chlorine pesticides; gas chromatography; critical level; drinking water; wastewater; regulatory compliance

1. Introduction

It is rare when analysing waters for organo-chlorine pesticides for the data user not to be concerned about the sensitivity of the method being used. The concentrations of biological concern are extremely low, generally well below the ability of currently available analytical technology to measure. For example, the United States Environmental Protection Agency (USEPA) has listed in its Criteria for Priority Toxic Pollutants (PTP) in water a value

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310903509294
http://www.informaworld.com

of 590 ng L^{-1} for 4,4′-DDT for human health protection [1]. The USEPA requires that laboratories analysing waters for 4,4′-DDT use USEPA Method 608 which combines a liquid-liquid extraction with analysis on a gas chromatograph (GC) with an electron capture detector (ECD). However, Method 608 cannot measure 4,4′-DDT at concentrations even approaching the above criterion value. The detection limit identified in the method is 12,000 ng L^{-1}. It is very common for a laboratory result from the analysis of 4,4′-DDT in water by Method 608 to be reported as 'less than' the lowest concentration which the laboratory can measure. Determining what that lowest reportable concentration, often called the reporting limit, is extremely important in this situation. Exactly how a laboratory determines a reporting limit is an extremely controversial issue, especially in the case of organo-chlorine pesticides in water.

The most widely recognised approach to determining reporting limits is the Kaiser Currie Model (KCM). Originally proposed by Dr. H. Kaiser in 1965 [2] and further developed and popularised by Dr. L. Currie [3], the KCM holds that for any laboratory, method and analyte combination (LMAC), there is some inherent noise which cannot be controlled and cannot be distinguished from a true signal generated by the presence of the analyte of interest in a sample. In a sample with a concentration of zero (Z sample), this noise could be incorrectly interpreted as a positive result, a false positive (FP). The KCM assumes that the noise would be distributed in a Gaussian fashion around a mean value corresponding to a concentration of zero.

The proposed solution that the KCM offers is to determine a statistical envelop centred on the value zero beyond which the probability of a Z sample erroneously being assigned a positive value would be below a fixed probability. This would be done by analysing a large number of Z samples and determine an upper statistical interval with a satisfactorily small probability of a Z sample producing a FP. Kaiser suggested a 1% probability which is widely used today but it is ultimately an arbitrary decision. To determine this threshold, Currie proposed an upper 99% $(1-\alpha)$ tolerance interval called the 'critical level' (L_C),

$$L_C = k_\alpha \sigma_Z \sim 1.6\sigma_Z,$$

where σ_Z is the standard deviation of the results of the analysis of the Z samples and k_α is the tolerance factor. The theory is that any value greater than L_C exceeds the upper 99% tolerance limit and thus the expected FP rate would be 1% or less for the analysis of Z samples. While it is important to know that a positive result has an acceptably low probability of not being zero, it tells one nothing of the bias or reproducibility of the positive value produced. To address this, Currie also proposed the quantitation level (L_Q), following the work of Adams *et al.* [4], which is the smallest amount of the analyte of interest that produces a relative standard deviation (RSD = s/mean * 100) of 10%.

$$L_Q = k_Q \sigma_Q \sim 10\sigma_z \sim 5L_C,$$

where k is $1/\mathrm{RSD}_Q$ and σ_Q is the standard deviation at Q amount which is greater than zero. The expectation is that at concentrations greater than Q, the %RSD would be smaller than 10% and at concentrations lower than Q the %RSD would be greater. This creates a two-tiered approach, results below the L_C, results between the L_C and L_Q, and results above the L_Q. Results above the L_Q are reported with numeric values while results below the L_C are typically reported as 'not detected' and results between these two threshold might be reported as 'detected but not quantified' although there are many variations.

Using the KCM, the USEPA also developed a similar two tier system of detection and quantitation limits based on statistical intervals. Corresponding to the L_C is the Method Detection Limit (MDL) and to the L_Q is the Minimum Level of Quantitation (ML). There are a few key differences between the USEPA's approach and Dr. Currie's. Instead of using Z sample, the USEPA requires the use of non-zero samples (N samples). Further, since the determination of the MDL must be economically practical, only a limited number of replicates can be taken, which means that the mean and standard deviation are not known, only estimated [5]. As a result, the EPA used an estimated mean (x) and standard deviation (s); so, the Student's t value is used instead of z, so that this confidence interval is $x + ts$, where the t value is determined by the confidence level desired and the number of replicates (e.g., for $\alpha = 0.99$, $n = 7$, $t = 3.14$). While the L_C procedure starts at zero with a Z sample and reaches up to determine the 99% tolerance interval, the MDL starts with an N sample and reaches downward until the lower confidence interval touches zero, so the MDL $= t * s$. The ML is calculated by multiplying the MDL by 3.18 and rounding the results to the number nearest to (1, 2, or 5) $\times$ 10n, where n is an integer' [6] (It is worth noting that the USEPA's Office of Drinking has developed an entire different non-KCM procedure based on the work of Hubeaux and Vos [7] called the Lowest Concentration–Minimum Reporting Limit [8]). In both cases, the quantitation limit (L_Q or ML) is a simple multiple of the detection limit (L_C or MDL).

Despite its long history, there has been little in the way of experimental evaluation of how well the KCM actually does at what it claims to do, determine the lowest quantifiable concentration for any given LMAC. The purpose of this paper is to determine if the KCM approach to quantitation limits, and in particular if the USEPA's adaptation of this approach, the ML, can determine a QL that has practical application.

2. Study design

The approach was to have laboratories calculate the L_C, L_Q, MDL, and ML and then compare these estimates of quantitation limits to the actual performance of these laboratories when they analyse of blind N and Z samples. In particular, data was collected to determine an 'Observed' DL and QL then these would be compared to the L_Q and ML to see how close these estimates were. Additionally, the ratios of detection limits and quantitation limits were examined to see if there was indeed a simple arithmetic relationship between the two. The USEPA established a Federal Advisory Committee on Detection and Quantitation (FACDQ) to assist in developing new approaches to the determining the MDL and ML. One component of that process was a large inter-laboratory pilot study to test the recommended statistical procedures developed by the FACDQ. The goal of this pilot study was to assess the relative merits of new and different applications of the KCM to both detection and quantitation for the Clean Water Act (CWA). The design and execution of this pilot study assumed that the KCM was both valid and useful for this application. The data was not collected for the purposes of this paper but the author, a member of the FACDQ, used a portion of the data collected during this study for this paper.

3. Study phases

The portion of the study used in this paper consisted of three phases. Phase 1 required the participating laboratories to submit the data from all artificially prepared Z samples

Table 1. Analytes and expected concentrations in samples in the third phase study. All units ng $L^{-1} \times 1000$.

Sample ID Method 608 – Analyte	1	2	3	4	5	6	7	8	9	10	11	12
A	0	2	5	10	20	50	75	100	200	500	800	1000
B	0	1	2	5	10	20	50	100	200	500	800	1000

Notes: A = 4,4′-DDD, 4,4′-DDE, 4,4′-DDT, Dieldrin, Endosulfan II, Endosulfan Sulphate, Endrin, Endrin Aldehyde,
B = Aldrin, α-BCHβ-BCH, δ-BCH, Endosulfan I, γ-BCH, γ-Chlordane, Heptachlor, Heptachlor Epoxide.

(also known as Laboratory Reagent Blanks) analysed as part of their routine analytical activities for six months prior to the beginning of the study. In Phase 2 the laboratories themselves prepared *N* samples at a concentration near where the laboratory anticipated its ML would be and then analysed it at least seven times on seven separate days. Phase 3 had the laboratories analyse 12 blind samples consisting of 11 *N* samples and one *Z* sample, with different concentrations of analytes (see Table 1) over several days. Six laboratories (designated Labs 29, 31, 32, 34, 35, and 37) participated in all three phases for the analysis of organo-chlorine pesticides using USEPA Method 608. Only those LMACs where there were at least seven Z sample results from the Phase 1 and produced results from Phases 2 and 3 were used for this study, of which there were 101.

4. Assessment

Phase 1 data was used to calculate the 99th percentile of *Z* samples would be the Observed Detection Limit (ODL), i.e. the concentration corresponding to a 1% FP rate. The standard deviation of the *Z* samples from Phase 1 results was used to calculate L_C and L_Q for each LMAC. From the Phase 2 data, the MDL and ML were calculated. The Phase 3 data was used to determine FP rates the *Z* samples as well as measure the bias and reproducibility of each LMAC at difference concentrations.

Currently, no standard for measurement accuracy at or near the L_Q or ML exists. In some situations, the USEPA uses an objective of +/−50% for results at or near the 'minimum reporting level', so this was used for this study [8]. *N* samples from the Phase 3 of the study that were within +/−50% of the expected value were judged to be accurately quantified while those with a greater bias were judged as inaccurate. Using this standard four different QLs were determined; first the lowest concentration where all ten replicates were within 50% of the target value (QL-10), the lowest concentration where the average concentration was within 50% of the target value (QL-Mean), and lowest concentration where at least one of the ten replicates was within 50% of the target value (QL-1). Finally, the *N* sample with the lowest concentration that had a %RSD of 10% or less was also determined and was considered an 'Observed QL' (OQL). Although this is not a measure of accuracy, it is the metric that the L_Q claims to achieve. How close the calculated L_Q and ML were to each of these four different observed QLs could then be measured. For the purposes of this study, the ML or L_Q for a given LMAC was considered accurate if it was within +/−50% of the one of the four measured observed QLs. Additionally, the ratio

of the ODL to OQL was determined for each LMAC to see if there is a simple arithmetic relationship between these two thresholds. These ratios could not always be determined however if the value was zero.

5. Results and discussion

Tables 2a–2r shows the mean results from individual mean, standard deviation, count, and ODL for the Z samples for each LMACs from Phase 1, the MDLs and MLs from Phase 2, and the QL-10, QL-mean, QL-1, and OQL from Phase 3 as well as the MDL published in Method 608 and the lowest criterion for PTP. Table 3 presents the number of FPs for all LMACs. Table 4 has the ratios of L_Q and ML to OQL, QL-10, QL-mean and QL-1

Table 2a. Summary of the observed and estimated detection and quantitation limits for 4,4′-DDD. MDL Published in Method 608 = 11,000, Criterion for PTP = 630. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	43	220	30	900	350	4800	2200	15,000	20,000	10,000	5000	2000
31	1500	5300	57	24,000	8600	14,000	53,000	45,000	10,000	50,000	20,000	2000
32	2600	8200	30	35,000	13,000	3000	81,900	9500	20,000	20,000	10,000	10,000
34	−8800	30,000	30	66,000	48,000	39,000	300,000	120,000	CND	50,000	50,000	20,000
35	53	2500	30	5500	3900	1300	25,000	4300	CND	20,000	10,000	5000
37	0	0	30	0	0	20,000	0	64,000	75,000	20,000	2000	2000

Table 2b. Summary of the observed and estimated detection and quantitation limits for 4,4′-DDE. MDL Published in Method 608 = 4000, Criterion for PTP = 590. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	0	0	30	0	0	4700	0	15,000	10,000	10,000	2000	2000
31	450	2400	57	13,000	3800	6000	24,000	19,000	100,000	50,000	50,000	10,000
32	−200	925	30	1500	1500	3000	9200	9400	50,000	50,000	20,000	10,000
34	430	16,000	30	37,000	25,000	19,000	160,000	60,000	50,000	50,000	20,000	20,000
35	−180	1000	30	120	1700	1500	10,000	4700	CND	75,000	5000	5000
37	0	0	30	0	0	12,000	0	39,000	10,000	50,000	2000	2000

Table 2c. Summary of the observed and estimated detection and quantitation limits for 4,4′-DDT. MDL Published in Method 608 = 12,000, Criterion for PTP = 590. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	4400	24,000	30	94,000	38,000	4600	240,000	15,000	20,000	10,000	5000	2000
31	3600	16,000	57	81,000	26,000	8200	160,000	26,000	500,000	50,000	20,000	2000
32	2600	8200	30	35,000	13,000	2200	82,000	7000	CND	20,000	10,000	2000
34	−1800	33,000	30	66,000	52,000	30,000	330,000	95,000	2000	50,000	50,000	50,000
35	850	2600	30	9900	4200	1500	26,000	4800	20,000	20,000	10,000	5000
37	0	0	30	0	0	21,000	0	66,000	10,000	10,000	2000	2000

Table 2d. Summary of the observed and estimated detection and quantitation limits for Aldrin. MDL Published in Method 608 = 4000, Criterion for PTP = 130. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	12,000	56,000	30	230,000	90,000	2100	560,000	6600	10,000	2000	2000	1000
31	2000	6300	57	25,000	10,000	8600	63,000	27,000	50,000	50,000	20,000	20,000
32	1500	3700	30	12,000	6000	9400	37,000	30,000	20,000	20,000	20,000	10,000
34	−12,000	30,000	30	57,000	48,000	25,000	300,000	81,000	20,000	CND	20,000	20,000
35	0	0	30	0	0	1800	0	5600	50,000	50,000	5000	2000
37	0	0	30	0	0	7500	0	24,000	10,000	10,000	10,000	10,000

Table 2e. Summary of the observed and estimated detection and quantitation limits for α-Chlordane. MDL Published in Method 608 = 14,000*, Criterion for PTP = 570*. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	0	0	30	0	0	2900	0	9100	10,000	800,000	2000	1000
31	0	0	57	0	0	31,000	0	97,000	50,000	1000	1000	1000
32	−100	1800	30	4900	2900	2800	37,000	8800	CND	200,000	20,000	20,000
34	−8600	15,000	30	28,000	2400	18,000	301,000	58,000	CND	20,000	10,000	10,000
37	0	0	30	0	0	22,000	0	70,000	CND	10,000	5000	2000

Note: *Chlordane is not distinguished by isomers in either Method 608 or in California Toxics Rule.

Table 2f. Summary of the observed and estimated detection and quantitation limits for α-BHC. MDL Published in Method 608 = 3000, Criterion for PTP = 3900. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	100	440	30	1900	700	4900	4300	16,000	100,000	2000	1000	1000
31	0	0	57	0	0	7200	0	23,000	50,000	50,000	50,000	50,000
32	730	3000	30	7900	4800	8600	30,000	27,000	CND	500,000	50,000	20,000
34	4500	7000	30	22,000	11,000	13,000	70,000	42,000	10,000	10,000	10,000	10,000
35	0	0	30	0	0	2000	0	6500	20,000	10,000	10,000	5000
37	0	0	30	0	0	13,000	0	40,000	CND	20,000	1000	1000

Table 2g. Summary of the observed and estimated detection and quantitation limits for β-BHC. MDL Published in Method 608 = 6000, Criterion for PTP = 1400. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	50	210	30	910	340	3300	2100	10,000	5000	2000	1000	1000
31	0	0	57	0	0	9100	0	29,000	5000	2000	2000	1000
32	−730	4400	30	8700	7100	11,000	44,000	35,000	CND	50,000	20,000	20,000
34	−3700	17,000	30	47,000	27,000	24,000	170,000	76,000	100,000	100,000	5000	1000
35	0	0	30	0	0	2400	0	7700	50,000	20,000	5000	1000
37	0	0	30	0	0	11,000	0	35,000	10,000	5000	2000	1000

Table 2h. Summary of the observed and estimated detection and quantitation limits for δ-BHC. MDL Published in Method 608 = 9000, Criterion for PTP = 1900. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	93	360	30	1500	570	3600	3600	11,000	10,000	2000	1000	1000
31	0	0	57	0	0	7300	0	23,000	50,000	50,000	50,000	20,000
32	2300	4100	30	16,000	6600	5600	41,000	18,000	CND	20,000	10,000	50,000
34	8800	16,000	30	45,000	25,000	17,000	160,000	55,000	100,000	50,000	20,000	20,000
35	0	0	30	0	0	1600	0	5100	20,000	10,000	10,000	5000
37	0	0	30	0	0	7600	0	24,000	50,000	5000	5000	1000

Table 2i. Summary of the observed and estimated detection and quantitation limits for Dieldrin. MDL Published in Method 608 = 2000, Criterion for PTP = 140. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	3	18	30	73	29	5500	180	18,000	200,000	5000	5000	2000
31	200	1500	57	5200	2400	5600	15,000	18,000	75,000	50,000	20,000	2000
32	670	2400	30	8700	3800	4300	24,000	14,000	CND	50,000	20,000	10,000
34	1700	15,000	30	39,000	25,000	19,000	150,000	62,000	50,000	50,000	20,000	20,000
35	180	770	30	3300	1200	1500	7700	4700	20,000	20,000	10,000	2000
37	0	0	30	0	0	14,000	0	44,000	10,000	2000	2000	2000

Table 2j. Summary of the observed and estimated detection and quantitation limits for Endosulfan I. MDL Published in Method 608 = 14,000, Criterion for PTP = 8700. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	13	57	30	250	91	2700	570	8600	CND	CND	10,000	1000
31	140	1100	57	3700	1700	5600	11,000	18,000	CND	20,000	2000	1000
32	−300	4800	30	16,000	7600	4000	48,000	13,000	CND	CND	CND	20,000
34	−2600	16,000	30	35,000	26,000	19,000	160,000	61,000	CND	CND	20,000	20,000
35	110	650	30	2700	1000	1600	6500	5100	CND	CND	5000	1000
37	0	0	30	0	0	6000	0	19,000	CND	CND	2000	1000

Table 2k. Summary of the observed and estimated detection and quantitation limits for Endosulfan II. MDL Published in Method 608 = 4000, Criterion for PTP = 8700. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	13	73	30	290	120	4700	730	15,000	CND	CND	50,000	2000
31	520	3300	57	14,000	5300	6600	33,000	21,000	CND	CND	2000	2000
32	67	3100	30	9500	5000	2900	31,000	9100	CND	CND	CND	20,000
34	(13,397)	31,647	30	59,360	50,636	37,000	320,000	120,000	CND	CND	20,000	5000
35	300	1000	30	4100	1600	1500	10,000	4700	CND	CND	5000	2000
37	0	0	30	0	0	13,000	0	41,000	CND	CND	50,000	2000

Table 2l. Summary of the observed and estimated detection and quantitation limits for Endosulfan Sulphate. MDL Published in Method 608 = 66,000, Criterion for PTP = 110,000. All units ng L^{-1}.

Lab	Mean	SD	*n*	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	20	92	30	390	150	4900	930	16,000	20,000	10,000	5000	2000
31	160	1200	57	4100	1900	6300	12,000	20,000	75,000	5000	2000	2000
32	4200	7200	30	22,000	12,000	8700	72,000	28,000	20,000	10,000	10,000	5000
34	−7900	34,000	30	70,000	54,000	42,000	340,000	130,000	1,000,000	50,000	50,000	10,000
35	98	390	30	1600	620	1600	3900	5100	200,000	20,000	5000	2000
37	0	0	30	0	0	15,000	0	47,000	20,000	2000	2000	2000

Table 2m. Summary of the observed and estimated detection and quantitation limits for Endrin. MDL Published in Method 608 = 6000, Criterion for PTP = 23,000. All units ng L^{-1}.

Lab	Mean	SD	*n*	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	730	3700	30	15,000	5900	5200	37,000	16,000	20,000	5000	5000	2000
31	950	4200	57	20,000	6800	8600	42,000	27,000	100,000	50,000	20,000	2000
32	370	3000	30	11,000	4500	5500	30,000	17,000	50,000	50,000	20,000	10,000
34	770	16,000	30	37,000	25,000	19,000	160,000	62,000	100,000	50,000	20,000	20,000
35	150	1100	30	3700	1700	2400	11,000	7600	CND	50,000	10,000	5000
37	0	0	30	0	0	13,348	0	42,445	10,000	2000	2000	2000

Table 2n. Summary of the observed and estimated detection and quantitation limits for Endrin aldehyde. MDL Published in Method 608 = 23,000, Criterion for PTP = 760,000. All units ng L^{-1}.

Lab	Mean	SD	*n*	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	70	210	30	770	330	5600	2100	18,000	200,000	75,000	10,000	5000
31	900	6400	57	24,000	10,000	6100	64,000	19,000	20,000	20,000	5000	2000
32	1300	6000	30	24,000	9500	4900	60,000	15,000	50,000	20,000	20,000	20,000
34	−15,000	46,000	30	81,000	74,000	57,000	460,000	180,000	500,000	75,000	50,000	10,000
35	490	1600	30	6300	2500	1500	16,000	4900	50,000	50,000	2000	2000
37	0	0	30	0	0	23,000	0	73,000	10,000	10,000	2000	2000

Table 2o. Summary of the observed and estimated detection and quantitation limits for γ-BHC. MDL Published in Method 608 = 9000, Criterion for PTP = 19,000. All units ng L^{-1}.

Lab	Mean	SD	*n*	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	27	98	30	420	160	2500	980	7800	2000	2000	1000	1000
31	1100	4100	57	19,000	6500	7000	41,000	24,000	50,000	50,000	20,000	20,000
32	900	2600	30	6700	4200	12,000	26,000	37,000	CND	500,000	20,000	20,000
34	3700	6700	30	20,000	11,000	12,000	67,000	37,000	1000	20,000	20,000	10,000
35	−1	7	30	0	12	2000	73	6500	20,000	10,000	5000	5000
37	0	0	30	0	0	7500	0	24,000	10,000	1000	1000	1000

Table 2p. Summary of the observed and estimated detection and quantitation limits for γ-Chlordane. MDL Published in Method 608 = 14,000*, Criterion for PTP = 570*. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	I	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	340	1100	30	4300	1800	2600	11,000	8100	10,000	5000	2000	1000
31	2500	7600	57	32,000	12,200	5700	76,000	18,000	20,000	20,000	10,000	1000
32	1200	5800	30	25,000	9300	9900	58,000	31,000	CND	200,000	20,000	20,000
34	33	18,000	30	45,000	29,000	22,000	180,000	69,000	CND	100,000	20,000	10,000
37	0	0	30	0	0	11,000	0	34,000	10,000	2000	1000	1000

*Chlordane is not distinguished by isomers in either Method 608 or in California Toxics Rule.

Table 2q. Summary of the observed and estimated detection and quantitation limits for Heptachlor. MDL Published in Method 608 = 3000, Criterion for PTP = 210. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	170	470	30	2000	750	2700	4700	8600	100,000	5000	2000	1000
31	1600	3900	57	16,000	6200	8800	38,000	28,000	50,000	20,000	10,000	1000
32	29,000	33,000	30	99,000	52,000	8200	330,000	26,000	CND	CND	1000	5000
34	3900	15,000	30	38,000	25,000	17,000	160,000	54,000	2000	50,000	20,000	20,000
35	170	760	30	3200	1200	1800	7600	5600	20,000	10,000	5000	2000
37	0	0	30	0	0	6700	0	21,000	10,000	1000	1000	1000

Table 2r. Summary of the observed and estimated detection and quantitation limits for heptachlor epoxide. MDL Published in Method 608 = 83,000, Criterion for PTP = 100. All units ng L^{-1}.

Lab	Mean	SD	n	ODL	L_C	MDL	L_Q	ML	OQL	QL-10	QL-m	QL-1
29	320	1500	30	6400	2400	2500	15,000	8100	10,000	5000	2000	1000
31	190	1400	57	4900	2200	7700	14,000	25,000	800,000	1000	1000	1000
32	−1500	2200	30	730	3500	4300	22,000	14,000	CND	200,000	20,000	20,000
34	−3900	15,000	30	31,000	24,000	18,000	150,000	56,000	100,000	20,000	20,000	20,000
35	−30	160	30	0	260	1500	1600	4900	10,000	10,000	5000	1000
37	0	0	30	0	0	8800	0	28,000	10,000	1000	1000	1000

including the maximum, minimum and median ratios as well as the number of LMACs which were the ML or LQ were within +/−50% of the measured QL plus the number of LMACs where the ML or LQ were more than 50% and less than 50% QL plus the number of LMACs where the ML or L_Q were more than 50% and less than 50%. These ratios could not always be determined, however. There were 27 LMAC where all of the Z samples analysed in Phase 1 were measured as zeros and so the standard deviation was also zero which meant that the ODL, L_C, and L_Q were zero. For two LMACs the mean and standard deviation of Phase 1 data were not zero but the ODL was still zero. Similarly some LMACs could not have a QL-10, QL-mean, QL-1 or OQL determined because there were no N samples that met the definitions, e.g. none of the N samples produced a %RSD of 10% or less or none of the results were within +50%. These were recorded as Could Not Determine (CND).

Table 3. Numbers of false positives by laboratory and analyte.

	Laboratory					
Analyte	29	31	32	34	35	37
4,4′-DDD	3	0	0	9	0	0
4,4′-DDE	1	1	0	9	0	0
4,4′-DDT	0	0	0	9	0	0
ALDRIN	4	1	0	8	0	0
α-CHLORDANE	0	0	0	9	NA	0
α–BHC	7	0	0	5	0	0
β–BHC	4	0	0	6	0	0
δ–BHC	4	0	0	6	0	0
DIELDRIN	0	0	0	10	0	0
ENDOSULFAN I	2	0	0	9	0	0
ENDOSULFAN II	0	0	0	9	0	0
ENDOSULFAN SULPHATE	1	0	0	8	0	0
ENDRIN	0	0	0	7	0	0
ENDRIN ALDEHYDE	0	0	0	9	0	0
γ-BHC	6	0	0	10	0	0
γ-CHLORDANE	3	0	0	3	NA	0
HEPTACHLOR	3	0	2	7	0	1
HEPTACHLOR EPOXIDE	0	0	0	3	0	0
Total False Positives	38	2	2	136	0	1
Total Determinations	190	190	190	190	170	190
Percent False Positives	20	1	1	72	0	<1

Table 4. Comparison of different estimates of QL to the OQL for LMACs with OQL > 0.

Ratio	OQL/L_Q	QL-10/L_Q	QL-m/L_Q	QL-1/L_Q	OQL/ML	QL-10/ML	QL-m/ML	QL-1/ML
Median	1.2	0.6	0.3	0.2	1.4	0.9	0.4	0.2
Minimum	0.006	0.004	0.003	0.002	0.02	0.04	0.03	0.01
Maximum	1095	137	68	68	39	18	3	3
N	52	65	74	76	74	88	99	101
<0.5	14	28	51	60	21	30	56	75
0.5≥ ≤1.5	14	15	12	10	16	26	32	22
1.5>	24	22	11	6	37	32	11	15

Notes: QL = Quantitation Limit.
OQL = Observed Quantitation Limit (10% RSD).
LQ = Limit of Quantitation (Currie).
ML = Minimum Level of Quantitation (USEPA).
QL-10 = Lowest concentration where all 10 *N* samples were within 50% of the target value.
QL-m = Lowest concentration where the mean of the 10 *N* samples were within 50% of the target value.
QL-1 = Lowest concentration where at least one of the 10 *N* samples was within 50% of the target value.

The KCM assumes that there is fixed ratio between the DL and QL. However, of the 101 LMACs in this study, only 50 had both a non-zero ODL and OQL so, they could be assessed. The median ratio of OQL to ODL for these 50 LMAC was 3 : 1 with a range from 0.03 to 2,740 and the mode was 1 : 1. For 12 of these LMACS, the OQL actually was less

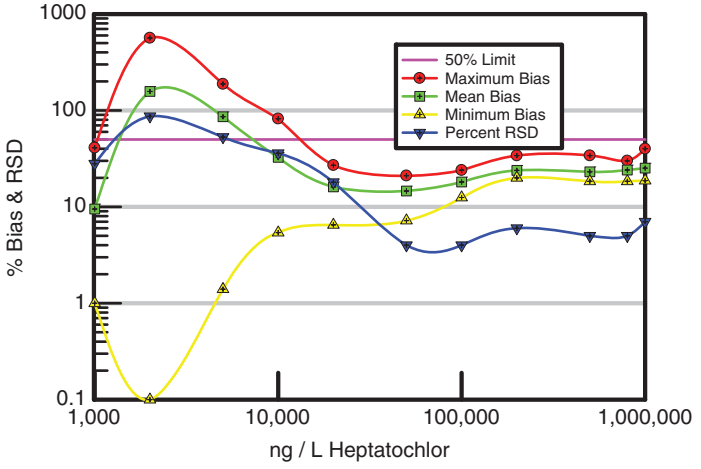

Figure 1. Bias & RSD in the Analysis of Heptachlor by GC-ECD at Lab 34.

than the ODL and for the remaining 38, the median ratio was 6 : 1 with a range from 1 : 1 to 2,740 : 1. Only 26 of the 101 LMACs had a ratio of OQL to ODL of between 1 : 1 and 10 : 1, around where both the L_Q and ML would be expected to be relative to the L_C and MDL respectively. DLs and QLs may both be zero, DLs may be of higher values than the QLs, or if the QL is higher than the DL, the ratios range over several orders of magnitude but no fixed ratios were observed.

The assumption of both the L_Q and ML is there would be range of concentrations where the %RSD would be below 10% and below this range the %RSD would be above 10% and the QL would mark the threshold between these two ranges. This relationship can be seen in Figure 1. All of the samples with concentrations of Heptachlor greater than 2,000 ng L^{-1} had a %RSD of less than 10% and the samples with concentrations less than this had a %RSD of greater than 10%. While this did happen for some LMACs where an OQL could be determined or was not zero, for others it did not. An example of this can be seen in Figure 2, where only two N samples analysed for DDT at Lab 29 produced a %RSD < 10, those at concentrations of 20,000 and 50,000 ng L^{-1}. All of the samples with higher concentrations produced results that had a %RSD > 10 as well those with lower concentrations. So while it is technically correct that some of the OQLs are indeed the lowest concentration measured that produced a 10% RSD, they are often also the highest concentrations as well, which does not really act as a threshold between ranges of low and high variability. Figure 3 shows that for some LMACs, all of the samples, no matter what the concentration, had a %RSD greater than 10%. In this case, no OQL could be determined.

The KCM assumes that Z samples will produce non-zero values, resulting in DLs and QLs that are non-zero as well. However, this turned out not to be the case, of the 3,671 Z samples analysed in Phase 1 by all laboratories, 2,776 (86%) were reported as zero and 367 (10%) were less than zero. Of the positive results (528) in Phase 1, over half (255) came from just one laboratory (Lab 34), a quarter (138) came from a second laboratory (Lab 32) while none came from a third laboratory (Lab 37). Similar results were obtained from

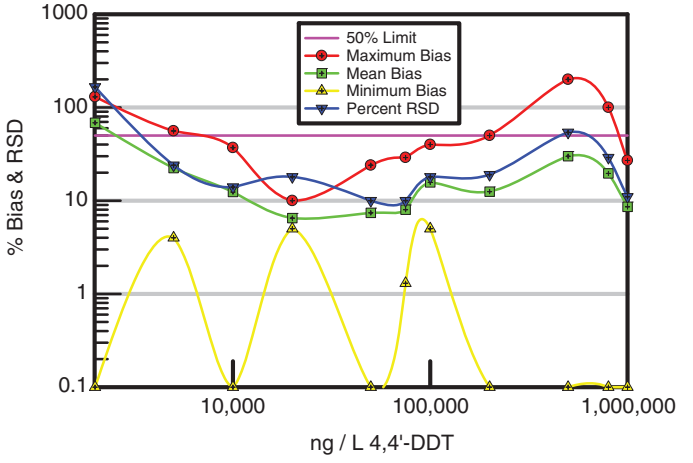

Figure 2. Bias & RSD in the Analysis of 4,4′-DDT by GC-ECD at Lab 29.

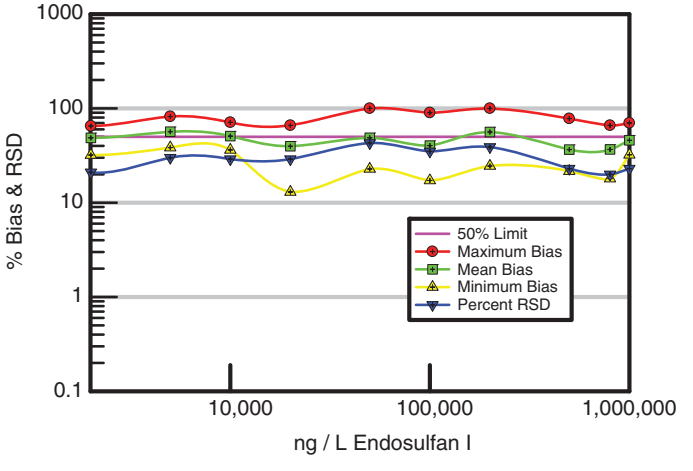

Figure 3. Bias & RSD in the Analysis of Endosulfan I by GC-ECD at Lab 37.

Phase 3, as can be seen in Table 3, as some laboratories produced few, if any, FP; almost all of the FP were produced by two laboratories. The different performance between the laboratories was the settings for peak rejection software, some laboratories minimised those settings while others did not. Suffice it to say, the assumption used in the Currie's L_C and the USEPA's MDL that the majority of values produced by the analysis of Z samples would be non-zero and normally distributed was not supported by the results of this study. This being so, there is no way that the L_C or MDL could be accurately determined and if the L_Q or ML are simple multiples of their respective DL, then they could not be accurately determined either.

This observation is born out in the results in Table 4. The ratio of the four measures of QL (OQL, QL-10, QL-mean, and QL-1) to either the USEPA's ML or Currie's LQ were

determined for each LMAC, when both values were available. Table 4 lists the median, maximum and minimum ratio as well as the number of LMACs where the ratio was between greater than 1.5 or less than 0.5 and those in between. What is quite clear is that there is a huge range of ratios, between three and seven orders of magnitude. There were LMACs where the OQL 1,000 times larger or smaller than the LQ while few of the LMACs where a ratio could be determined were within 50% of the expected value.

Again using the DDT determination by Lab 29 as an example, of the 30 *Z* samples analysed as part of Phase 1, 26 were zero but the standard deviation was 23,500 ng L^{-1} so the L_C was 94,300 ng L^{-1} and the L_Q was 235,000 ng L^{-1}. Similarly, the MDL and ML as determined from seven replicate *N* samples in Phase 2 were 4,600 and 14,700 ng L^{-1} respectively. However, the lowest Phase 3 blind *N* sample analysed by Lab 29 for DDT that had a %RSD of 10% or less was 20,000 ng L^{-1}, which is less than 1/10th of the L_Q but only 26% higher than the ML. However, all ten of the replicates of the *N* sample with 20,000 pg L^{-1} DDT analysed by Lab 29 were within 10% of the target value and seven were within 5%. Even at 5,000 ng L^{-1}, this laboratory was able to get nine replicates to be within 50% of the target value, and four replicates were within 10%. This laboratory was able to accurately analyse *N* samples with concentrations well below the MDL, L_C, ML, and L_Q. As the results in Table 4 make clear, these results were entirely typical for this study.

A significant portion of these unexpected results is due to variability between the days of analysis. Using the same example of Lab 29's analysis of DDT, the 110 *N* samples were analysed over a three week period. At least two and as many as three *N* samples were analysed at each of the 11 concentrations during each one week period). In the first week, 27 were analysed and the mean bias for all samples (at least two and as many as three *N* samples were analysed at each of the 11 concentrations during this period). The mean bias for all *N* samples during this period at all concentrations was 7.9% with three *N* samples having a bias of 0% (including one at the lowest concentration of 2,000 pg L^{-1}) and a maximum bias of 24%. Another 38 *N* samples were analysed in the second week but with a mean bias of 19% and a maximum of 130% and minimum of zero. Four *N* samples had a bias of greater than 50, all with a concentration less than 10,000 ng L^{-1} (there were a minimum of three *N* samples per concentration). The remaining 44 *N* samples were analysed during the third week and had a mean bias of 26% with a maximum of 200% and a minimum bias of 0% and six *N* samples with a bias greater than 50%. Of the nine *N* samples with a bias of 50% or greater, six had concentration of 2,000 ng L^{-1} and the other three were all analysed on the same day. By all measures, the laboratory's performance was dramatically less accurate at the end of the study as compared to the beginning. As might be expected the deterioration of accuracy, and precision, was most dramatic at the lower concentrations.

6. Conclusions and recommendations

Neither the L_Q nor the ML appeared to be very useful in estimating the lowest reportable concentration, whether that was defined in terms of bias or reproducibility. L_Q did not produce an estimate of a concentration that would produce a 10% RSD nor was it clear that even if it had, that such a value corresponded in any way to a critical concentration that would function usefully as a reporting limit and the ML did not perform any better. This in part because contrary to theory, there was no general arithmetic relationship

between the 99th percentile of values of Z samples and the lowest concentration of N samples that had a certain bias or reproducibility. Additionally, both the L_C and MDL are based on the assumption that the analysis of Z samples produce non-zero values that are distributed in a Gaussian fashion, which was not supported by the results of this study [9].

Even if all of the assumptions of the KCM were in fact sound, they would at best only be useful on the day that they were determined. The results of this study indicate that sensitivity can change dramatically over a short amount of time which changes performance at low concentrations and thus significantly alters what might constitute a reporting limit. In case of Lab 29's analysis of DDT, the accuracy and precision changed dramatically over just a few weeks. No matter how a QL is determined, it is clear that a QL must be evaluated on an ongoing basis. The USEPA has been moving in this direction in certain situations. The Laboratory Certification Manual [10] for the analysis of water samples for the Safe Drinking Water Act (which is not applicable to CWA laboratories) does suggest that the lowest reportable concentration be confirmed on a regular basis.

Rather than trying to determine reporting limits based on statistical intervals, it might be more useful to set them based on the parameters of interest. A QL is at least implicitly a measure of the lowest concentration that produces accurate results, then a reporting limit based on the lowest concentration that can be analysed with that level of bias, which might be more useful [11,12]. Further, rather than conducting a study periodically to statistically estimate a reporting limit, it might be more to the point to determine, or at least confirm, that instrument sensitivity has not shifted. In any event, it is clear that the KCM approach is fundamentally flawed and a different approach is needed.

Acknowledgements

The design of this interlaboratory study was conducted by a sub-committee of the FACDQ which included Zonetta English, Louisville and Jefferson Counties Metropolitan Sewer District, Dr. Richard Rediske, Annis Water Resources Institute, Dr. Richard Burrows, Test America, Larry LaFleur, National Council for Air and Stream Improvement, Inc., Dick Redding, USEPA Office of Water, Engineering and Analysis Division, and Bob Avery, Michigan Department of Environmental Quality, Environmental Laboratory Services. The author would like to offer special thanks to Ken Miller of Computer Science Corporation who was a technical consultant to the USEPA ODW and provided technical support to the FACDQ.

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