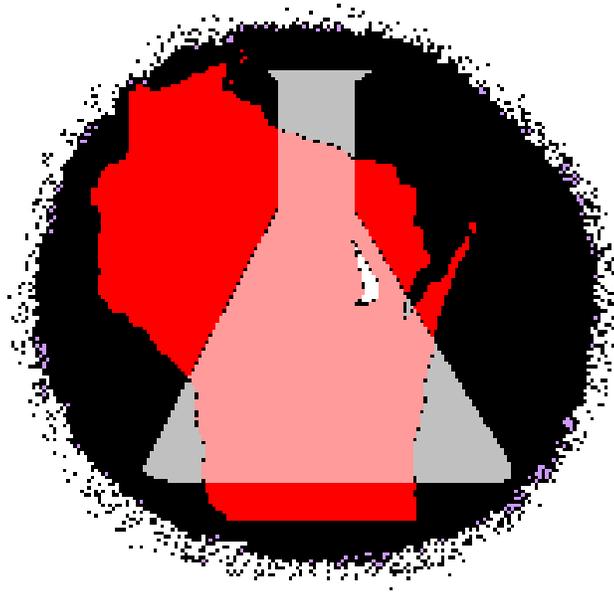


# **Method Detection Limit Survey Results and Analysis**



**Kerilynn M. Carden  
Wisconsin Department of Natural Resources  
Laboratory Certification Program**

**December 1998**

**PUBL-SS-930-98**

## ABSTRACT

Since 1990, the Wisconsin Department of Natural Resources (DNR) has published several rules requiring laboratories to report analytical data down to their established limits of detection (chapters NR 149, 105 and 809, Wis. Adm. Code). The DNR is concerned about data at these low levels because the earliest possible detection of toxic or potentially carcinogenic chemicals in the environment is paramount in the DNR's mission to protect human health, wildlife, fish, and the environment. Low level data is important information needed by agency decision makers. In cases where health-based standards fall below typical laboratory detection limits, low level data are critical for making the correct choices when designing site remediation strategies, alerting the public to health threats, and protecting wildlife from toxic chemicals.

Data users that know how to properly interpret low level environmental data understand analytical variability near the detection limit. This variability occurs both within and across laboratories. As the DNR began implementing new low level reporting rules, the laboratory certification program realized the need to determine the range of capabilities across Wisconsin certified and registered laboratories. The primary purpose of the spring 1998 survey was to gather information on the range and variability of method detection limits (MDLs) calculated by Wisconsin certified and registered laboratories for a select list of compounds of special concern. These compounds were selected based upon the magnitude of their health-based standards and the DNR's perception of analytical capabilities in the laboratory industry. The report includes a summary of the statistics, quartiles, and other useful information about MDLs calculated by Wisconsin certified and registered laboratories.

## DEFINITIONS AND ACRONYMS

Listed below are definitions, acronyms, and abbreviations used in this report.

**Acute Toxicity Criteria (ATC):** This is the maximum daily concentration of a substance which ensures adequate protection of sensitive species of aquatic life from the acute toxicity of that substance and will adequately protect the designated fish and aquatic life use of the surface water if not exceeded more than once every 3 years. (chapter NR 105.03, Wisconsin Administrative Code)

**Cold Vapor Atomic Absorption (CVAA):** This is a technique used for mercury analysis.

**Detection Reporting Requirement List:** A list of analytes that have a health based environmental standard in chapters NR 105, 140, 720, and 809, Wisconsin Administrative Code, below or near the detection limit. Laboratories are required to report all data for these substances down to their limit of detection. (Appendix A)

**Enforcement Standard (ES):** This is a numerical value expressing the maximum allowable concentration of a substance in groundwater which is adopted under s. 160.07, Stats., and s. NR 140.10 or s. 160.09, Stats., and s. NR 140.12. These standards are toxicologically derived to protect human health. Analytical values above the ES trigger remediation and additional monitoring.

**Extraction/Concentration and Atomic Absorption (Extraction/AA):** This is a technique occasionally used for the analysis of samples with very low metal concentrations (most commonly hexavalent chromium).

**Flame Atomic Absorption (FLAA):** This is a single element analysis in which a flame is used to dissociate the atoms of an aspirated sample into the free atomic state, rendering them available for the absorption of light.

**Gas Chromatography (GC):** This is a technique used for the separation and identification of organic compounds.

**Gas Chromatography/Mass Spectrometry (GC/MS):** This is a specific **gas chromatography** technique that uses a mass-sensitive detector to identify the compounds of interest.

**Graphite Furnace Atomic Absorption (GFAA):** This is similar to **flame atomic absorption**, except a programmable graphite furnace is used instead of a flame.

**High-Performance Liquid Chromatography (HPLC):** This is a technique similar to **gas chromatography**, except the separation of individual compounds takes place in the liquid phase instead of the gaseous phase. HPLC-UV is the technique with an ultra violet detector and HPLC-F is with a fluorescence detector.

**Human Cancer Criteria (HCC):** This is the maximum concentration of a substance or mixture of substances established to protect humans from an unreasonable incremental risk of cancer resulting from contact with or ingestion of surface waters of the state and from ingestion of aquatic organisms taken from surface waters of the state. (chapter NR 105.09, Wisconsin Administrative Code)

**Inductively Coupled Plasma (ICP):** A multiple element analysis technique to test for metals, during which samples are aspirated through a hot plasma torch.

**Inductively Coupled Plasma/Mass Spectrometry (ICP/MS):** This technique is a refinement of the **ICP** technique. After the ions are generated in the torch plasma, they are directed to a mass spectrometer.

**Inductively Coupled Plasma-Axial Modified Torch (ICP-Trace):** This technique is a modification of the conventional **ICP**, in which the torch is mounted horizontally rather than vertically. This allows the sample to pass through the plasma torch for a longer period of time, which results in an increase in emission intensity and lower detection limits.

**Limit of Detection (LOD):** This is the lowest concentration level that can be determined to be statistically different from a blank (99% confidence). The LOD is typically determined to be in the region where the signal to noise ratio is greater than 5. Limits of detection are matrix, method, and analyte specific. Unless specified differently, it is assumed that the numerical value of the LOD is the same as the **MDL**.

**Limit of Quantitation (LOQ):** This is the level above which quantitative results may be obtained with a specified degree of confidence. The LOQ is mathematically defined as equal to 10 times the standard deviation of the results for a series of replicates used to determine a justifiable **limit of detection**. Limits of quantitation are matrix, method, and analyte specific.

**Low-Level Mercury:** For the purposes of this study, low-level techniques are defined as technologies that provide detection capability of 0.02 ug/L or less (i.e. an order of magnitude below generally recognized detection capabilities). Generally, this indicates the use of cold vapor atomic fluorescence technology.

**Method Detection Limit (MDL):** This the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. MDLs are matrix specific, and must be calculated according to the procedure outlined in Chapter 40, Code of Federal Regulations, part 136, Appendix B, rev. 1.11 (Appendix B).

**Preventive Action Limit (PAL):** The PAL is a numerical value expressing the maximum allowable concentration of a substance in groundwater before additional monitoring is required. PALs are adopted under s. 160.15, Stats., and s. NR 140.10, 140.12 or 140.20. The PAL is typically set at 1/10<sup>th</sup> of the **enforcement standard** if the substance is carcinogenic, mutagenic, teratogenic or has a synergistic effect. The PAL is 20% of the enforcement standard for other substances of public health concern. (NR 140.05(17) & 140.10 note)

**Wildlife Criteria (WC):** This is the concentration of a substance which if not exceeded protects Wisconsin's wildlife from adverse effects resulting from ingestion of surface waters of the state and from ingestion of aquatic organisms taken from surface waters of the state. (chapter NR 105.07, Wisconsin Administrative Code)

## INTRODUCTION

The Department of Natural Resources (DNR) requires laboratories to report monitoring data down to their limit of detection for many types of samples, including wastewater, drinking water and groundwater. The earliest possible detection of trace chemicals in the environment is paramount to the protection of human health and the environment. Regulators base environmental policy decisions on the detection of toxic chemicals at levels that are perceived to have environmental consequences. For many substances, health-based environmental standards are promulgated without regard to analytical capabilities. Where health-based standards fall below analytical capabilities, accurate determinations of laboratory detection limits are important for interpreting low-level data. This requires that data users understand analytical variability near the detection limit. This variability occurs both within and across laboratories. When a laboratory reports a value as “less than” or “not detected” without specifying the detection limit, interpretation is difficult. To assist with low-level data interpretation, regulators require laboratories to use standardized procedures to calculate their detection limits.

The Wisconsin Department of Natural Resources requires certified and registered laboratories to calculate detection limits using the U.S. Environmental Protection Agency Method Detection Limit (MDL) procedure found in Title 40 Code of Federal Regulations Part 136 (40 CFR 136, Appendix B, revision 1.11). Method detection limits are statistically determined values that define how easily measurements of a substance by a specific analytical protocol can be distinguished from measurements of a blank (background noise). Method detection limits are matrix, instrument and analyst specific and require a well-defined analytical method. Variation in method detection limits among laboratories is attributable to differences in technique and instruments, sample contamination, choice of method, spike level, analytical bias, gross error (systematic), and random error (Draper et.al., 1998). Method detection limits provide a useful mechanism for comparing different laboratories' capabilities with identical methods as well as different analytical methods within the same laboratory. The MDL procedure is simple, and has wide applicability in environmental monitoring. The Wisconsin laboratory certification and registration program has developed guidance to assist laboratories and generate meaningful detection limits (WDNR, 1996).

In support of the Department's efforts to quantify and interpret low level data, the laboratory certification and registration program designed a survey to compile information about detection limit capabilities across Wisconsin certified and registered laboratories. The primary purpose of this survey was to gather information on the range and variability of MDLs calculated for a select list of compounds of special concern. These compounds were chosen because their health-based standards are similar in magnitude to detection limits achievable in the environmental laboratory industry.

The DNR had the following objectives for the limit of detection survey:

1. Determine the percentage of laboratories that correctly calculate MDLs and identify the most common errors laboratories make when calculating MDLs.

2. Gather information on the range and variability of reagent water MDLs reported by laboratories for selected analytes on the Detection Reporting Requirement list (included as Appendix A).
3. Compare calculated MDLs with reported detection limits to discover the level of detection that is routinely achievable for the compounds on the Detection Reporting Requirement list.

This report fulfills the first two objectives; summarizing the calculated method detection limits and investigating problems with the MDL determinations. The information presented in this report is useful for comparing MDLs across laboratories, but does not investigate specific situations where the calculated MDL is not analytically feasible. Calculated MDLs may not reflect real-world detection limits for several reasons (WDNR, 1996). Most importantly, calculated MDLs are often determined using reagent water spiked with the analyte of interest, rather than a specific matrix such as wastewater or soils using the same procedure. Reagent water MDLs can be described as "best case limits", and the detection limits achievable in clean samples may not be analytically achievable in other matrices. Nonetheless, calculating the MDL in reagent water is useful for comparing detection limits among many laboratories. The Department intends to investigate the detection limit data in more detail and hopes to release future reports that will focus specifically on how calculated MDLs compare to routinely achievable detection limits in real world samples.

## MATERIALS AND METHODS

The DNR began this detection limit investigation in January, 1998. First, the DNR designed and mailed a survey to laboratories certified or registered for the compounds on the Detection Reporting Requirement list (Appendix A). The survey requested information about how laboratories calculated MDLs, LODs, and limits of quantitation (LOQs). After all of the laboratories had responded, the DNR compiled the data into a database and the results were validated based upon the requirements of the MDL procedure in 40 CFR 136 (Appendix B). Method detection limits that did not meet the necessary criteria were removed from the data set. Finally, the Department conducted a statistical analysis (e.g. range, mean, median, and quartiles) of the valid data.

### Survey Development

The analytes chosen for this survey can be found on the Detection Reporting Requirement list (Appendix A). This list of analytes includes all primary drinking water contaminants specified in chapter NR 809, Wis. Adm. Code, and those substances specified in chapters NR 105, 140 and 720, Wis. Adm. Code, that have health-based environmental standards below or near the detection limit. All certified or registered laboratories analyzing for these substances were required to submit their MDL, LOD, and LOQ information to the Department to comply with Wisconsin regulations. Specifically, the survey requested that the laboratories submit instrument type, methods used, spike concentrations, replicate results, and the mean and standard deviation of the replicates. The laboratories had the option of submitting their detection limit data electronically or by mail to the Department. A copy of the request letter and the spreadsheet can be found in Appendix C.

### Database Construction

The Department entered the information into a database as it was received from the laboratories. The data were checked for consistency. All results were to be reported in micrograms per liter ( $\mu\text{g/L}$ ). If other units were reported the data were adjusted to make the units consistent. The method numbers had to be consistent with the instrument used. Once all of the data was standardized (e.g. units, spelling, methods), each submittal was reviewed to determine if it met the necessary criteria and could be used in the analysis.

### Data Validation

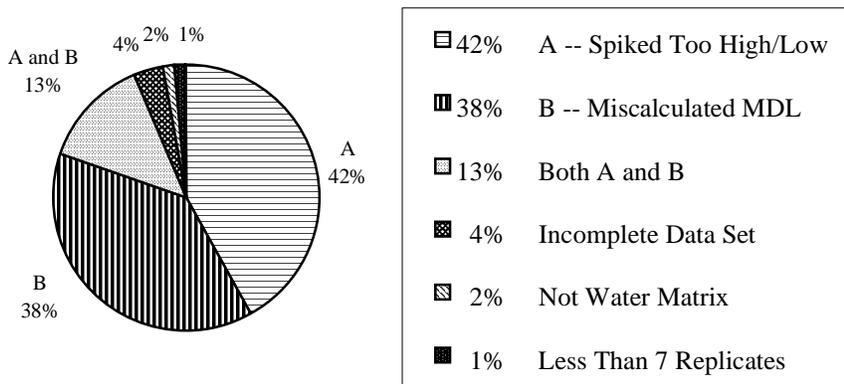
The Department validated the data using the following criteria:

1. **Incomplete Data Set** – A laboratory was contacted if it did not submitted all of the information requested or if there were inconsistencies with their data. If the laboratory could not supply the necessary information, the data were not used in this report.
2. **Not a Water Matrix** – The DNR requested that laboratories report all detection limit data based on a reagent water matrix. If an alternative matrix (e.g. soil, oil, sediment) was used, that specific data point was removed from this report.

3. **Less Than 7 Replicates** – According to the EPA’s procedure for calculating the MDL, at least seven replicates have to be used to calculate the MDL. MDL determinations that did not use a minimum of seven replicates were excluded.
4. **Spike Too High/Low** – The EPA’s MDL procedure has specific spiking criteria, requiring that laboratories spike at concentrations less than ten times the calculated MDL. Spiked concentrations should also be greater than the calculated MDL. The spike level specifications are important to minimize variability between laboratories. Data that did not meet the spiking criteria were excluded.
5. **Miscalculated MDL** – The data set was checked to determine if the MDLs were calculated correctly. To allow for rounding, a ten percent margin was used when checking for miscalculated MDLs. Miscalculated MDLs were not used in the analysis.

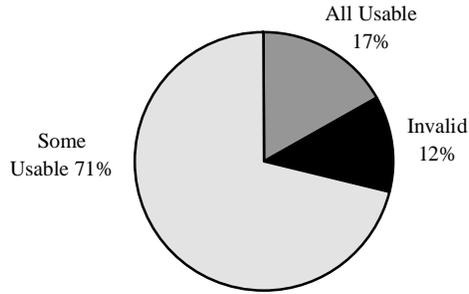
Twenty-six percent (26%) of the submitted results were not used because they failed to meet all of the criteria listed above. Figure 1 presents a summary of the discarded data.

**Figure 1: Breakdown of Discarded Data.**



Of the 122 laboratories that submitted MDL data, it is noteworthy that only 17% of the laboratories returned data that met the criteria for each analyte. Of the remaining 83%, 71% returned surveys that met the criteria for some analytes, but not others while 12% of the surveys had to be discarded completely (Figure 2).

**Figure 2:** Percent of Laboratories Submitting Usable Data Sets



### **Statistical Analysis**

Statistical analyses were conducted on the remaining data set to determine the percentage of reported results that were at or below the PAL. Quartiles of the MDL data (25%, 50%, 75%, and 100%) were constructed. The MDL ranges, means, and medians for each analyte by instrument type were also determined. The following results, discussion, and conclusions are based on a data set of over 2,313 MDL results.

## RESULTS AND DISCUSSION

The calculated MDLs were compared to groundwater standards (PALs) and surface water quality standards to determine if current technology is capable of detecting these analytes at these levels. It is important to note that the wildlife criteria (WC) are implemented to protect the health of wildlife. The 25% quartile demonstrates the detection limits that 25% of the laboratories could be expected to achieve, the median (50% quartile) represents the detection limit achievable by 50% of the laboratories, and so forth. The one-hundredth percentile, or fourth quartile, is equal to the highest MDL reported for a given analyte. All laboratories participating in the survey are capable of detecting the analyte at this level. The quartile representation is also a way to estimate what MDLs a laboratory can be expected to achieve for specific analytes. The ranges, means, and medians for each analyte of interest were calculated to help determine if a particular analytical method consistently produced lower MDLs. The following discussion is divided into six sections: metals, volatile organic compounds (VOCs), semivolatile organic compounds, pesticides, PAHs, and PCBs.

### Metals

Although several metals are listed on the Detection Reporting Requirement list (Appendix A), only the MDLs submitted for cadmium (Cd), hexavalent chromium (Cr<sup>+6</sup>), lead (Pb), mercury (Hg), and thallium (Tl) were analyzed in this report. These metals are introduced into the environment as byproducts of industrial processes such as metal plating and machining or in municipal wastewater effluents.

The DNR was interested in determining if current analytical technologies are capable of detecting metals at the PAL. The MDLs for cadmium, lead, thallium, and mercury were compared to the PALs (Figure 3). A laboratory using a graphite furnace atomic absorption (GFAA) or inductively coupled plasma/mass spectrometry (ICP/MS) instrument should be able to consistently achieve a MDL at or below the PAL. On the contrary, laboratories that use flame atomic absorption (FLAA) or inductively coupled plasma (ICP) instruments are not likely to be able to detect these metals at levels at or below the PAL. It is noteworthy that at this time the PAL for thallium is beyond the reach of current technology. All of the methods used to test for mercury can consistently detect it at or below the PAL.

**Figure 3: Percent of Metal MDLs that Met the PAL**

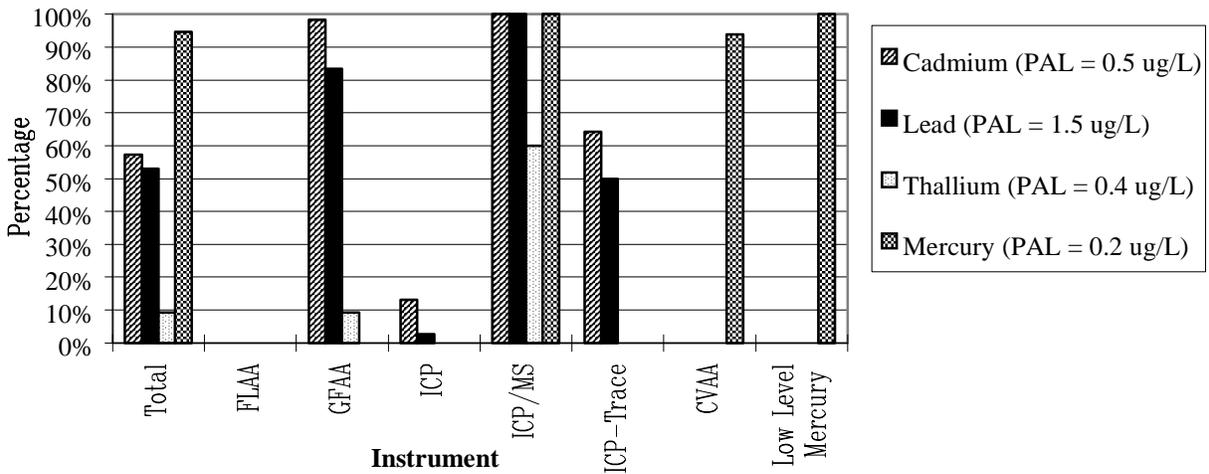


Table 1 is a summary of the MDL quartiles for metals. Each metal is divided by instrument or detector type. It is important to note that the information for thallium by FLAA and mercury by ICP/MS is limited because very few values were reported.

**Table 1: MDL Quartiles for Metals**

	25%	50%	75%	100%
<b>Cadmium (Cd)</b>	0.118	0.353	2.5	19
FLAA	3.17	4.83	8.9	19
GFAA	0.0815	0.116	0.19	0.51
ICP	1.47	2.5	3.58	9.6
ICP/MS	0.037	0.061	0.101	0.2
ICP-Trace	0.257	0.386	0.603	2.9
<b>Chromium, Hexavalent (Cr<sup>6+</sup>)</b>	1.51	2.88	6.53	126
Extraction/AA	1.3	2.6	5.6	8.3
Colorimetric	1.89	3.19	6.68	126
<b>Lead (Pb)</b>	0.85	1.39	16.5	100
FLAA	27.5	37.7	61.8	100
GFAA	0.696	0.9	1.355	3.3
ICP	17.5	28.7	37.4	86.7
ICP/MS	0.078	0.096	0.155	0.621
ICP-Trace	1.285	1.55	2.1	16.7
<b>Mercury (Hg)</b>	0.033	0.0705	0.11	0.6
Cold Vapor AA	0.0515	0.076	0.12	0.6
Low Level	0.0029	0.0062	0.0088	0.161
ICP/MS	NA	NA	NA	0.02
<b>Thallium (Tl)</b>	0.8635	2.06	5.3	327.0
FLAA	NA	NA	NA	60.0
GFAA	0.715	1.0	1.405	5.0
ICP	22.35	50.0	84.7	327.0
ICP/MS	0.015	0.04	0.0506	0.51
ICP-Trace	2.76	3.83	5.0	9.7

\*All units are in µg/L

Each metal is discussed individually below. The information includes a table containing a summary of the ranges, mean, and medians.

### **Cadmium (Cd)**

When very low detection limits are necessary, conventional ICP and FLAA are not generally capable of producing detection limits comparable to newer technology. The Inductively Coupled Plasma-Axial Modified Torch (ICP-Trace) instruments are becoming more widely used, and with some refinements may eventually be able to achieve MDLs closer to those calculated using GFAA and ICP/MS techniques. It is interesting to note that GFAA and ICP had almost the same number of results, yet the median ICP MDL was more than one order of magnitude greater than the GFAA MDLs.

<b>Cadmium</b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
Total	152	19	0.005	1.72	0.353	0.5
FLAA	14	19	1.9	7.45	4.83	
GFAA	56	0.51	0.02	0.15	0.12	
ICP	46	9.6	0.024	2.84	2.5	
ICP/MS	8	0.2	0.005	0.07	0.06	
ICP-Trace	28	2.9	0.16	0.6	0.39	

\*All units are in µg/L

### **Lead (Pb)**

The MDL results from FLAA and ICP instruments are significantly higher than the alternative methods. As more laboratories use the ICP-Trace technologies, consistently lower MDLs and results at or below the PAL may be increasingly obtainable.

<b>Lead</b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
Total	170	100	0.005	11.35	1.4	1.5
FLAA	14	100	9.6	44.14	37.69	
GFAA	78	3.3	0.23	1.09	0.9	
ICP	37	86.7	0.121	30.87	28.7	
ICP/MS	7	0.62	0.005	0.17	0.096	
ICP-Trace	34	16.7	0.58	2.45	1.55	

\*All units are in µg/L

### **Thallium (Tl)**

The data show that the majority of the instruments currently used to test for thallium are not sufficiently sensitive to meet groundwater criteria. ICP/MS appears to be the most promising technology available for low level detection of thallium.

<b>Thallium</b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
Total	87	327	0.004	16.7	2.1	0.4
FLAA	3	60	26	48.67	60	
GFAA	43	5	0.2	1.26	1	

<b>Thallium</b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
ICP	15	327	5.9	77.92	50	
ICP/MS	5	0.509	0.004	0.12	0.04	
ICP-Trace	21	9.7	2	4.17	3.83	

\*All units are in µg/L

### Hexavalent Chromium (Cr<sup>6+</sup>)

Hexavalent chromium does not have a PAL associated with it. However, an water quality standard for hexavalent chromium is the acute toxicity criteria (ATC) found in chapter NR 105. The ATC for all aquatic life for this compound is 16.02 µg/L. Only one result was above this level. Although the Extraction/Concentration and Atomic Absorption (Extraction/AA) method is capable of detecting hexavalent chromium at slightly lower levels, it is not often used by environmental laboratories. The Extraction/AA method is more expensive and time consuming than colorimetric procedures.

<b>Hexavalent Chromium (Cr<sup>6+</sup>)</b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>	<b>ATC</b>
Total	26	126	0.58	8.78	2.88	NA	16.02
Extraction/AA	5	8.3	0.58	3.68	2.6		
Colorimetric	20	126	0.6	10.44	3.19		
ICP-Trace	1	---	---	---	0.91		

\*All units are in µg/L

### Mercury (Hg)

Cold Vapor Atomic Absorption (CVAA) has the ability to detect mercury at or below the PAL. However, this type of analysis is more prone to false positives caused by contamination in sampling and analytical procedures because there is ambient mercury in the laboratory. In January 1996 a low level method for mercury analysis was approved by EPA. The low level method compresses the sample to get a stronger signal for mercury. Since the PAL is not the lowest water quality standard, the results for mercury were also compared to the wildlife criteria (WC) value found in chapter NR 105. The WC for mercury is 0.0013 µg/L. Only two of the reported results were below this level. The technologies being used to detect mercury at low levels are improving due to increased awareness and initiatives to reduce sources of mercury contamination in the laboratory.

<b>Mercury</b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>	<b>WC</b>
Total	74	0.6	0.00014	0.085	0.071	0.2	0.0013
CVAA	65	0.6	0.0054	0.0955	0.076		
Low Level	7	0.0161	0.00014	0.0065	0.0062		
ICP/MS	2	0.02	0.0129	0.016	---		

\*All units are in µg/L unless otherwise specified.

## **Summary of Metal Results**

There are numerous methods currently available to test for metals in water. For cadmium, lead, and thallium, ICP/MS consistently produced the lowest MDL results. The second lowest MDL results for these metals came from GFAA instruments. The more recent ICP-Trace instruments are capable of producing low MDLs, but still cannot detect metals at the same levels as GFAA and ICP/MS. As more laboratories use the ICP-Trace technology, consistently lower MDLs and results at or below the PAL may be increasingly obtainable. Using FLAA or ICP to test for cadmium, lead, and thallium resulted in an average MDL 10 to 100 times greater than the other methods. The MDL results for mercury demonstrate that the current technologies allow laboratories to consistently meet the PAL. The colorimetric method does not produce the lowest MDLs, but remains the most common procedure for determining hexavalent chromium.

## **Volatile Organic Compounds (VOCs)**

Nine of the thirteen volatile compounds on the Detection Reporting Requirement list (Appendix A) were analyzed in this report. Volatile organic compounds (VOCs) are introduced into the environment from a variety of sources, including spent solvents, leaky storage tanks, and landfills.

All of the MDLs for VOCs were evaluated in relation to the PALs. Figure 4 summarizes the percentage of MDLs that met the PAL. In all cases, a slightly higher percentage of MDLs obtained by GC were able to meet the PAL than MDLs obtained by GC/MS. For five of the nine compounds, at least 60% of the total reported MDLs were at or below the PAL. In the instances where the PAL was not met or only met by a few laboratories, the PALs are extremely low. Current technology may not be sufficiently sensitive to consistently detect those analytes at or below the PAL.

**Figure 4:** Percent of VOC MDL Results that Meet the PAL

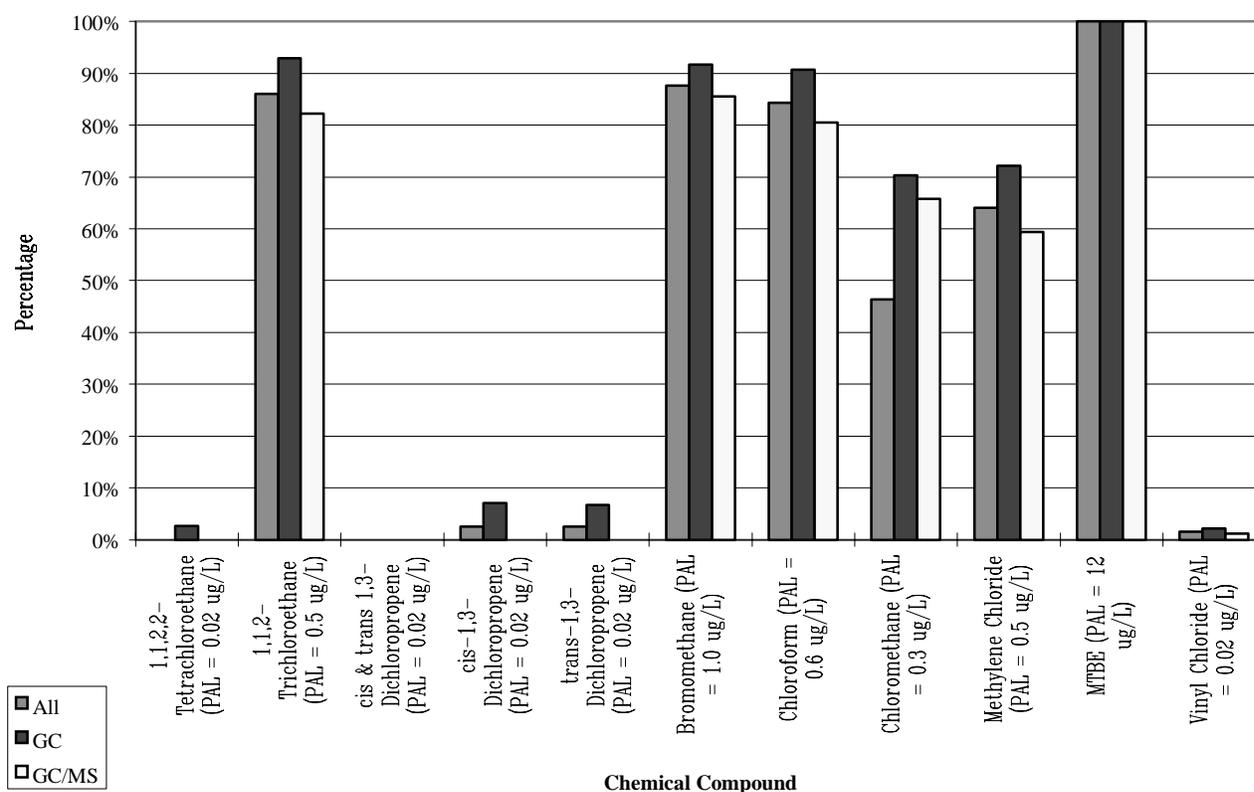


Table 2 summarizes the results of the laboratories' capabilities for detecting VOCs. As with metals, each analyte has been subdivided by instrument type. For the majority of the VOCs the MDL values at the first and second quartiles (25% and 50%, respectively) are relatively similar. At the third quartile (75%) a larger difference between GC and GC/MS can be seen. In this case all of the third quartile results are greater than the GC MDL results. The fourth quartile (100%) values for GC and GC/MS lack a definite pattern, possibly due to outliers at the upper end of the scale.

**Table 2:** MDL Quartiles for VOCs

	25%	50%	75%	100%
<b>1,1,2,2-Tetrachloroethane</b>	0.1305	0.24	0.465	2.51
GC	0.13	0.233	0.3	2.51
GC/MS	0.132	0.245	0.57	2.27
<b>1,1,2-Trichloroethane</b>	0.15	0.227	0.364	7.2
GC	0.15	0.196	0.3	2.14
GC/MS	0.15	0.23	0.41	7.2
<b>1,3-Dichloropropene (cis &amp; trans)</b>	0.12	0.25	0.43	2.18
GC	0.103	0.22	0.37	0.581
GC/MS	0.12	0.286	0.47	2.18
<b>cis-1,3-Dichloropropene</b>	0.107	0.175	0.273	1.89
GC	0.123	0.212	0.256	1.89
GC/MS	0.106	0.155	0.389	1.374

	25%	50%	75%	100%
<b>trans-1,3-Dichloropropene</b>	0.13	0.189	0.46	6.29
GC	0.122	0.2	0.243	2.12
GC/MS	0.133	0.184	0.574	6.29
<b>Bromomethane</b>	0.17	0.32	0.75	5.84
GC	0.2	0.336	0.611	3.6
GC/MS	0.17	0.317	0.83	5.84
<b>Chloroform</b>	0.117	0.2	0.391	6.12
GC	0.128	0.213	0.337	1.89
GC/MS	0.109	0.198	0.503	6.12
<b>Chloromethane</b>	0.16	0.317	0.635	6.61
GC	0.172	0.34	0.59	5.88
GC/MS	0.16	0.31	0.65	6.61
<b>Methylene Chloride</b>	0.2	0.36	0.678	5.87
GC	0.225	0.302	0.55	2.54
GC/MS	0.15	0.42	0.84	5.87
<b>Methyl tert-butyl ether (MTBE)</b>	0.159	0.299	0.6	6.7
GC	0.17	0.292	0.445	6.7
GC/MS	0.13	0.32	0.78	2.58
<b>Vinyl Chloride</b>	0.15	0.25	0.5	5.81
GC	0.147	0.25	0.45	2.22
GC/MS	0.15	0.233	0.58	5.81

\*All units are in µg/L

The following information contains a statistical analysis for each VOC analyzed in this report. The information includes a table containing a summary of the ranges, mean, and medians for each volatile.

### 1,1,2,2-Tetrachloroethane

GC and GC/MS instruments obtained similar ranges, means, and medians demonstrating that the two methods are not significantly different for this compound.

<b>1,1,2,2-Tetrachloroethane</b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
Total	103	2.51	0.013	0.385	0.24	0.02
GC	37	2.51	0.013	0.318	0.233	
GC/MS	66	2.27	0.027	0.422	0.245	

\*All units are in µg/L

### 1,1,2-Trichloroethane

The data indicate that GC is slightly more sensitive than GC/MS for analyzing 1,1,2-Trichloroethane.

<b>1,1,2-Trichloroethane</b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
Total	115	7.2	0.015	0.37	0.227	0.5
GC	42	2.14	0.015	0.28	0.196	
GC/MS	73	7.2	0.044	0.43	0.23	

\*All units are in µg/L

## 1,3-Dichloropropene

The median for each isomer, by each method, was about one order of magnitude greater than the PAL. With current technology it is not realistic for a laboratory to detect 1,3-dichloropropene at 0.02 µg/L. GC and GC/MS MDL results are comparable.

<b>1,3-Dichloropropene</b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
1,3-Dichloropropene (cis & trans)	58	2.18	0.05	0.36	0.25	0.02
GC	21	0.58	0.054	0.25	0.22	
GC/MS	37	2.18	0.05	0.43	0.286	
cis-1,3-Dichloropropene	40	1.89	0.019	0.301	0.175	0.02
GC	14	1.89	0.019	0.31	0.212	
GC/MS	26	1.37	0.031	0.3	0.155	
trans-1,3-Dichloropropene	41	6.29	0.016	0.49	0.19	0.02
GC	15	2.12	0.016	0.34	0.2	
GC/MS	26	6.29	0.049	0.59	0.184	

\*All units are in µg/L

## Bromomethane

The ranges, means, and medians between GC and GC/MS demonstrate little variability between the two instrument types. Due to the fact that bromomethane is a gas and volatilizes readily, the reported MDLs are higher. Nonetheless, current methods and instruments used for detecting bromomethane are capable of quantifying this compound at or below the PAL.

<b>Bromomethane</b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
Total	105	5.84	0.052	0.62	0.32	1.0
GC	36	3.6	0.052	0.55	0.336	
GC/MS	69	5.84	0.06	0.658	0.317	

\*All units are in µg/L

## Chloroform

As seen for many of the volatile organic compounds, the MDL range from GC/MS instruments is much greater than that of GC. The medians for the two methods are very similar. Again, the current methods are able to detect chloroform at low levels.

<b>Chloroform</b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
Total	115	6.12	0.017	0.374	0.2	0.6
GC	43	1.89	0.017	0.284	0.213	
GC/MS	72	6.12	0.038	0.428	0.198	

\*All units are in µg/L

## Chloromethane

Detection of chloromethane in environmental samples is hampered because it is a gas that readily volatilizes at room temperature, which increases the MDL. The ranges, means, and medians for the two methods were very similar showing that the two instruments are comparable. The current technologies available for analyzing chloroform produce similar results, but refinements are necessary if lower detection levels are required.

<u>Chloromethane</u>	<u># of Results</u>	<u>Maximum</u>	<u>Minimum</u>	<u>Mean</u>	<u>Median</u>	<u>PAL</u>
Total	110	6.6	0.051	0.66	0.32	0.3
GC	37	5.88	0.051	0.68	0.34	
GC/MS	73	6.61	0.053	0.66	0.31	

\*All units are in µg/L

## Methylene Chloride

The range for GC/MS is wider than that of other GC instruments; therefore, more consistent MDL results are seen with GC instruments. Methylene chloride is a common laboratory solvent, and poor laboratory ventilation increases analytical variability and detection limits.

<u>Methylene Chloride</u>	<u># of Results</u>	<u>Maximum</u>	<u>Minimum</u>	<u>Mean</u>	<u>Median</u>	<u>PAL</u>
Total	100	5.87	0.026	0.678	0.36	0.5
GC	36	2.54	0.026	0.487	0.3015	
GC/MS	64	5.87	0.031	0.786	0.408	

\*All units are in µg/L

## Methyl tert-butyl ether (MTBE)

GC/MS detection allows for greater sensitivity because MTBE tends to coelute with the solvent front in GC determinations. The coelution diminishes sensitivity of the photoionization detector (PID) used with GC. As a result, the GC/MS MDL range was smaller than that found with GC instrumentation.

<u>MTBE</u>	<u># of Results</u>	<u>Maximum</u>	<u>Minimum</u>	<u>Mean</u>	<u>Median</u>	<u>PAL</u>
Total	113	6.7	0.029	0.55	0.3	12.0
GC	66	6.7	0.041	0.6	0.292	
GC/MS	47	2.58	0.029	0.48	0.32	

\*All units are in µg/L

## Vinyl Chloride

The wide range in the GC/MS MDL data shows that there is greater variability when analyzing vinyl chloride by GC/MS compared to GC.

<u>Vinyl Chloride</u>	<u># of Results</u>	<u>Maximum</u>	<u>Minimum</u>	<u>Mean</u>	<u>Median</u>	<u>PAL</u>
Total	131	5.81	0.0049	0.47	0.25	0.02
GC	45	2.22	0.013	0.354	0.25	

<b><u>Vinyl Chloride</u></b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
GC/MS	86	5.81	0.0049	0.535	0.23	

\*All units are in µg/L

### Summary of VOC Results

Overall, about half of the PALs for the volatile compounds analyzed here were achievable using available technologies. It is important to note that almost twice the number of laboratories are using GC/MS as GC to analyze volatile samples. A smaller range was seen with the GC instruments which may be attributed to the smaller sample size or that the GC instruments are more sensitive than GC/MS. According to the Student's t-test statistical analysis, the reported MDLs for GC and GC/MS are not significantly different for any of the volatile analytes discussed above.

### Semivolatile Organic Compounds

Four semivolatile organic compounds were analyzed: 2,4-dinitrotoluene, 2,6-dinitrotoluene, di(2-ethylhexyl)phthalate, and pentachlorophenol. Ninety-five percent (95%) of the MDLs were generated with GC/MS with the remaining 5% by GC. The PALs for these compounds were significantly lower than the capability of the laboratories surveyed.

The results for semivolatile organic compounds are summarized in Table 3. Each analyte is subdivided by instrument type, where applicable.

**Table 3:** MDL Quartiles for Semivolatile Organic Compounds

	<b>25%</b>	<b>50%</b>	<b>75%</b>	<b>100%</b>
<b>2,4-Dinitrotoluene</b>	0.69	1.2	2.0	5.9
GC/MS	0.84	1.25	2.03	5.9
<b>2,6-Dinitrotoluene</b>	0.605	1.4	2.46	6.32
GC/MS	0.75	1.42	2.6	6.32
<b>Di(2-ethylhexyl)phthalate</b>	1.18	1.9	2.7	16.7
GC/MS	1.15	2.0	2.71	16.7
<b>Pentachlorophenol</b>	0.823	2.02	3.63	17.9
GC/MS	1.02	2.2	3.9	17.9
GC	0.058	0.68	2.82	3.33

\*All units are in µg/L

Below is a statistical analysis for each semivolatile organic compound analyzed in this report. The information includes a summary of the ranges, mean, and medians for each analyte and method.

#### 2,4-Dinitrotoluene

The data indicate that the available technologies are not sufficiently sensitive to detect 2,4-dinitrotoluene at or near the PAL (0.005). The GC MDLs are much lower than the GC/MS MDLs, but a larger sample size is necessary to draw more definitive conclusions.

<b><u>2,4-Dinitrotoluene</u></b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
----------------------------------	---------------------	----------------	----------------	-------------	---------------	------------

<b><u>2,4-Dinitrotoluene</u></b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
Total	42	5.9	0.0163	1.67	1.2	0.005
GC/MS	40	5.9	0.11	1.76	1.25	
GC	2	0.0274	0.0163	0.022	NA	

\*All units are in µg/L

## **2,6-Dinitrotoluene**

As with 2,4-dinitrotoluene, technology for detecting 2,6-dinitrotoluene is not sensitive enough to detect at or near the PAL.

<b><u>2,6-Dinitrotoluene</u></b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
Total	39	6.32	0.0214	1.7	1.4	0.005
GC/MS	37	6.32	0.11	1.79	1.42	
GC	2	0.0266	0.0214	0.024	NA	

\*All units are in µg/L

## **Di(2-ethylhexyl)phthalate**

The range of the MDLs for di(2-ethylhexyl)phthalate is wide; extending from 0.61 to 16.7 µg/L. The wide range can be attributed to the fact that this is a common laboratory contaminant and will interfere in the analysis. As seen with the previous two semivolatile organic compounds, the GC/MS methods being used today are not capable of detecting this compound at the PAL.

<b><u>Di(2-ethylhexyl)phthalate</u></b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
Total	44	16.7	0.61	2.36	1.9	0.5
GC/MS	42	16.7	0.61	2.42	2.0	
GC	2	1.27	1.19	1.23	NA	

\*All units are in µg/L

## **Pentachlorophenol**

As with all of the other semivolatile organic compounds, the PAL is not routinely achievable using current GC/MS instruments.

<b><u>Pentachlorophenol</u></b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
Total	52	17.9	0.006	2.99	2.02	0.1
GC/MS	41	17.9	0.028	3.45	2.2	
GC	11	3.33	0.006	1.25	0.68	

\*All units are in µg/L

## **Summary of Semivolatile Organic Results**

The four semivolatile organic compounds analyzed in this report demonstrate that the available technologies for detecting these compounds at the PAL are not sufficient. The low precision of these methods, exhibited by the wide range of MDLs, suggests that these analytes are difficult to detect. Very few laboratories use GC technology to detect the semivolatile organic compounds.

More MDL results by GC are necessary to draw any conclusions about the relationship between GC and GC/MS.

## Pesticides

Seven pesticides were analyzed in this study: alachlor, heptachlor epoxide, dichlorodiphenyltrichloroethane (DDT), dimethoate, heptachlor, lindane, and parathion. Less than ten MDL results were reported for alachlor, dimethoate, and parathion. The other pesticides had at least forty MDLs reported.

Unlike semivolatile organic compounds, the methods for detecting pesticides in water were more capable of detecting pesticides at or below the PALs (Figure 5). It is interesting to note that the analyte with the highest PAL, dimethoate, resulted in the lowest percentage of results being reported at or below the PAL. For the other four chemicals, at least 60% of the MDLs were at or below the respective PALs.

**Figure 5:** Percent of Pesticide MDL Results that Meet the PAL

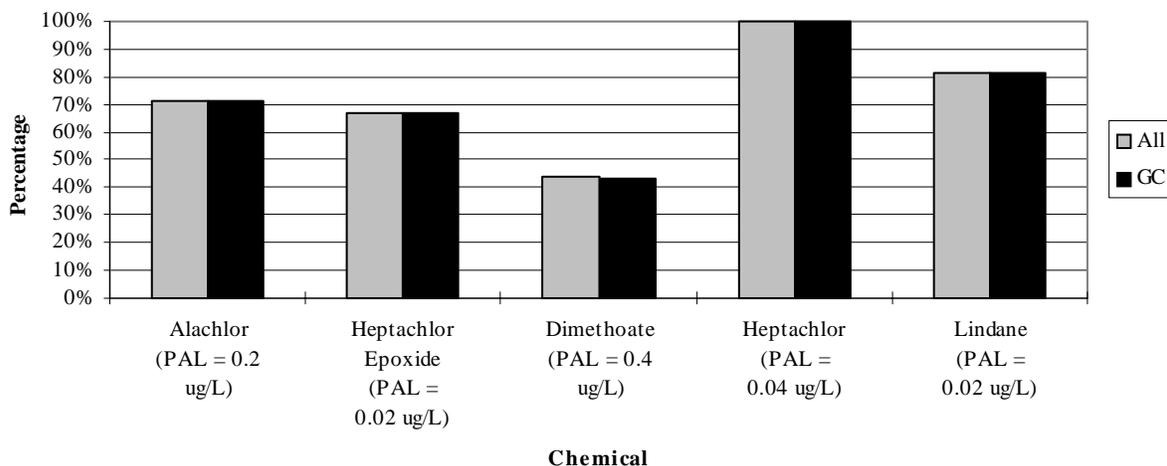


Table 4 summarizes laboratories pesticide capabilities. Each analyte has been subdivided by instrument type unless only one type of instrument was reported.

**Table 4:** MDL Quartiles for Pesticides

	25%	50%	75%	100%
<b>Alachlor</b> (all by GC)	0.034	0.079	0.232	1.3
<b>Heptachlor Epoxide</b> (all by GC)	0.003	0.0074	0.022	0.082
<b>DDT</b> (all instrument types)	0.0079	0.0144	0.03	0.093
GC	0.0077	0.137	0.03	0.093
<b>Dimethoate</b> (all instrument types)	0.23	0.377	0.774	0.99
GC	0.19	0.352	0.751	0.99
<b>Heptachlor</b> (all instrument types)	0.0049	0.009	0.017	0.038
GC	0.0048	0.009	0.016	0.038

	25%	50%	75%	100%
<b>Lindane</b> (all instrument types)	0.004	0.0069	0.015	0.06
GC	0.0036	0.0069	0.015	0.06
<b>Parathion</b> (all instrument types)	0.072	0.15	0.311	2.0
GC	0.063	0.15	0.16	0.69

\*All units are in µg/L

The following information contains a statistical analysis for each pesticide analyzed in this report. The information includes the ranges, mean, and medians for each pesticide.

### Alachlor

Although very few laboratories certified or registered by the State of Wisconsin perform tests for alachlor, it is a widely used nitrogen pesticide for broad leaf weed control in corn and soybean crops. A larger sample size would produce more conclusive results about this compound.

<u>Alachlor</u>	# of Results	Maximum	Minimum	Mean	Median	PAL
Total (all by GC)	7	1.3	0.0087	0.27	0.079	0.2

\*All units are in µg/L

### DDT

Although DDT has been banned in Wisconsin since 1970, it remains a threat to wildlife. DDT is very insoluble in water and is seldom detected by laboratories which test water and wastewater. Based on a sample size of 42 reported MDL results, 50% reported a MDL of less than 0.016 µg/L. The wildlife criteria (WC) for DDT is 0.000011 µg/L. None of the laboratories were able to detect DDT at this low health-based standard. Most laboratories use GC to determine DDT.

<u>DDT</u>	# of Results	Maximum	Minimum	Mean	Median	PAL	WC
Total	40	0.093	0.0009	0.0217	0.0144	NA	0.000011
GC	39	0.093	0.0009	0.0215	0.0137		
GC/MS	1	NA	NA	0.03	NA		

\*All units are in µg/L

### Dimethoate

Dimethoate is a phosphoric insecticide used on crops such as corn and soybeans; however, very few laboratories are certified or registered by the State to test for this compound. As with alachlor, a larger sample size would produce more conclusive results.

<u>Dimethoate</u>	# of Results	Maximum	Minimum	Mean	Median	PAL
Total	8	0.99	0.11	0.484	0.377	0.4
GC	6	0.99	0.11	0.471	0.352	
GC/MS	2	0.75	0.3	0.524	NA	

\*All units are in µg/L

## Heptachlor

All of the laboratories were capable of detecting heptachlor below the PAL.

<u>Heptachlor</u>	<u># of Results</u>	<u>Maximum</u>	<u>Minimum</u>	<u>Mean</u>	<u>Median</u>	<u>PAL</u>
Total	40	0.038	0.001	0.012	0.0092	0.04
GC	39	0.038	0.001	0.012	0.009	

\*All units are in µg/L

## Heptachlor Epoxide

Heptachlor epoxide is a degradation product of heptachlor. Heptachlor epoxide has a larger MDL range than heptachlor implying that this compound is more difficult to detect.

<u>Heptachlor Epoxide</u>	<u># of Results</u>	<u>Maximum</u>	<u>Minimum</u>	<u>Mean</u>	<u>Median</u>	<u>PAL</u>
Total (all by GC)	41	0.082	0.001	0.016	0.0074	0.02

\*All units are in µg/L

## Lindane

Lindane is one isomer of hexachlorobenzene. Currently available GC and GC/MS technologies are sufficiently sensitive to detect lindane at or below the PAL..

<u>Lindane</u>	<u># of Results</u>	<u>Maximum</u>	<u>Minimum</u>	<u>Mean</u>	<u>Median</u>	<u>PAL</u>
Total	41	0.06	0.001	0.0128	0.0069	0.02
GC	40	0.06	0.001	0.0127	0.0069	
GC/MS	1	NA	NA	0.02	NA	

\*All units are in µg/L

## Parathion

Parathion is an orthophosphate insecticide which does not have a PAL. It does have an acute toxicity criteria (ATC) for all aquatic life which is 0.057 µg/L. Three of the 10 results were below the ATC. Fifty percent (50%) of the reported MDLs were at or below 0.15 µg/L. It is difficult to draw more definitive conclusions from a sample size of ten MDL results.

<u>Parathion</u>	<u># of Results</u>	<u>Maximum</u>	<u>Minimum</u>	<u>Mean</u>	<u>Median</u>	<u>PAL</u>	<u>ATC</u>
Total	10	2	0.019	0.37	0.15	NA	0.057
GC	9	0.69	0.019	0.19	0.15		
GC/MS	1	NA	NA	2.0	NA		

\*All units are in µg/L

## Summary of Pesticide Results

Due to the large amount of agriculture in Wisconsin, accurate quantitation of trace levels of pesticides in surface and groundwater is important. The current technologies do an average job of detecting these compounds at low levels. With the limited number of responses to the survey for pesticides, it is difficult to draw conclusions about current analytical capabilities.

### Polynuclear Aromatic Hydrocarbons (PAHs)

The only PAH that is on the Detection Reporting Requirement list is benzo(a)pyrene. This compound is typically found near coal piles and oil and gas spills and is considered to be very carcinogenic.

Table 5 below summarizes the quartile information for the PAH benzo(a)pyrene. The two HPLC methods for detecting this compound result in substantially lower detection limits than GC or GC/MS.

**Table 5:** MDL Quartiles for PAHs

	25%	50%	75%	100%
<b>Benzo(a)pyrene</b>	0.029	0.435	1.33	6.7
GC/MS	0.6	1.21	2.2	6.7
GC	0.545	1.07	1.29	1.5
HPLC-UV	0.0181	0.045	0.065	0.22
HPLC-F	0.0066	0.017	0.03	0.07

\*All units are in  $\mu\text{g/L}$

Below are the ranges, means, and medians for benzo(a)pyrene. High-performance liquid chromatography-fluorescence (HPLC-F) is the only way to consistently detect benzo(a)pyrene at the PAL of 0.02  $\mu\text{g/L}$ . More than half of the MDL results are reported by GC/MS, but none of those results were at or below the PAL.

<b>Benzo(a)pyrene</b>	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>	<b>PAL</b>
Total	71	6.7	0.0017	0.92	0.435	0.02
GC/MS	41	6.7	0.026	1.51	1.24	
GC	3	1.5	0.205	0.86	1.07	
HPLC-UV	10	0.22	0.00765	0.066	0.045	
HPLC-F	17	0.07	0.0017	0.021	0.017	

\*All units are in  $\mu\text{g/L}$

### Polychlorinated Biphenyls (PCBs)

The final class of chemicals analyzed in this study are polychlorinated biphenyls (PCBs). Historically, PCBs have found widespread industrial uses including as an insulator in electrical transformers and as a dye solvent carrier in carbonless copy paper. Although the sale and production of PCBs has been banned in the United States since 1977 there are still transformers in use that contain PCB contaminated oil. The PCBs consist of a group of similar congeners that

differ in the number and position of chlorine atoms on benzene rings. PCBs are insoluble in water, but are found in sediment and bioaccumulate in the food chain. There are no PALs for the seven congeners evaluated in this study. However, there is a PCB human cancer criteria (HCC) of 0.003 ng/L that can be used for discussion purposes. None of the laboratories were able to detect PCBs down to that level.

Table 6 summarizes the PCB detection limit quartiles. The quartiles are similar for each congener.

**Table 6: MDL Quartiles for PCBs**

	<b>25%</b>	<b>50%</b>	<b>75%</b>	<b>100%</b>
<b>Aroclor 1016 GC</b>	0.054	0.145	0.255	0.9
<b>Aroclor 1221 GC</b>	0.096	0.167	0.394	1.02
<b>Aroclor 1232 GC</b>	0.088	0.164	0.293	0.71
<b>Aroclor 1242 GC</b>	0.119	0.19	0.325	0.83
<b>Aroclor 1248 GC</b>	0.057	0.182	0.259	0.86
<b>Aroclor 1254 GC</b>	0.055	0.114	0.197	0.81
<b>Aroclor 1260 GC</b>	0.07	0.12	0.223	0.68

\*All units are in µg/L

A summary of the ranges, means, and medians for the PCBs is listed below in Table 7

**Table 7: PCB Summary Statistics**

	<b># of Results</b>	<b>Maximum</b>	<b>Minimum</b>	<b>Mean</b>	<b>Median</b>
<b>Aroclor 1016</b>	46	0.9	0.008	0.186	0.145
<b>Aroclor 1221</b>	39	1.02	0.0175	0.247	0.167
<b>Aroclor 1232</b>	39	0.71	0.018	0.222	0.164
<b>Aroclor 1242</b>	47	0.83	0.01	0.224	0.19
<b>Aroclor 1248</b>	48	0.86	0.0004	0.2	0.182
<b>Aroclor 1254</b>	49	0.806	0.0206	0.16	0.114
<b>Aroclor 1260</b>	52	0.68	0.0071	0.167	0.12

\*All units are in µg/L

\*\*All results by GC

## CONCLUSIONS

Detection limits vary considerably, both between laboratories and between procedures. Different analytical technologies have different abilities to detect chemicals of concern at low levels. From the information gathered for this report, several important conclusions can be made about the detection limit capabilities of Wisconsin certified and registered laboratories:

- ◆ Of the 33 compounds in this study, 14 of them can reasonably be detected in a clean water matrix at or near levels of concern. They include:
  - ◆ Cadmium
  - ◆ Hexavalent Chromium
  - ◆ Lead
  - ◆ Mercury
  - ◆ 1,1,2-Trichloroethane
  - ◆ Bromomethane
  - ◆ Chloroform
  - ◆ Methylene Chloride
  - ◆ MTBE
  - ◆ Alachlor
  - ◆ Heptachlor Epoxide
  - ◆ Dimethoate
  - ◆ Heptachlor
  - ◆ Lindane
- ◆ Of the 33 compounds in this study, it is possible to reliably quantitate within one order of magnitude 6 compounds. They include:
  - ◆ Thallium
  - ◆ 1,3-Dichloropropene (cis) and 1,3-Dichloropropene (trans)
  - ◆ Chloromethane
  - ◆ Vinyl Chloride
  - ◆ Di(2-ethylhexyl)phthalate
  - ◆ Parathion
- ◆ Of the 33 compounds in this study, improvements in analytical capability or alternate methodologies are necessary to detect 14 compounds at or near the level of concern. They include:
  - ◆ 1,1,2,2-Tetrachloroethane
  - ◆ 1,3-Dichloropropene (cis & trans)
  - ◆ 2,4-Dinitrotoluene
  - ◆ 2,6-Dinitrotoluene
  - ◆ Pentachlorophenol
  - ◆ DDT
  - ◆ Benzo(a)pyrene
  - ◆ PCB Aroclors (1016, 1221, 1232, 1242, 1248, 1254, 1260)
- ◆ 26% of the reported MDLs could not be used. The following reasons are of most concern:
  - ◆ Spiking replicate samples either too high or too low.

- ♦ Miscalculating the MDL, either by using the wrong Student's t-value or by substituting the sample standard deviation with the population standard deviation.
- ♦ Using less than 7 replicates for the determination.
- ♦ Only 17% of the laboratories reported completely usable data.
- ♦ The detection limits for all compounds vary by at least one order of magnitude.
- ♦ To detect metals at the PAL, ICP/MS and GFAA consistently produced the best results.
- ♦ For volatile organic compounds, when both GC and GC/MS are used, neither technique is more consistent at producing low MDLs.
- ♦ Both GC and GC/MS are capable of consistently detecting volatile organic compounds at the PAL.
- ♦ Current instrumentation is not capable of detecting the low semivolatile PALs.
- ♦ HPLC-F is the only technique that can consistently detect benzo(a)pyrene at the PAL.
- ♦ GC is capable of detecting PCBs below part per billion (ppb) levels.

### **ACKNOWLEDGEMENTS**

I would like to thank all of the laboratories in the Laboratory Certification Program that submitted data for this study. I would also like to thank the Laboratory Certification Staff and Paul Rasmussen for all of their help.

## REFERENCES

- Definition and Procedure for Determination of the Method Detection Limit. Revision 1.11.  
Appendix B to Part 136. Federal Register, 49 FR 43430 (10/26/84), 50 FR 694 (1/4/85),  
and 51 FR (6/30/86).
- Draper, W.M. ET AL. Detection Limits of Organic Contaminants in Drinking Water. *Journal  
AWWA*, 90:6:82 (June 1998).
- Wisconsin Department of Natural Resources, "Analytical Detection Limit Guidance and  
Laboratory Guide for Determining Method Detection Limits", PUBL-TS-056-96, April  
1996.

## APPENDIX A

---

### *DETECTION REPORTING REQUIREMENT*

---

#### 1. INORGANICS

##### Metals

Antimony  
Beryllium  
Cadmium  
Lead  
Thallium  
Mercury  
Chromium (Hexavalent)

#### 2. ORGANICS

##### Acids/Phenols

Pentachlorophenol (PCP)

##### Benzidines

Benzidine

##### Haloethers

Bis(chloromethyl)ether

##### Nitroaromatics

2,4-Dinitrotoluene  
2,6-Dinitrotoluene

##### Polynuclear Aromatic

##### Hydrocarbons

Benzo(a)pyrene

#### 2. ORGANICS

##### Phthalates & Adipates

Di(2-ethylhexyl)phthalate

##### Nonpurgeable Chlorinated

##### Hydrocarbons

Hexachlorobenzene

##### Dioxins/Furans

Dioxin

##### PCBs

Polychlorinated biphenyls

##### Chlorinated Pesticides

DDT and Metabolites  
Heptachlor  
Heptachlor epoxide  
Lindane  
Toxaphene

##### Carbamate Pesticides

Aldicarb

##### Nitrogen Pesticides

Alachlor  
Dimethoate  
Parathion  
Trifluralin

#### 2. ORGANICS

##### Volatiles

1,1,2,2-Tetrachloroethane  
1,1,2-Trichloroethane  
1,3-Dichloropropene (cis/trans)  
Bromodichloromethane  
Bromoform  
Bromomethane  
Chloroform  
Chloromethane  
Methyl tert-butyl ether (MTBE)  
Methylene Chloride  
Vinyl Chloride  
Dibromochloropropane (DBCP)  
Ethylene dibromide (EDB)

## APPENDIX B

### APPENDIX B TO PART 136—DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT— REVISION 1.11

#### *Definition*

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte.

#### *Scope and Application*

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific, and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

#### *Procedure*

1. Make an estimate of the detection limit using one of the following:
  - (a) The concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5.
  - (b) The concentration equivalent of three times the standard deviation of replicate instrumental measurements of the analyte in reagent water.
  - (c) That region of the standard curve where there is a significant change in sensitivity, i.e., a break in the slope of the standard curve.
  - (d) Instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the initial estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferant concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferant). The interferant concentration is presupposed to be normally distributed in representative samples of a give matrix.
3.
  - (a) If the MDL is to be determined in reagent (blank) water, prepare a laboratory standard (analyte in reagent water) at a concentration which is at least equal to or in the same concentration range as the estimated detection limit. (Recommend between 1 and 5 times the estimated detection limit.) Proceed to Step 4.
  - (b) If the MDL, is to be determined in another sample matrix, analyze the sample. If the measured level of the analyte is in the recommended range of one to five times the estimated detection limit, proceed to Step 4.

If the measured level of analyte is less than the estimated detection limit, add a known amount of analyte to bring the level of analyte between one and five times the estimated detection limit.

If the measured level of analyte is greater than five times the estimated detection limit, there are two options.

- (1) Obtain another sample with a lower level of analyte in the same matrix if possible.
  - (2) This sample may be used as is for determining the method detection limit if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance at lower analyte concentrations.
4.
    - (a) Take a minimum of seven aliquots of the sample to be used to calculate the method detection limit and process each through the entire analytical method. Make all computations according to the defined method with final results in the method reporting units. If a blank measurement is required to calculate the measured level of analyte, obtain a separate blank measurement for each sample aliquot analyzed. The average blank measurement is subtracted from the respective sample measurements.
    - (b) It may be economically and technically desirable to evaluate the estimated method detection limit before proceeding with 4a. This will: (1) Prevent repeating this entire procedure when the costs of analyses are high and (2) insure that the procedure is being conducted at the correct concentration. It is quite possible that an inflated MDL will be calculated from data obtained at many times the real MDL even though the level of analyte is less than five times the calculated method detection limit. To insure that the estimate of the method detection limit is a good estimate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower concentration of analyte will not result in significant lower method detection limit. Take two aliquots of the sample to be used to calculate the method detection limit and process each through the entire method, including blank measurements as described above in 4a. Evaluate these data:
      - (1) If these measurements indicate the sample is in desirable range for determination of the MDL, take five additional aliquots and proceed. Use all seven measurements for calculation of the MDL.
      - (2) If these measurements indicate the sample is not in correct range, reestimate the MDL, obtain new sample as in 3 and repeat either 4a or 4b.
  5. Calculate the variance ( $S^2$ ) and standard deviation (S) of the replicate measurements as follows:

$$S^2 = \frac{1}{n-1} \left[ \sum_{i=1}^n X_i^2 - \left( \sum_{i=1}^n X_i \right)^2 / n \right]$$

$$S = (S_2)^{1/2}$$

where:

$X_i$ ;  $i=1$  to  $n$ , are the analytical results in the final method reporting units obtained from the sample aliquots and  $S$  refers to the sum of the  $X$  values from  $i=1$  to  $n$ .

6. (a) Compute the MDL, as follows:

$$MDL = t_{(n-1, 1-\mu=0.99)} (S)$$

where:

MDL = the method detection limit

$t_{(n-1, 1-\mu=0.99)}$  = the students' t value appropriate for a 99% confidence level and a standard deviation estimate with  $n-1$  degrees of freedom. See Table.

$S$  = standard deviation of the replicate analyses.

(b) The 95% confidence interval estimates for the MDL, derived in 6a are computed according to the following equations derived from percentiles of the chi square over degrees of freedom distribution ( $X^2/df$ ).

$$LCL = 0.64 MDL$$

$$UCL = 2.20 MDL$$

where: LCL and UCL are the lower and upper 95% confidence limits respectively based on seven aliquots.

7. Optional iterative procedure to verify the reasonableness of the estimate of the MDL and subsequent MDL determinations.

(a) If this is the initial attempt to compute MDL based on the estimate of MDL formulated MDL based on the estimate of MDL formulated in Step 1, take the MDL as calculated in Step 6, spike the matrix at this calculated MDL and proceed through the procedure starting with Step 4.

(b) If this is the second or later iteration of the MDL calculation, use  $S^2$  from the current MDL calculation and  $S^2$  from the previous MDL calculation to compute the F-ratio. The F-ratio is calculated by substituting the larger  $S^2$  into the numerator  $S^2_A$  and the other into the denominator  $S^2_B$ . The computed F-ratio is then compared with the F-ratio found in the table which is 3.05 as follows: if  $S^2_A/S^2_B < 3.05$ , then compute the pooled standard deviation by the following equation:

$$S_{pooled} = \left[ \frac{6(S^2)_A + 6(S^2)_B}{12} \right]^{1/2}$$

If  $S^2_A/S^2_B > 3.05$ , respoke at the most recent calculated MDL and process the samples through the procedure starting with Step 4. If the most recent calculated MDL does not permit qualitative identification when samples are spiked at that level, report the MDL as a concentration between the current and previous MDL which permits qualitative identification.

(c) Use the  $S_{pooled}$  as calculated in 7b to compute the final MDL according to the following equation:

$$MDL = 2.681(S_{pooled})$$

where 2.681 is equal to  $t_{(12, 1-\mu=0.99)}$ .

(d) The 95% confidence limits for MDL derived in 7c are computed according to the following equations derived from percentiles of the chi squared over degrees of freedom distribution.

$$LCL = 0.72 MDL$$

$$UCL = 1.65 MDL$$

where LCL and UCL are the lower and upper 95% confidence limits respectively based on 14 aliquots.

TABLES OF STUDENTS' t VALUES AT THE 99 PERCENT CONFIDENCE LEVEL

Number of replicates	Degrees of freedom (n-1)	$t_{(n-1, .99)}$
7 .....	6	3.143

8 .....	7	2.998
9 .....	8	2.896
10 .....	9	2.821
11 .....	10	2.764
16 .....	15	2.002
21 .....	20	2.528
26 .....	25	2.485
31 .....	30	2.457
61 .....	60	2.390
¥ .....	¥	2.326

*Reporting*

The analytical method used must be specifically identified by number of title and the MDL for each analyte expressed in the appropriate method reporting units. If the analytical method permits options which affect the method detection limit, these conditions must be specified with the MDL value. The sample matrix used to determine the MDL must also be identified with MDL value. Report the mean analyte level with the MDL and indicate if the MDL procedure was iterated. If a laboratory standard or a sample that contained a known amount analyte was used for this determination, also report the mean recovery.

If the level of analyte in the sample was below the determined MDL or exceeds 10 times the MDL of the analyte in reagent water, do not report a value for the MDL.

[49 FR 43430, Oct. 265, 1984; 50 FR 694, 696, Jan. 4 1985, as amended at 51 FR 23703, June 30, 1986]

*Adapted from the Code of Federal Regulations by the Wisconsin Department of Natural Resources*

## **APPENDIX C**

Appendix C contains a sample copy of the request letter and a blank spreadsheet that were sent to the laboratories that participated in the study.



**State of Wisconsin \ DEPARTMENT OF NATURAL RESOURCES**

Box 7921  
101 South Webster Street  
Madison, Wisconsin 53707-7921  
TELEPHONE 608-266-2621  
FAX 608-267-3579  
TDD 608-267-6897

Tommy G. Thompson, Governor  
George E. Meyer, Secretary

1/13/98

FID

SUBJECT: Low Level Detection Reporting Requirement Information Request

Dear

Section NR 149.11(5) and NR 149.15 Wis. Adm. Code, require certified or registered laboratories to have determined their limit of detection (LOD) and limit of quantitation (LOQ) for substances on the Detection Reporting Requirement list by January 1, 1997. **Consequently, in accordance with section NR 149.06(3) of the Laboratory Certification code, we are requiring that all laboratories currently certified or registered for any of the substances on the list submit their LOD and LOQ for those substances in a water matrix.**

The substances on the list which your laboratory is currently certified or registered for are listed below. You will need to submit both an LOD and LOQ for these substances. In addition, your laboratory must report 1) the analytical method used, 2) how the LOD and LOQ were calculated and 3) any analytical judgment or reasoning used to adjust or average the values. We strongly encourage the use of the enclosed diskette, which contains an electronic spreadsheet, to submit this information, but will accept paper reports if your lab cannot use it. Simply open the file (a:\lodreqst.wq1) in your spreadsheet program (Excel, QuattroPro, Lotus 123, etc.) and fill out the appropriate sections for the analytes listed in the table below. Save the changes to the same 3.5" disk and mail it using the enclosed disk mailer.

Category #	Group	Analytes
08	Metal	Cadmium
08	Metal	Lead
08	Metal	Mercury
08	Metal	Thallium
10	Volatile	1,1,2,2-Tetrachloroethane
10	Volatile	Chloroform
10	Volatile	Methylene Chloride
10	Volatile	Vinyl Chloride
11	Acid Phenol	Pentachlorophenol by GC
13	PAH	Benzo(a)pyrene by HPLC
15	Petro. Volatile	Methyl tert-butyl ether (MTBE)
18	SDWA Metal	Beryllium in Drinking Water
18	SDWA Metal	Cadmium in Drinking Water
18	SDWA Metal	Lead in Drinking Water

**All data must be received by the Laboratory Certification Program within 60 days of the date of this letter.**

Please contact either Mike Kvitrud at (608) 261-8459 or Jeff Ripp at (608) 267-0579 of my staff if you have any questions.

Sincerely,

John R. Sullivan, Chief  
Analytical and Statistical Services  
Bureau of Integrated Science Services

