



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MAR 18 1994

OFFICE OF
WATER

Dear Colleague:

EPA's Office of Wastewater Enforcement and Compliance (OWEC) formed a workgroup in 1991 to address the issue of implementing and enforcing water quality-based effluent limits (WQBELs) set below analytical detection/quantitation levels. Members included representatives from EPA Headquarters, Regions, and States (attachment 1). The purpose of this letter is to transmit the product of that group, the draft "National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-based Effluent Limitations Set Below Analytical Detection/Quantitation Levels" (attachment 2), for your review and comment.

Previous EPA guidance (Dioxin Strategy - 5/90 & TSD - 3/91) recommended that minimum levels (MLs) be used to evaluate compliance with WQBELs set below quantitation. This guidance goes a step further and makes recommendations for calculating interim MLs when promulgated MLs for a particular analytical method do not yet exist, and for reporting results below quantitation. The purpose of this document is to encourage national consistency in this area by providing recommendations for addressing those WQBELs until analytical chemistry has advanced enough to measure to them.

The four major elements in this guidance are: 1) a permit limit is expressed as the calculated WQBEL; 2) the ML is used as the quantitation level and is included in the permit as a footnote to the WQBEL; 3) where a promulgated ML is not available, an "interim ML" is calculated using a factor of 3.18 times the method detection limit (MDL); and 4) analytical results below the ML are reported as "0."

The workgroup for this project includes representatives from EPA Headquarters, EPA Regions, EPA Office of Research and Development, and five States (FL, MD, NJ, TX & WI). The first working draft of this document was released to the workgroup and the Regions for review in December 1992. A draft was released to the same group in October 1993. The two major areas we received comments on were: how to develop interim MLs, and how to report analytical results below quantitation.

The rationale and justification for the major recommendations included in the document are as follows:



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1. Permit limits are expressed as the calculated WOBEL
 - This statement is in conformance with the Clean Water Act (CWA) and EPA regulations at 40 CFR 122.44(d) that require limits to be protective of water quality standards.
2. ML is used as the quantitation level and is included in the permit as a footnote to WOBEL
 - The Strategy for the Regulation of Discharges of PCDDs and PCDFs from Pulp and Paper Mills to Waters of the United States (May 21, 1990) recommends that the permit writer specify the ML as the compliance evaluation level in permits that limit dioxin.
 - March 1991, EPA expanded its guidance on quantitation levels in the Technical Support Document for Water Quality-based Toxics Control to include all other pollutants.
 - The ML is a concept originated by EPA's Office of Water Engineering and Analysis Division in developing the 1600 series analytical methods.
 - The ML is the concentration in a sample that is equivalent to the lowest calibration standard analyzed by a specific analytical procedure.
 - MLs were developed to cope with the high level of variability among laboratories, analytes, and matrices when developing MDLs.
3. Where promulgated MLs are not available, an "interim ML" is calculated by multiplying 3.18 times the MDL.

MDL Component of Interim ML:

- The MDL is the cornerstone of the ML. The MDL has withstood court challenges and has generally been accepted by the regulated community. It is also defined in EPA regulations at 40 CFR Part 136, Appendix B.
- Resources are not available at this time to derive a new endpoint for the methods.
- MDLs are being developed for metals, and MDLs are not too expensive to generate.

Factor of 3.18:

- The relationship between the ML and MDL varies between 2.7 - 5.0, depending on the analyte. Multiple laboratory confirmation indicates that MLs are closer to 2.7 - 3.3 times the MDL.

- The factor of 3.18 is scientifically based, consistent and documented by the American Chemical Society (ACS) and the International Union of Pure and Applied Chemistry (IUPAC) for a limit of quantitation.
 - Multiplying 3.18 times the MDL contains the practical procedures necessary for calibrating analytical instruments and making environmental measurements.
 - The EPA Office of Water Analytical Methods Staff used this factor in deriving MLs for the 1600 series methods.
 - The development of interim MLs should be based on the same principles as the MLs. It should contain the operational procedure of the MDL. A factor of 3.18 times the MDL should be applied in order to derive interim MLs.
 - We recommend that 3.18 be used until a promulgated factor is derived, additional MLs are derived, or the scientific basis of 3.18 changes.
4. Analytical results which fall below the ML should be reported as "0."
- Defensible compliance tool: This approach avoids taking an enforcement action based on results falling in a region of uncertainty (below the ML). Where the analytical value is at or above the ML (i.e., non-zero) it provides certainty that a violation has indeed occurred. (This approach is successfully being used by Region VI for dioxin limits.)
 - Will result in consistency of reporting values below quantitation and calculating monthly averages.
 - Easy and cost effective to implement. Requires no change to reporting or tracking systems (e.g. PCS).
 - The majority of commenters on October 1993 draft favored the use of zero.

The recommendations presented in this guidance will not satisfy everyone's concerns, however, they are based on current regulations, science, and policy and they are defensible. Please keep in mind that this document is guidance only and it does not offer a permanent solution to the issue of implementing and enforcing WQBELS below quantitation. The approach presented is an interim solution and, as science and technology in this area evolves, it will need to be revised.

Please send your comments to Jackie Romney (mail code: 4203) or Kathy Smith (4202) of my staff by Friday, April 29, 1994. At this time, we are also sending the document for review by EPA Regions, States, workgroup members, and other external groups. We will consider all comments received by April 29 and expect to have a final document in June 1994.

Sincerely yours,

A handwritten signature in black ink, appearing to read "Michael B. Cook". The signature is written in a cursive, slightly slanted style.

Michael B. Cook
Director
Office of Wastewater Enforcement
and Compliance

Attachment

DRAFT

MARCH 22, 1994

**NATIONAL GUIDANCE FOR THE
PERMITTING, MONITORING, AND ENFORCEMENT OF
WATER QUALITY-BASED EFFLUENT LIMITATIONS
SET BELOW ANALYTICAL DETECTION/QUANTITATION LEVELS**

I. PURPOSE

Regions and States have expressed a need for guidance regarding the implementation and enforcement of water quality-based effluent limitations (WQBELs) set below analytical detection levels. The problem is that science has not kept pace with policy in this area. The purpose of this document is to provide interim guidance until analytical chemistry can measure such low levels.

This guidance contains interim techniques for establishing compliance at the WQBEL. Existing EPA guidance and this guidance recommend that minimum levels (MLs) be used to make a compliance determination. The ML is a concept originated by the Office of Water, Engineering and Analysis Division, in developing the 1600 series methods. Currently, methods 1624 and 1625 are the only EPA methods promulgated under Section 304(h) that have MLs. However, other 1600 series methods have been or are presently being proposed and contain MLs. The most notable proposed method is Method 1613, for chlorinated dioxins and furans. Use of this method has been required for permit compliance monitoring since its proposal in February 1991. EPA's 600 series methods contain method detection limits (MDLs), not MLs. This document provides guidance for developing interim MLs from MDLs in those instances in which MLs do not exist. These interim MLs are intended to be temporary--to be used only until minimum levels are promulgated. This approach addresses the immediate need to provide interim quantitation levels to determine compliance with WQBELs.

Alone, this guidance does not adequately address values below analytical detection. Progress in advancing technology must continue, including development of minimum levels, new analytical methods with lower detection limits, and better quality assurance/quality control techniques. This progress will require prioritization and commitment of resources. Only with that commitment and the subsequent advancement of technology will we truly achieve national consistency in addressing WQBELs below detection levels. As science and technology in this area evolves, this document will need to be revised.

The spirit behind this guidance is that even in the absence of more sensitive promulgated methods, laboratories should do their best to measure as closely as possible to WQBELs. Since as an agency, our ultimate goal is to protect the Nation's surface

waters, and eventually achieve the goal of "no discharge of toxics in toxic amounts," we recommend that every effort be made to use the best available techniques for measuring these low levels.

This document was developed using current information and is EPA's approach to using 40 CFR Part 136 and other analytical methods to achieve WQBELs set below analytical detection levels. In addition, this document represents guidance. As such, it is a general statement of policy. It does not establish or affect legal rights or obligations. It does not establish a binding norm and is not finally determinative of the issues addressed. Agency decisions in any particular case will be made by applying the law and regulations on the basis of specific facts and actual action.

In some cases, this guidance reiterates statutory or regulatory requirements and provides citations to the relevant statutory or regulatory provisions. Otherwise, this guidance makes recommendations only. These recommendations are not accompanied by statutory or regulatory citations.

The recommendations in this document will not be appropriate in all situations. It is the responsibility of the regulatory authority to use all available information to assess the situation and then to implement additional or more stringent requirements, as necessary, to protect aquatic life and human health from the impacts of pollutants being discharged in amounts below analytical detection.

II. EXECUTIVE SUMMARY

As a result of the increasing use of WQBELs in National Pollutant Discharge Elimination System (NPDES) permits, a significant number of permits now contain limits that fall below the detection/quantification capability of current analytical technology for certain analytes. A major concern to permit writer, permittee, and enforcement authority is how to:

- Incorporate calculated limits below detection levels into permits
- Monitor effluent and require that analytical methods used in effluent monitoring measure the lowest accurately quantifiable level possible
- Report analytical results when data fall below detection levels
- Determine compliance with limits that fall below detection levels

- Track analytical results
- Facilitate advances in technology

The EPA Offices of Wastewater Enforcement and Compliance (OWEC) and Office of Science and Technology (OST) have developed this guidance to address these concerns.

This document includes the five following basic elements:

- WQBELs are to be imposed as NPDES permit limits when necessary to protect the designated uses of the receiving waters, even when the WQBEL is less than the analytical detection level.
- The quantification level to be used in analyzing samples and reporting the results is the ML. Guidance for incorporating MLs into NPDES permits, developing MLs where they are not currently available, and translating analytical values below the ML into the discharge monitoring report (DMR) data for compliance evaluations is provided in this document.
- The existing analytical data reporting and tracking mechanisms, the DMR and permit compliance system (PCS), respectively, will continue to be used with no changes to their structures. This document provides guidance and examples for reporting analytical values that are at or below the ML. The ML has an indirect role in compliance evaluations. The ML is the threshold for recording the analytical data that will then be used to calculate and report summary information on the DMR.
- Enforcement criteria are consistent with those set forth in the EMS guidelines, and compliance evaluations continue to be made directly between the DMR information and the permit limit (which is the WQBEL in cases where water quality is the most stringent limitation).
- Important permitting and compliance issues, such as addressing matrix interferences, using internal outfalls in permit writing, driving technology to achieve lower detection levels, specifying analytical protocols in NPDES permits, and determining the ability of laboratories to achieve specified MLs are also addressed in this guidance.

III. BACKGROUND

At present, EPA Regions and NPDES-authorized States use a wide variety of approaches for establishing water quality-based permit limits, including the imposition of MDLs, Practical

Quantification Levels (PQLs), Minimum Quantification Levels (MQLs), Quantification Levels (QLs), MLs, Practical Detection Levels (PDLs), Limits of Detection (LODs), and/or setting levels as an unspecified non-detect. While the rationale supporting these approaches may differ, the basis for each is shared, that is, the need to establish a level in the permit that can be measured for evaluating compliance.

The Office of Water issued *Final Guidance on Section 304(1): Listing and Permitting of Pulp and Paper Mills* (March 15, 1989) (hereinafter the 304(1) Guidance) recommending that where calculated WQBELs are less than the detection level for the specified analytical method, the calculated WQBEL should be included as a requirement of the permit. This guidance is in conformance with the Clean Water Act (CWA) and EPA regulations at 40 CFR 122.44(d) that require limits to be protective of water quality standards. This guidance also stated that the detection level of the analytical method should be the threshold for compliance/noncompliance determinations. The detection level issue was also raised in the *Strategy for the Regulation of Discharges of PCDDs and PCDFs from Pulp and Paper Mills to Waters of the United States* (May 21, 1990) (hereinafter the Dioxin Strategy). This modified the March 15, 1989 guidance by recommending that the permit writer specify the ML as the compliance evaluation level in permits that limit dioxin.

In March 1991, EPA further expanded its guidance on detection levels in the *Technical Support Document for Water Quality-based Toxics Control* (hereinafter the TSD). On page 111 of the TSD, EPA recommended applying the concepts contained in the Dioxin Strategy to analytical detection levels for all pollutants. Despite the support for the use of MLs, obstacles exist that prevent their wider use. These obstacles include the availability of MLs, the historical misuse of detection and quantification levels, and the inconsistent definitions representing these levels.

IV. INTRODUCTION

This guidance outlines the responsibilities of both the permittee and the permitting authority to ensure accurate monitoring, reporting, and tracking as analytical technology advances to meet lower detection levels necessary to protect water quality. Specific guidance is included to assist the permit writer and compliance officer in writing and enforcing permits with WQBELs that fall below detection levels.

This guidance is designed to provide an interim way to deal with analytical results that fall below detection until advances in technology are made that allow lower detection levels and thus increase the ability to ensure protection of the Nation's waters, as well as to encourage source reduction that will limit the

discharge of the pollutants. Figure 1, which appears on the next page, demonstrates the problems created by WQBELs that fall below detection levels. It depicts how future technical advances in analytical chemistry detection and quantification levels can resolve the problems created by WQBELs that are below these levels.

This document was developed with significant input from the Regions, States, and other EPA Offices. EPA's Office of Research and Development (ORD) is currently conducting a method validation study for trace metals by inductively-coupled plasma (ICP) spectroscopy. That study is designed to address issues related to method detection limits. ORD's definitive study should produce an appropriate data base for defining and evaluating detection limits and quantification levels as well as state-of-the-art MDLs and MLs for toxic metals.

This guidance is consistent with EPA's May 1990 Dioxin Strategy as well as other pertinent permitting and enforcement documentation (e.g., Quarterly Noncompliance Report (QNCR) guidance, the TSD, and the Permit Compliance System (PCS) Policy Statement).

In summary, the goals of this guidance are: (1) to outline objectives for achieving consistency in establishing permit pollutant limitations for pollutants that are set below detection and quantification levels, taking into consideration the current capabilities and uncertainties of science and technology, and (2) to provide specific guidance on implementing the objectives of this approach in a rational and defensible manner.

This document is organized in four sections: (1) Key Definitions, (2) Permitting Principles and Strategy, (3) Compliance Monitoring and Enforcement Principles and Strategy, and (4) Additional Permitting and Enforcement Strategy Issues. The appendices provide: (1) a list of available quantitation/detection levels taken from 40 CFR Part 136, (2) procedures for reviewing discharge-specific MDLs, (3) recommended permit writing boilerplate language, (4) recommended permittee procedures for reporting, (5) compliance evaluations in accordance with this guidance, and (6) recommended permit writer procedures for calculating WQBELs at internal outfalls.

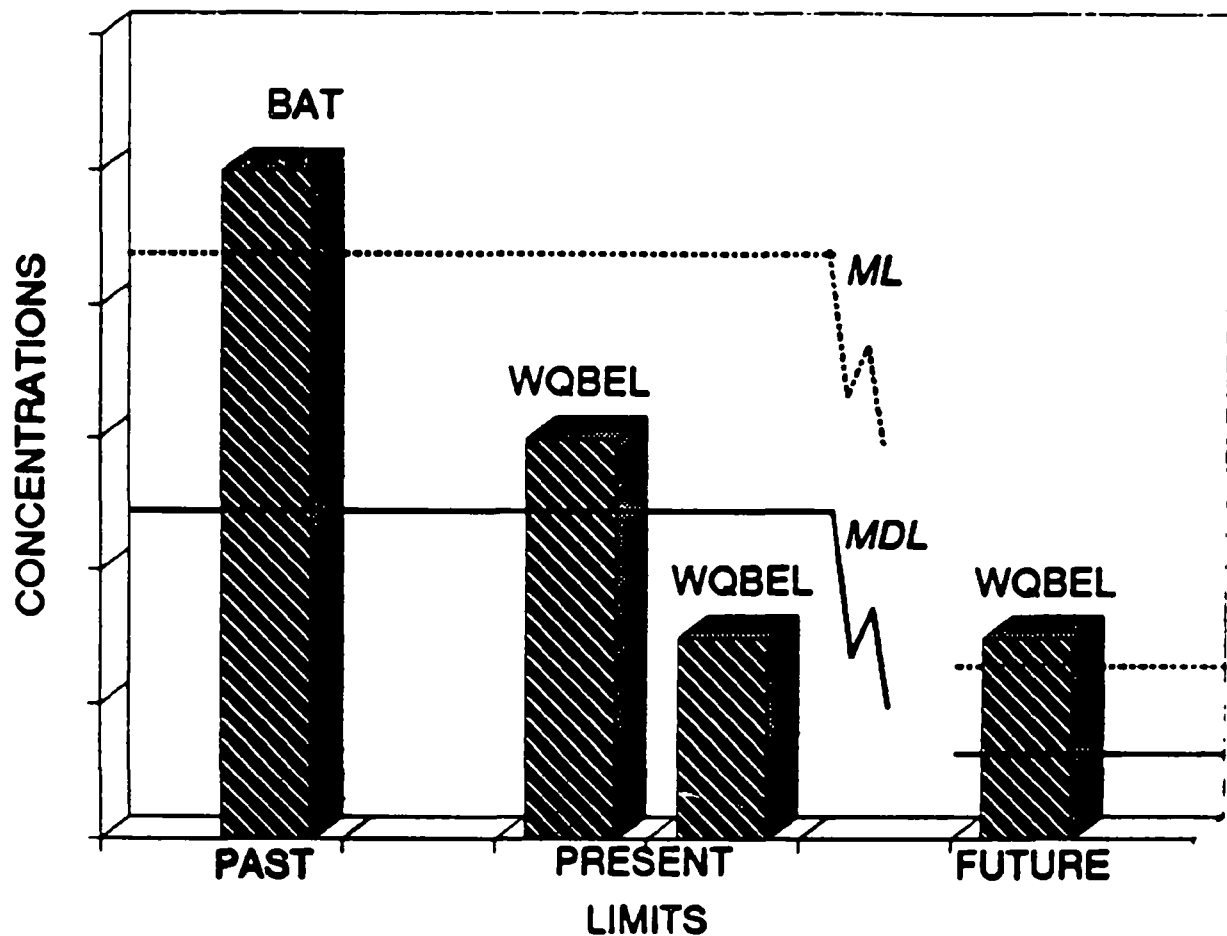
V. KEY DEFINITIONS

The following terms are used in this document; they are consistent with EPA regulations and existing EPA guidance.

Detection Limit (DL)

The lowest concentration or amount of the target analyte that can be determined to be different from zero by a single

**FIGURE 1
DETECTION/QUANTIFICATION OF
WQBELS**



Best Available Technology limits, by definition, are set at concentrations that are quantifiable. Water Quality-based Effluent Limitations, to be protective, are often set below the Minimum Level and sometimes below the Method Detection Level. In the future, as analytical chemistry improves, the MLs and MDLs will become more sensitive and approach the lower WQBEL.

measurement at a stated level of probability.

Interim Minimum Level (Interim ML)

The interim ML is calculated when a method-specified ML does not exist. It is equal to 3.18 times the method-specified MDL rounded to the nearest multiple of 1, 2, 5, 10, 20, 50, etc. The interim ML should be used until an analytically developed ML can be established.

Method Detection Limit (MDL)

The minimum concentration of an analyte that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero as determined by a specific laboratory method (40 CFR Part 136). [An MDL is usually determined in reagent water, but a discharge-specific MDL is sometimes developed using effluent. The use of reagent water is for two purposes: (1) reagent water as a reference matrix is available to all laboratories who can then reproduce the work, and (2) it is necessary to determine the MDL at very low concentrations of analyte. It may not be possible to find concentrations this low in a wastewater effluent.] The procedure for determination of an MDL is in 40 CFR Part 136, Appendix B.

Minimum Level (ML)

The concentration at which the entire analytical system must give a recognizable signal and acceptable calibration point. The ML is the concentration in a sample that is equivalent to the concentration of the lowest calibration standard analyzed by a specific analytical procedure, assuming that all the method-specified sample weights, volumes, and processing steps have been followed. Quantifying measurements below the ML requires extrapolation of the calibration relationship below the range of data used to establish the calibration. Such an extrapolation is not a preferred practice and leads to greater uncertainty in the quantitative result.

Minimum Quantification Level (MQL)

An MQL is a concentration identified by EPA Region 6 based on a thorough evaluation of current literature and analytical capabilities to be used until more analytically developed MLs can be established.

Practical Quantification Level (PQL)

A quantification limit that is approximately 3 to 10 times the MDL and that is greater than the concentration of a

chemical that can be detected by current laboratory methods, thereby providing a less demanding, "practically-based" analytical limit. This definition of the PQL is different from the PQL defined by the Office of Solid Waste, and published in earlier versions of SW-846 methods. The PQL is not used in this guidance.

Quantification Level (QL)

A measurement of the concentration of a chemical obtained by using a specified laboratory procedure, at a specified concentration above the detection level. Examples are the ML and PQL.

Water Quality-Based Effluent Limitation (WQBEL)

The limitation developed in a wastewater discharge permit to control all pollutants that will cause, have the reasonable potential to cause, or contribute to an excursion above any State or Federal water quality standard or criteria. WQBELs are imposed in NPDES permits when it has been determined that more stringent limits than technology-based effluent guidelines must be applied to a discharge to protect the designated use of the receiving waters.

The Best Available Technology Economically Achievable, by definition, sets limits at concentrations that are quantifiable. WQBELs, to be protective, are often set below the ML and sometimes below the MDL. As analytical chemistry technologies improve, MLs and MDLs are likely to be lowered such that measurement of the WQBEL becomes possible.

Summary of Concepts:

LESS THAN (<) MDL	Not Detected
GREATER THAN OR EQUAL TO (≥) MDL BUT LESS THAN (<) ML	Not Quantified
GREATER THAN OR EQUAL TO (≥) ML	Quantified (Numerical Result Reported)

VI. PERMITTING PRINCIPLES AND STRATEGY FOR WATER QUALITY-BASED EFFLUENT LIMITS THAT FALL BELOW ANALYTICAL METHOD DETECTION LEVELS

A. Permitting Principles

This permitting strategy is based on the following principles:

- Principle I: Permit requirements must be protective of water quality.
- Principle II: Permits must be written to avoid ambiguity and ensure enforceability.
- Principle III: Permit requirements must support the achievement of the lowest accurately quantifiable level possible when WQBELs fall below detection levels.

B. Permitting Strategy

EPA's NPDES regulations at 40 CFR Part 122 state that permit limitations must reflect the most stringent of technology-based or water quality-based controls, or other standards required by the CWA. Once it has been determined that a WQBEL is needed to protect water quality, consideration must be given to the capability of available analytical chemistry to measure at the WQBEL. Permitting authorities must increasingly contend with enforcing WQBELs that fall below what can be measured using current analytical chemistry techniques.

Reasonable Potential (RP)

The first step in developing a water quality-based limit is to determine whether a limit is needed. Permitting authorities must determine whether a discharge causes, has the reasonable potential to cause, or contributes to an excursion above a water quality standard. The procedures used in making this determination are discussed in Chapter 3 of the TSD. When monitoring results are at levels above analytical quantification levels, they are easily compared to the water quality standard to determine reasonable potential.

However, when monitoring results are below analytical quantification levels, a decision must be made on how to interpret the data to determine RP. In this case, necessity for the reasonable potential procedure should be based on the likelihood that the pollutant is present in the discharge(s) resulting from operation of the facility. Once this determination is made, the following guidance offers recommendations on how to interpret data to make a reasonable potential analysis.

When determining reasonable potential, actual analytical results should be used whenever possible. When an analytical result is below the ML, the Agency recommends that the permit writer set this result equal to zero because the result is not quantifiable.

When the effluent data consist of non-quantifiable/non-detectable values, the regulatory authority should consider other

that limits be protective of water quality. The use of the ML as an analytical chemistry performance standard provides an unambiguous and rational means to demonstrate that the best chemistry available at the time of permit issuance is being used in conjunction with WQBELs that are below quantification levels.

The Agency is recommending the use of the ML when WQBELs are below analytical detection and quantification levels to address the problems associated with recording and reporting. EPA believes that the use of MLs encourages permittees to maintain the highest quality assurance/quality control (QA/QC) standards, as well as strict standard operating procedures, which, in turn, will ensure that the self-monitoring data reported to the permitting and enforcement authority will be as accurate as possible.

The ML should be included in a footnote to the WQBEL in the NPDES permit. These MLs are to be used as quantification levels for recording and reporting purposes and are not to be confused with the compliance level, which is the WQBEL. As part of this guidance, a summary of available quantification and detection levels has been provided in Appendix A. In the absence of promulgated MLs, interim MLs should be used. The basis for the interim ML is the MDL, and the procedure for calculating interim MLs follows on page 12.

EPA recognizes that not all analytical methods approved under 40 CFR Part 136 have MDLs or MLs and therefore recommends that permit writers explicitly require analyses in accordance with the most sensitive technique within those approved methods. The method improvement provisions in the quality control section of some methods (e.g., 40 CFR 136, Appendix A) allow the analyst to use more sensitive techniques than those given in the method. In addition, 40 CFR Parts 136.4 and 136.5 provide procedures for using alternate test procedures (ATPs) which may allow for a lower level of detection.

Permit writers should also require calibration of laboratory equipment with standards that include a concentration equivalent to the ML. The Agency believes that it is appropriate to specify the analytical method since specified MLs are based on a specific laboratory technique, and facilities must perform analyses in accordance with that technique or an analogous technique to achieve the ML. Additionally, since the ML is defined as equivalent to the lowest calibration standard, it is appropriate to specify that the ML be used as the lowest calibration standard.

The Agency recommends that reporting requirements in permits specify that actual analytical results be reported whenever possible. When analytical results are below the minimum level that can be quantified (i.e., below the ML or interim ML), the

Agency recommends reporting "zero." This recommendation provides a two-fold advantage: (1) it ensures a margin of relief to the permittee seeking to avoid false positives which lead to violations, and (2) in the cases where the analytical value is non-zero, it provides certainty to the compliance personnel that a violation has indeed occurred where such is noted on the DMR.

This recommendation will not satisfy everyone's concerns. Some people will interpret this approach to imply that EPA believes that there are no pollutants in results that fall below the ML. In the context of this guidance, zero is a numeric symbol selected by the Office of Wastewater Enforcement and Compliance to represent non-measurable data and thereby facilitate consistency in DMR calculations and reporting.

EPA recognizes this approach introduces some bias to the data and does not drive technology to achieve lower detection levels. In developing this guidance, a number of different approaches were considered. The use of zero was chosen because it is defensible and is successfully being used by the Agency to issue and enforce permits with dioxin limits, and because it can be implemented without changes to EPA monitoring and reporting systems. This approach is meant to be an interim solution which should be periodically re-evaluated and improved as improvements in technology occur.

EPA believes compliance with permit limitations that are derived from "no discharge" or "no detectable amounts" effluent limitations guidelines are to be determined by qualifying samples as less than the MDL. For these limitations, which are established to essentially prohibit any addition of a pollutant to the receiving water, the standard of compliance is set at the minimum level of detection as opposed to a level of quantitation (e.g., the ML). The application of the MDL in instances of no discharge or no detectable amounts limitations will provide assurance to the 99th percentile against a false positive. Permit limitations based on such effluent limitations should clearly establish the standard of compliance at the MDL in the fact sheet and state compliance with the no discharge standard will be established by reporting analytical results below the approved MDL as zero on the DMR.

This approach is required for situations where the discharge standard has been established to effectively prohibit any further addition of a specific pollutant to waters of the U.S. One example of this situation is at 40 CFR Part 423, the effluent limitations guidelines for the steam electric category. This effluent guideline has several limitations which establish a no discharge in detectable (not quantifiable) amounts, specifically the prohibition on the discharge of PCBs and priority pollutants other than chromium and zinc in chemicals added for cooling tower maintenance (see 40 CFR 423.13(a) and 423.13(d)(1)). Compliance

with permit limitations based on these effluent guidelines would be shown by analytical results demonstrating that there was no pollutant of concern in detectable amounts, i.e. at levels at or above the MDL. Results at or below the MDL would be reported as zero on the DMR.

Permits should require that the permittee provide information that will be needed when reissuing the permit. In support of permitting Principle II, EPA recommends that the permit writer require the permittee to report the achieved ML and the number of occurrences during the month when analytical results were below the ML (i.e., number reported as zero) in the comment field of the DMR form or on an attachment to the DMR form. This allows gathering of sufficient information for use in reasonable potential calculations, as well as for other uses.

EPA recommends that permits that have pollutant limits for aquatic life that are set below analytical detection levels include the requirement to perform whole effluent toxicity (WET) tests. WET testing provides the only mechanism available to measure the cumulative toxic effects of one or more pollutants and counteract the potentially misapplied "benefit of the doubt" provided to a facility by the translation of data less than the ML.

Additionally, EPA supports the use of other measures to protect water quality. For example, mercury being discharged in amounts below quantitation may be suspected of impacting the benthic community. In such situations, the regulatory authority should go beyond the recommendations in this guidance and require bioaccumulation or sediment studies, pollution reduction/prevention plans, or other measures to protect water quality.

As part of this guidance, EPA has provided, in Appendix C, boilerplate language that includes requirements for setting limitations and specifying monitoring and reporting.

Interim MLs

Basis for MLs:

Analytical data are characterized by many different terms. A true detection level connotes the lowest concentration that can be detected. The quantitation level connotes the lowest concentration that can be quantified reliably. This guidance uses the quantitation level as a threshold for compliance with water quality-based limits.

For purposes of this guidance, the use of the ML as the compliance level has been established. EPA's position that the ML is a valid scientific and regulatory concept is consistent

with the "May 1990 Dioxin Permitting Strategy" and the "1991 TSD".

The ML is defined as the lowest concentration that gives recognizable signals and an acceptable calibration point. It is the equivalent concentration of the lowest calibration standard analyzed by a specific analytical procedure, assuming that all the method-specified sample weights, volumes, and processing steps have been followed. MLs are analyte and method specific and are established during the development and validation of the method. The 1600 Series EPA methods are currently the only Agency methods that explicitly include MLs.

MDL Component:

An interim ML is needed when a promulgated ML is not available for a pollutant. The following discussion explains why the interim ML should be based on the MDL, and how it should be derived.

The MDL is a well-established part of the foundation of the NPDES program, as defined in 40 CFR Part 136. MDLs have withstood court challenges and are generally accepted by the regulated community. Attempting to use a level other than the MDL as the basis for determining the quantitation level would be resource intensive and would have extensive repercussions.

EPA's procedure for determining the MDL calls for making an initial estimate of the detection limit using one of the following: (1) the concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5, (2) the concentration equivalent to three times the standard deviation of replicate instrumental measurements of the analyte in reagent water, (3) 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, or (4) instrumental limitations. If the initial MDL is suspected of being too low or too high, the MDL procedure can be iterated to determine the reasonableness of the initial value and to arrive at a final value.

In the region of the MDL, the absolute variance of analytical measurements (measured as the standard deviation) remains approximately constant. Above the ML, the absolute variance increases with increasing concentration, whereas the relative variance (measured as the relative standard deviation; coefficient of variation) remains approximately constant (i.e., the variance is proportional to the concentration). Between the MDL and the ML, there is a region of transition from constant to proportional variance as the concentration increases. Because the variance is approximately constant in the region of the MDL, changes in test concentrations in this region will result in a constant MDL value. However, as the test concentration increases

significantly above the MDL, a point will be reached at which the calculated MDL will begin to rise. Because the ML is based on the MDL, the ML procedure requires iteration of the spiking and measurement processes until the calculated MDL is within a factor of 5 of the spike level. This iteration assures that the MDL, and therefore the ML, will not be overstated.

As the MDL is determined by the analyses of a series of replicate samples, its applicability to single sample analysis is open to question. The MDL may not take into account bias, analyst proficiency, inter-laboratory variability, matrix effects, and other considerations that affect analytical results. Furthermore, because the statistical derivation of the MDL is designed to minimize the occurrence of false negative results, it has been suggested that using the MDL as the compliance threshold may lead to unacceptable levels of false positive results, and thus potential permit violations.

MDL values determined in a clean matrix such as reagent water are useful indicators of a laboratory's capabilities in a clean matrix, but may not necessarily be achievable in other matrices, such as NPDES effluents. However, EPA's experience has shown that effluents from well-designed and well-operated "best available technology (BAT)" treatment systems behave much as reagent water in the analytical process, primarily because the concentrations of the analytes of interest and of interfering substances are reduced to undetectable or very low levels. Therefore, although there may be a few instances in which MDL values in reagent water do not reflect MDL values in NPDES effluents, the number of instances can be expected to be small. The procedure for determining the MDL and ML in this guidance can be applied to either reagent water, NPDES effluent, or other matrices to arrive at an ML that reflects the detection and quantitation levels that can be achieved under actual operating conditions.

If the MDL is set as a compliance threshold, any concentration above the MDL would be considered a violation when the permit limit was below the MDL. The uncertainty of measurements between zero and the ML, and the certainty of measurements at or above the ML, makes the MDL unreliable for compliance determinations. If the MDL does not offer the level of certainty needed to make a compliance determination, the question becomes, what level will offer a reasonable level of certainty?

Relationship Between Promulgated ML and the MDL

First, it is important to look at the definition and the nature of the Limit of Quantitations (LOQ) as defined by the American Chemical Society (ACS). The LOQ, as adopted by ACS and by the International Union of Pure and Applied Chemistry (IUPAC),

is a statistically based level that has been defined as the "level above which quantitative results may be obtained with a specified degree of confidence". The ACS recommends an LOQ set at 10 standard deviations above the average level of a well characterized blank. These 10 standard deviations correspond to an (estimated) quantitative uncertainty of ± 30 percent at a 99 percent confidence level.

In order to compare the ACS LOQ with the EPA ML, it is important to first understand the nature of the EPA MDL. As defined in Appendix of B to 40 CFR Part 136, the MDL is "the minimum concentration of a substance that can be ...measured and reported with 99 percent confidence that the analyte concentration is greater than zero". The MDL is statistically derived from data based on the analysis of at least seven replicate samples containing a known concentration of each analyte of interest. Specifically, the MDL is calculated by multiplying the standard deviation of the seven replicates by 3.14. The 3.14 value is the multiplier used for seven replicates according to the student's t-test.

The OW Office of Science and Technology (OST) currently uses the MDL to calculate the ML. OST has recently refined this approach by using a multiplier of 3.18 which reflects the 10 standard deviations above zero that is used by ACS and normalizes the ML to reflect the difference produced by the 3.14 multiplier used in MDL determinations. As a result, both the ML and the LOQ are statistically derived values that correspond to an estimated uncertainty of ± 30 percent at 99 percent confidence. The remaining difference between the ML and LOQ is that the ML is rounded to allow calibration at practical levels, as described below, and because rounding simplifies entries and compliance calculations on the DMR.

For the sake of being consistent with ACS guidelines for reporting results beyond the calibration range of the instrument, OST utilizes the ML as the lowest point on the calibration curve. Because calibration of instruments at exact numbers such as 4.86 or 13.9 is not practical, OST rounds the calculated ML to the nearest multiple of 1, 2, 5, 10, 20, 50, 100, 200, 500, etc. Rounding is done because it simplifies instrument calibrations and reduces the potential for error in the preparation of calibration solutions.

The above approach is the basis for developing the promulgated MLs and the same rationale was used to develop interim MLs.

Developing an Interim ML

In the absence of promulgated MLs and the definition of the MDL concept, EPA believes that interim ML values can be derived

most effectively as a multiple of the existing MDL value for a given analyte.

Thus, the interim ML should be developed by multiplying the published MDL for the analyte from a specific analytical method approved under Section 304(h) or previously approved for use by the permitting authority by 3.18, and rounding the calculated ML as explained above.

For metals, the soon-to-be-proposed MDLs will be used to calculate the MLs. When neither the ML nor the MDL is available, 3.18 times the best estimate of the detection level should be used. When a range is given instead of a detection level, the lower end of the range should be used.

EPA's rationale for selecting a factor of 3.18 is based on the following:

- The 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..." (40 CFR 136, Appendix B). The MDL is equal to 3.14 times the standard deviation of seven replicate measurements.
- The American Chemical Society has defined the Limit of Quantitation (LOQ) as the level at which a sample can be reasonably measured (quantified) at 10 standard deviations above the average blank measurement using graphical and statistical techniques. Since the MDL is equal to 3.14 standard deviations about the replicate measurements, dividing this into 10 provides a multiplier of 3.18 between the MDL and the calculated ML.
- The calculated ML is then rounded to 1, 2, 5, 10, 20, 50, etc. Rounding is consistent with the established scientific and mathematical principle of rounding a number after all calculations, not before.
- Rounding the result to the nearest whole number also makes the preparation of calibration standards a straight forward process, given that the standards are typically prepared by serial dilution of a stock solution.
- Similarly, rounding simplifies reporting results, as analytes that are not detected will be associated with a whole number value.

Proposed New Science for Deriving Detection and Quantitation Levels

The American Chemical Society (ACS), American Standard Testing Methods (ASTM), and EPA (Office Ground Water & Drinking Water) are currently developing an alternative approach for deriving detection and quantitation levels. The approach would go beyond the existing LODs and LOQs and would work toward reducing the false negatives and false positives around the detection and quantitation levels. This effort is in its formative stages and has not yet been peer reviewed or documented. Until an alternative approach is developed and documented, our guidance is consistent with the ACS's current recommendation to use a multiplier of 3.18 times the MDL to calculate a LOQ (which is equivalent to our interim ML). As science changes in this area, our guidance should be reviewed and revised as needed.

VII. COMPLIANCE MONITORING AND ENFORCEMENT PRINCIPLES AND STRATEGY FOR WATER QUALITY-BASED EFFLUENT LIMITATIONS BELOW ANALYTICAL METHOD DETECTION LEVELS

A. Enforcement Principles

This enforcement strategy is based on four principles:

- Principle I: Permittees are responsible for attaining and maintaining permit compliance and for the quality of the monitoring data they submit.
- Principle II: Enforcement authorities will evaluate self-monitoring data quality to ensure program integrity.
- Principle III: Enforcement authorities will assess compliance through discharger data reviews and confirm compliance through inspections, audits, and other independent monitoring or review activities.
- Principle IV: Enforcement authorities will enforce effluent limits, reporting and other requirements, and compliance schedules to ensure the protection of water quality.

B. Enforcement Strategy

When a facility's WQBEL is set below detection, the facility is in compliance with the limit when it has demonstrated that it is capable of measuring concentrations at the required ML using the designated analytical method (Principle I). To ensure the enforceability of WQBELs when analytical values are below the ML, and because the region below the ML is one of greater uncertainty

than the region at or above the ML, EPA recommends that values below the ML be represented as zero for determining maximums and averages for DMR submittal.

EPA recognizes that this approach is a compromise that introduces some bias into the data, and does not ensure compliance with WQBELs. There is an indirect relationship between the ML and the compliance level. The WQBEL is used to determine compliance; MLs are used as the analytical measure by which a laboratory determines the concentration of an analyte in a given sample. When the analysis of a sample indicates that the analyte is present above some detection level, some quantitative assessment must be made of the concentration in order for it to be used for DMR reporting purposes. Once the quantifiable level has been achieved, that value can be used to report data on the DMR. Consistent with previous EPA guidance, such as the March 15, 1989 Section 304(l) Guidance and the May 21, 1990 Dioxin Strategy, this approach involves the use of a threshold value (i.e., ML) for purposes of reporting DMR data for compliance evaluations. EPA Region VI has been successfully using a similar approach since 1992.

The major advantage to this approach is that, in situations of high uncertainty, it gives the permittee a small margin of relief to avoid false positives leading to violations. The purpose of this approach is to provide us with a temporary, consistent way to report values below quantification levels until better analytical technology is developed.

Based on this guidance, EPA sees no need to modify the PCS database to accommodate data where analytical results are at less than detectable levels. As with all self-monitoring data that are submitted on DMRs, these data will also be entered into PCS. Data shall be reported as positive numbers or as zero. No less than (<) or minus (-) signs accompanying the data or alpha characters (such as "ND" for non-detect) representing the data are deemed necessary, based on this approach. Use of zero and positive numbers will address the current problem of inconsistent reporting of these data. For permits that require reporting a maximum value, the number of analytical results exceeding the ML and the maximum value of the reporting period will be entered. For average values, the calculated average as it appears on the DMR will be entered.

Any reported DMR value showing a concentration above the specified WQBEL is considered an effluent violation when the stated ML or interim ML for the pollutant in the most sensitive analytical method promulgated at 40 CFR Part 136 is at or below the WQBEL. When the stated ML or interim ML for that method is above the WQBEL, an effluent violation has occurred when the concentration is equal to or greater than the ML.

The ML is not to be misconstrued as the level by which compliance is determined. In support of Enforcement Principle II, the ML is used to ensure the sensitivity of the permittee's analytical method. In general, any violation involving WQBELs established at levels less than quantifiable are considered to be of concern to the regulatory authority and should receive thorough review. This is because the pollutants that are covered under the description of "non-detectable" have been deemed to have potential water quality impacts at such low concentrations that detection alone is of concern. Appendices D and E provide examples of the monitoring, reporting, tracking, and the enforcement process.

To ensure protection of water quality from pollutants of concern, the permit writer should specify in the permit any methods to be used by the permittee to demonstrate compliance with WQBELs included in the permit. Clear permit requirements are essential for effective compliance evaluation and enforcement of WQBELs. Facilities that are not in compliance with their permit requirements must be required to return to compliance promptly. EPA's approach to enforcement (Enforcement Principles III and IV) is set forth below:

- **Effluent Violations:** Though any violation that has been deemed to cause a water quality impact may be placed on the "Quarterly Non-compliance Report (QNCR)," the QNCR regulations contained as an appendix to 40 CFR Part 123.46 dictate the following minimum:

The application of EPA's "Enforcement Management System" (EMS) guidelines treats these parameters according to their group designation: Group I (Technical Review Criteria (TRC) of 1.4 times the monthly average effluent limit) and Group II (TRC of 1.2 times the monthly average effluent limit). A reportable noncompliance (RNC) status is achieved and the violation placed on the QNCR if a facility has two exceedances of either 1.4 times the monthly average effluent limit or greater (Group I pollutants) or 1.2 times the monthly average effluent limit or greater (Group II pollutants) in 6 months, or four exceedances or more of any magnitude in a 6-month period. These criteria apply to all Group I and Group II pollutants, defined below.

Just as all other QNCR-reportable permit effluent violations are considered significant noncompliance (SNC) and must receive timely and appropriate enforcement activity, these limits are held to the same standards. In accordance with the EMS, when a WQBEL has been violated and the determination has been made that the violation has the potential to cause a water quality impact, enforcement action should be prompt. Initial

Group I Pollutants - TRC = 1.4

Biochemical Oxygen Demand	Total Suspended Solids (Residues)
Chemical Oxygen Demand	Total Dissolved Solids (Residues)
Total Oxygen Demands	Other Solids
Total Organic Carbon	
Other Oxygen Demand	MBAS
	NTA
Inorganic Phosphorus	Oil and Grease
Compounds	Other Detergents or Algicides
Inorganic Nitrogen Compounds	
Other Nutrients	
Calcium	Total Alkalinity
Chloride	Total Hardness
Fluoride	Other Minerals
Magnesium	
Sodium	Aluminum
Potassium	Cobalt
Sulfur	Iron
Sulfate	Vanadium

Group II Pollutants - TRC = 1.2

Other Metals Not Specifically Listed Under Group I

Cyanide
Total Residual Chlorine

All Organics Except Those Specifically Listed Under Group I

activity may be in the form of a 308 letter requesting additional information about the violation. The formal enforcement action that follows will be tailored to the circumstances surrounding the facility to achieve the most efficient return to compliance. The action may be an administrative order (with or without penalties) or a judicial action, depending on the severity and duration of the violation. Either approach should require compliance by a specified date met via a compliance schedule requiring milestone achievement by certain dates and progress reports at frequent intervals. Enforcement may also encourage a facility to pursue pollution prevention activities or, when appropriate, a Toxicity Identification Evaluation (TIE)/Toxicity

Reduction Evaluation (TRE) as long as this effort does not delay compliance.

- **Schedule Violations:** Permit writers have no latitude to grant extensions for compliance with WQBELs, unless State regulations specify such and the permit writer knows that the facility will need time to comply (e.g., where construction to provide additional treatment is needed). Where State regulations do not allow for compliance extensions, compliance schedules will need to be set forth as part of enforcement actions (i.e., enforcement orders). Permit writers may, however, establish compliance schedules in permits for conducting TIES/TREs and/or pollution prevention studies, establishing best management practices, or other such special conditions. Where such a schedule is established, EPA recommends the use of milestone dates and the submission of routine progress reports to evaluate progress and minimize delays. The following milestones are considered SNC when 90 or more days overdue: start construction, end construction, and attain compliance with permit. Slippage of these milestones of 90 days or more must be reported on the QNCR.

Violations of schedules of 90 days or more, or reporting violations in which progress report due dates are missed by 30 days or more, are signs that the facility may not meet a final compliance date. These violations should be addressed with formal enforcement actions to quickly resolve the delay and retain the expected schedule.

- **Reporting or Other Violations:** Treatment of reporting violations is consistent with existing EMS guidelines.

Submittal of data determined to be invalid (i.e., failing to meet the specified ML) is a reporting violation equivalent to nonsubmittal of the data. The facility must perform a second analysis and submit the corrected data.

- **Administrative Penalty Orders (APOs):** APOs may be used in conjunction with an Administrative Order for permit violations. The CWA Civil Penalty Policy should be used for determining which class of APO to pursue.

The EMS guidelines for addressing violations of pollutant limits or excursions that have potential to cause a water quality impact require an enforcement action (Administrative Order or State equivalent mechanism, judicial action, etc. with a compliance schedule and date of final compliance) to be taken.

Noncompliance may be resolved (designated as having been returned to compliance on the QNCR) when a facility has returned to compliance from a particular violation or as a whole with the requirements of its permit for one full quarter. Timely and appropriate enforcement actions in accordance with the EMS are required to prompt a facility to return to compliance. A failure to take prompt enforcement action (within two quarters of a facility appearing on the QNCR as being in SNC) will require the facility to be placed on the Exceptions List.

The EPA-recommended boilerplate language is designed to provide for the reporting of data on DMRs that are consistent and that facilitate compliance evaluation, development of NPDES permit limits, and preparation of studies and reports. The data provided for compliance evaluation purposes will reflect noncompliance only when noncompliance has indeed occurred. An example of a compliance evaluation is shown in Appendix E.

VII. ADDITIONAL RECOMMENDATIONS

To improve the quality of analytical data, EPA recommends the use of clean techniques and extraction/concentration techniques to aid in the lowering of detection and quantitation levels, and the use of data quality objectives to facilitate an understanding of results required.

A. Clean Techniques

The term "clean techniques" refers to practices used to reduce contamination and interference during the accurate and precise measurement of trace level pollutants. Data quality may be compromised due to contamination of samples during collection, preparation, storage, and analysis. Clean techniques begin with the field sampling procedures and continue through all sample processing and analysis steps. Examples of clean techniques include wearing latex or polyethylene gloves during all steps of the sampling and sample preparation process, using acid-washed plastic equipment for trace metals, and analyzing blanks. Although the Agency has not yet issued protocols for clean techniques, specifications for apparatus and materials, quality control, and sample collection, preservation, and handling are included for each analytical method in 40 CFR Part 136, Appendix A, and these procedures, while not exactly analogous to the clean techniques described in the literature for trace metals, are minimum requirements for sampling and analysis. The Agency believes that field and laboratory use of clean techniques may be critical for lowering the detection and quantitation levels of analytical methods to achieve or approach WQBELs.

EPA has included general, interim guidance on the use of clean techniques as part of the *Office of Water Policy and Technical Guidance on Interpretation and Implementation of*

Aquatic Life Metals Criteria issued on October 1, 1993. EPA plans to develop protocols on the use of clean techniques and is coordinating this effort with the United States Geological Survey. Draft protocols are expected in early 1994.

B. Sample Extraction/Concentration

Concentrating the sample by evaporation of water is a technique that has been shown to lower detection levels when analyzing for specific chemicals. For example, volume reduction during digestion has been shown to aid in the determination of metals in the nanogram per liter range. Extracting samples and concentrating the sample extract prior to instrumental analysis is an established, universally accepted technique used to enhance the range of detectability for organic compounds.

The following questions are commonly asked by the permitting authority in reference to concentrating samples:

- 1) Are the techniques for concentrating samples allowed under 40 CFR Part 136? and
- 2) How easily are the techniques employed?

For metals analyses, concentrating samples can be easily accomplished through the existing regulations under 40 CFR Part 136. References to concentration techniques in the regulations exist for some of the analytical methods, but not all. Where a method does not include procedures for concentrating samples, a method modification would be required.

Concentrating samples is a proven, highly successful technique that may be utilized to lower analytical laboratory detection levels. Concentration of samples is straightforward; however, problems sometimes occur prior to analysis, such as matrix interferences, precipitation of some of the components, or solidification. There are well-documented solutions to each of these problems, although solutions differ from facility to facility, and among production processes using different chemicals within a facility. Among the solutions is the use of other instrumentation methods. For example, an ion chromatographic technique may be substituted for the Technicon analyzer for minerals/nutrients analysis.

In the absence of methods in 40 CFR Part 136 that can measure below the detection level, EPA recommends methodologies for concentrating and extracting samples and the use of cleanup or clean techniques. Such techniques allow the permittee to measure as close as possible to the WQBELs, thereby meeting the goal of this guidance.

C. Data Quality Objectives

In support of the development of technology-based limits and WQBELs and determining compliance with those limits, EPA recommends the use of data quality objectives (DQOs).

The "DQO Process" is a series of planning steps designed to ensure that the type, quantity, and quality of environmental data used in decision making are appropriate for the intended application. It is a planning tool that allows decision makers to define their data requirements and acceptable levels of decision errors during planning, before they collect data.

EPA's Quality Assurance Management Staff recently issued an interim final document entitled, Guidance for Planning for Data Collection in Support of Environmental Decision Making Using the Data Quality Objectives Process (EPA QA/G-4). This document describes seven distinct steps that make up the DQO Process, the value of such a process, when it should be used, and who should participate.

EPA's Office of Wastewater Enforcement and Compliance also issued guidance titled "NPDES Permit Writer's Guide on Data Quality Objectives" (December 3, 1990).

VIII. ADDITIONAL PERMITTING AND ENFORCEMENT ISSUES

While EPA believes that the above guidance for permitting and enforcing WQBELs that fall below detectable levels is appropriate, there are several issues of concern.

A. Using Internal Outfalls to Ensure Compliance with WQBELs

Potential Issue: Often effluent limits are below detection levels because of dilution following treatment of the wastewater which contains only trace levels of pollutants (e.g., non-contact cooling water). Where technology-based limits are applied, setting limits at an internal outfall at the end-of-process is common. However, since WQBELs are applied at the end-of-pipe, an internal outfall appears to be inappropriate.

Approach: EPA fully supports the use of internal outfalls to determine compliance even where permit limits are water quality-based. EPA believes that internal outfalls can be especially appropriate where a pollutant of concern is very concentrated at an internal outfall and is co-mingled with discharges from other outfalls prior to discharge, causing dilution or matrix interference. Also, there are internal and external censor devices that are easily installed on the

treatment system pipes and that allow sampling to be conducted before the wastewater is diluted.

Flow variability for internal waste streams is an issue that can be accounted for by installing a flow meter that allows flows to be quantified and eliminates the "uncertainty" for nonlinear flow.

Appendix F of this guidance provides an example of the use of internal outfalls in determining compliance with WQBELs, which, if applied at the final outfall, would be below detectable levels. The example in Appendix F shows that assuming no contribution of pollutants from the dilution waste stream will demonstrate whether the concentrated waste stream would result in a violation of the WQBEL.

Rationale: Internal waste stream limits are used to account for pollutants prior to dilution. Applying limits at an internal outfall to determine compliance with WQBELs is consistent with 40 CFR 122.45(h), which allows for the use of an internal outfall where dilution or interference makes detection of the pollutants impracticable at the otherwise established monitoring point.

[This is consistent with Permitting Principles I and II.]

B. Driving the Technology to Achieve Lower Detection Levels

Potential Issue: Providing permittees with an ML may result in the use of the ML as an easily met performance level and thus not drive technology to achieve lower detection levels.

Approach: The ML is a quantification level used in reporting analytical results, not a compliance evaluation level. Facilities are required to comply with the WQBEL. This is demonstrated in Appendix E, which shows examples of compliance evaluations.

EPA recommends that, in expectation of improved analytical methods, permit writers include generic re-opener clauses that are sufficient to provide permitting authorities the means to reopen, modify, and reissue the permit as analytical methods are revised and/or promulgated. At a minimum, improved analytical methods and quantification levels should be incorporated in the permit at the time of reissuance.

Rationale: EPA believes that WQBELs set below detection levels, regardless of the use of MLs, will encourage development of improved analytical methods and better quality assurance/quality control techniques. In some

cases, facilities will violate the WQBEL simply when detecting a pollutant. Thus, any exceedance of the ML will be a violation. Technology will be driven to lower detection levels when facilities make efforts to quantify pollutants below the ML in order to avoid exceedances of WQBELs. This is also true when trying to negate a demonstration of reasonable potential and thus eliminate the need for a limit altogether.

[This is consistent with Permitting Principle III.]

C. Specifying Analytical Methods in NPDES Permits

Potential Issue: Facilities may challenge EPA's authority for requiring analyses by a specific method and calibration at a specific concentration.

Approach: EPA believes it is appropriate and necessary to include specific language for reporting compliance with the ML, the quantification level used by the permittee, and the use of the ML concentration as a calibration standard.

Rationale: EPA already limits the specific methods that may be employed to those proposed or promulgated under Section 304(h) or approved by the permitting authority in advance. In the case of many pollutants, there is a limited set of approved methods. Specificity ensures that the ML can be measured and that the laboratory is conducting analyses by the most sensitive method available. Pursuant to 40 CFR 122.43, permit writers may include additional conditions in a permit that "provide for and assure compliance with all applicable requirements of the CWA and regulations." Based on this authority, permit writers should establish special monitoring and reporting requirements pertaining to WQBELs that are less than detectable levels.

[This is consistent with Permitting Principle II and Enforcement Principle I.]

D. Dealing With Matrix Interferences

Potential Issue: Matrix interferences may, in some cases, result in laboratories being unable to meet the stated or interim MLs.

Approach: In most cases, EPA believes that wastewater of high quality will have very little matrix interference. EPA acknowledges that some facilities will have matrix interference. Appendix B to 40 CFR Part 136 sets forth procedures that facilities must follow when establishing discharge-specific MDLs. Procedures for reviewing

discharge-specific MDL and ML submittals are provided in Appendix B to this guidance.

Rationale: EPA acknowledges that some facilities may be unable to meet the specified MLs due to matrix interferences. However, EPA believes that it is important to distinguish between instances when MLs are not achieved due to poor laboratory technique and when matrix interferences do indeed occur. To make this determination, guidelines and procedures under which facilities must conduct studies and, if appropriate, develop discharge-specific MLs must be set forth. Without such, facilities are likely to develop less stringent MDLs for use as quantification levels that have no technical basis.

[This is consistent with Permitting Principle II and Enforcement Principle I.]

B. Providing Time Extensions for Meeting the Specified Analytical Method and Achieving the ML

Potential Issue: Many facilities may be unable to meet the ML specified in the permit, particularly where they have laboratory equipment that performs analyses in accordance with an alternate test procedure approved under 40 CFR Part 136.4.

Approach: EPA recognizes that facilities may experience delays in meeting specified analytical requirements for certain parameters until in-house capabilities are established. However, it is recommended that permitting authorities not provide compliance extensions for permittees to gain the capability of measuring the ML using a specified method. If permittees do not meet the required methods and ML specified in the permit, schedules for meeting them should take place through enforcement action which may be issued concurrently with the permit.

Rationale: Since analytical capabilities for conducting analyses in accordance with specified methods are readily available, the Agency feels that compliance schedules are not necessary. Schedules, when set forth, should include milestone dates to be fully enforceable and avoid ambiguity.

[This is consistent with Permitting Principles I and II, and Enforcement Principles I and IV.]

F. Determining Whether Failure to Achieve MLs Is Caused by Poor Lab Performance or Other Factors

Potential Issue: While specifying monitoring and reporting requirements in a permit is appropriate and should result in

consistency in permitting as well as compliance from the majority of permittees, this will not assist EPA in determining whether exceedances of the ML are actual exceedances of the WQBEL or the result of other problems such as poor laboratory technique or some other problem.

Approach: Permittees are responsible for knowing and understanding the terms and conditions of their permit, attaining and maintaining compliance, and ensuring the quality of monitoring data collected and submitted. Where permittees experience problems, they must identify the cause and develop a solution. EPA does, however, recommend use of oversight mechanisms to identify actual or potential problems.

In accordance with established procedures, major permitted facilities and minor facilities of concern will be inspected at minimum frequency of once per year. EPA recommends that inspections of permittees that discharge pollutants that are limited below the ML should be particularly thorough and conducted by inspectors with analytical experience. All permittees should comply with QA/QC procedures for sample collection, storage, transport, analysis, instrument maintenance, calibration, etc. The possibility of not achieving the specified ML and thus being noncompliant as a result of sample contamination or technician error is greater at low pollutant concentrations. Sampling and handling procedures and proper QA/QC are addressed in 40 CFR Part 136 for each method. A work group of the Environmental Monitoring Management Council is addressing this aspect of analytical testing in its *Agency Standardization of Methods*. EPA recommends that laboratory procedures and records be evaluated during inspections and audits to ensure that the data are generated under acceptable procedures and that submitted self-monitoring data are reflective of the underlying raw data.

Rationale: Inspections/audits are used to verify the permittee laboratory's capability to perform analyses necessary to reach the required ML. EPA maintains, however, that requiring facilities to report the ML that they achieve will assist EPA in identifying facilities that may not be meeting the ML. These factors can then be used to subsequently target facilities for in-depth performance audit inspections. This will allow EPA to determine whether problems are caused by poor laboratory technique or matrices interference.

[This is consistent with Permitting Principle II and Enforcement Principle III.]

G. Addressing Potential Water Quality Problems That May Not Be Addressed Where Analytical Data Cannot Be Quantified

Potential Issue: Despite the measures proposed by EPA as part of this guidance to more accurately and consistently quantify pollutant discharges, water quality problems still may occur.

Approach: EPA acknowledges that measures intended to demonstrate compliance with WQBELs will not necessarily ensure compliance with water quality. Thus, EPA recommends that permits that have pollutant limits for aquatic life below analytical detection levels should include the requirement to perform WET testing in the permit. Additionally, EPA supports the use of other measures to protect water quality including bioaccumulation or sediment studies, pollution reduction/prevention plans, or other such special requirements.

Any information provided to the permitting and enforcement authority from EPA or State sources, citizens groups, etc., that indicate water quality problems may be used to initiate a more thorough investigation of the facility. For example, fish/shellfish tissue samples that demonstrate a bioaccumulative effect of pollutants otherwise not detected or a chemical mass balance that shows the release of large quantities of pollutants in a discharge may be used to initiate additional activities that will further quantify pollutants. In response to noted problems, EPA may conduct an inspection, issue a request for information pursuant to Section 308 of the CWA, or require studies. Ultimately, the permit may be reopened to include more stringent requirements that result in water quality protection and/or a compliance agreement may be negotiated that includes pollution prevention/reduction goals.

Rationale: Permits must be protective of water quality.

[This is consistent with Permitting Principle I and Enforcement Principle III.]

VIII. SUMMARY

This guidance includes the five following basic elements:

- WQBELs are to be imposed as NPDES permit limits when necessary to protect the designated uses of the receiving waters, even if the WQBEL is less than the analytical detection level.

- The quantification level to be used in analyzing samples and reporting the results is the ML. Guidance for incorporating MLs into NPDES permits, developing MLs where they are not currently available, and translating analytical values below the ML into DMR data for compliance evaluations is provided in this guidance and the accompanying appendices.
- The existing analytical data reporting and tracking mechanisms (the DMR and PCS, respectively) will continue to be used with no changes to their structures. This document provides guidance and examples for reporting analytical values that are at or below the ML. The role of the ML in compliance evaluations is not direct; rather, it is the threshold for recording the analytical data, which will then be used to calculate and report summary information on the DMR.
- Enforcement criteria are consistent with those set forth in the EMS guidelines, and compliance evaluations continue to be made directly between the DMR information and the permit limit (which is the WQBEL in cases where water quality is the most stringent limitation).
- Important permitting and compliance issues, such as matrix interference, the use of internal outfalls in permit writing, driving technology to achieve lower detection levels, specifying analytical protocol in NPDES permits, and the ability of laboratories to achieve specified MLs, are also addressed in this guidance.

APPENDIX A

**MDLs, IDLs AND OTHER ANALYTICAL QUANTITATION
LEVELS FOR EPA APPROVED ANALYTICAL METHODS**

ACHIEVABLE DETECTION LEVELS FOR ORGANIC PRIORITY POLLUTANTS

		ORGANIZATION					
		40 CFR Part 136 Approved ¹					
		EPA		EPA		EPA	
		EPA		EPA		EPA	
		EPA		EPA		EPA	
		EPA		EPA		EPA	
		EPA		EPA		EPA	
		EPA		EPA		EPA	
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ACHIEVABLE DETECTION LEVELS (Continued)

		ORGANIZATION				
		40 CFR Part 136 Approved ¹				
		EPA-CW ²		USGS ³		ASTM ⁴
Pollutant	EDL (ug/L)	EDL (ug/L)	Method	EDL (ug/L)	Method	Method
Perachloroethane	10	0.03 1.0	GC/MS 912 "Chlorinated Hydrocarbons" GCMS 625 "Semi-Volatile and Aromatic" GCMS 1625 "Semi-Volatile Organic Compounds by Isotope Dilution"	5	GCMS 0-3118 "Semi-Volatile Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
1,1-dichloroethane	10	0.07 4.7	GC/MS 901 "Purgeable Hydrocarbons" GCMS 624 "Purgeable" GCMS 1624 "Volatile Organic Compounds by Isotope Dilution"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
1,1,2-trichloroethane	10	0.03 5.0	GC/MS 901 "Purgeable Hydrocarbons" GCMS 624 "Purgeable" GCMS 1624 "Volatile Organic Compounds by Isotope Dilution"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
1,1,2,2-tetrachloroethane	10	0.03 5.0	GC/MS 901 "Purgeable Hydrocarbons" GCMS 624 "Purgeable" GCMS 1624 "Volatile Organic Compounds by Isotope Dilution"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
chloroethane	10	0.03 5.0	GC/MS 901 "Purgeable Hydrocarbons" GCMS 1624 "Volatile Organic Compounds by Isotope Dilution"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
1,2-dichloroethyl ether	10	0.2 5.7	GC/MS 911 "Hydrocarbons" GCMS 625 "Semi-Volatile and Aromatic" GCMS 1625 "Semi-Volatile Organic Compounds by Isotope Dilution"	5	GCMS 0-3118 "Semi-Volatile Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
2-chloroethyl vinyl ether (mixed)	10	0.13	GC/MS 901 "Purgeable Hydrocarbons" GCMS 1624 "Volatile Organic Compounds by Isotope Dilution"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
2-chloronaphthalene	10	0.04 1.0	GC/MS 912 "Chlorinated Hydrocarbons" GCMS 625 "Semi-Volatile and Aromatic" GCMS 1625 "Semi-Volatile Organic Compounds by Isotope Dilution"	5	GCMS 0-3118 "Semi-Volatile Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
2,4,6-trichlorophenol	10	0.04 2.7	GC/MS 904 "Phenols" GCMS 625 "Semi-Volatile and Aromatic" GCMS 1625 "Semi-Volatile Organic Compounds by Isotope Dilution"	1	GCMS 0-3117 "Acid Extraction Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
perchloromethyl cresol (4-chloro-3-methylphenol)	1.0	0.28	GC/MS 904 "Phenols"			
chloroform	0.2	0.02 1.0	GC/MS 901 "Purgeable Hydrocarbons" GCMS 624 "Purgeable"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	GC/MS 13073 "Test Method for Low Molecular Weight Halogenated Hydrocarbons in Water"
1,1-dichloroethane	10	0.03 1.0	GC/MS 901 "Purgeable Hydrocarbons" GCMS 625 "Semi-Volatile and Aromatic" GCMS 1625 "Semi-Volatile Organic Compounds by Isotope Dilution"	1	GCMS 0-3117 "Acid Extraction Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	GC/MS 13073 "Test Method for Phenols in Water by Gas Liquid Chromatography"

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ACHIEVABLE DETECTION LEVELS (Continued)

		ORGANIZATION					
		40 CFR Part 136 Approved ¹					
		EPA-CIN ²		USGS ³		ASTM ⁴	
Pollutant	EDL (ug/L)	EDL (ug/L)	Method	EDL (ug/L)	Method	EDL (ug/L)	Method
di-(2-ethylhexyl) phthalate	10	2.8 2.8	QCIC 808 "Phthalate Ester" GCMS 825 "Benzothiadiazole and Acids" GCMS 1625 "Benzothiadiazole Organic Compounds by Isotope Dilution"	5	GCMS 0-3118 "Benzothiadiazole Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
butyl benzyl phthalate	10	0.34 2.8	QCIC 808 "Phthalate Ester" GCMS 825 "Benzothiadiazole and Acids" GCMS 1625 "Benzothiadiazole Organic Compounds by Isotope Dilution"	5	GCMS 0-3118 "Benzothiadiazole Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
di-n-butyl phthalate	10	0.34 2.8	QCIC 808 "Phthalate Ester" GCMS 825 "Benzothiadiazole and Acids" GCMS 1625 "Benzothiadiazole Organic Compounds by Isotope Dilution"	5	GCMS 0-3118 "Benzothiadiazole Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
di-n-octyl phthalate	10	3.0 2.8	QCIC 808 "Phthalate Ester" GCMS 825 "Benzothiadiazole and Acids" GCMS 1625 "Benzothiadiazole Organic Compounds by Isotope Dilution"	5	GCMS 0-3118 "Benzothiadiazole Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
dimethyl phthalate	10	0.48 1.8	QCIC 808 "Phthalate Ester" GCMS 825 "Benzothiadiazole and Acids" GCMS 1625 "Benzothiadiazole Organic Compounds by Isotope Dilution"	5	GCMS 0-3118 "Benzothiadiazole Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
dimethyl phthalate	10	0.29 1.8	QCIC 808 "Phthalate Ester" GCMS 825 "Benzothiadiazole and Acids" GCMS 1625 "Benzothiadiazole Organic Compounds by Isotope Dilution"	5	GCMS 0-3118 "Benzothiadiazole Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
benzo (a) anthracene	10	7.8 0.012	GCMS 825 "Benzothiadiazole and Acids" HPLC/DV 810 "Polynuclear Aromatic Hydrocarbons" GCMS 1625 "Benzothiadiazole Organic Compounds by Isotope Dilution"	5 1	GCMS 0-3118 "Benzothiadiazole Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry" HPLC/DV 0-3113 "Polynuclear Aromatic Hydrocarbons (PNA), Total Recoverable, High-Performance Liquid Chromatography"		
benzo (a) pyrene	10	2.8 0.023	GCMS 825 "Benzothiadiazole and Acids" HPLC/DV 810 "Polynuclear Aromatic Hydrocarbons" GCMS 1625 "Benzothiadiazole Organic Compounds by Isotope Dilution"	5 1	GCMS 0-3118 "Benzothiadiazole Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry" HPLC/DV 0-3113 "Polynuclear Aromatic Hydrocarbons (PNA), Total Recoverable, High-Performance Liquid Chromatography"		
3,4-benzofluoranthene (benzo (b) fluoranthene)	0.05	4.8 0.018	GCMS 825 "Benzothiadiazole and Acids" HPLC/DV 810 "Polynuclear Aromatic Hydrocarbons"	5	GCMS 0-3118 "Benzothiadiazole Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
benzo (b) fluoranthene	10	7.8 0.018	GCMS 825 "Benzothiadiazole and Acids" HPLC/DV 810 "Polynuclear Aromatic Hydrocarbons" GCMS 1625 "Benzothiadiazole Organic Compounds by Isotope Dilution"	5	GCMS 0-3118 "Benzothiadiazole Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		

ACHIEVABLE DETECTION LEVELS (Continued)

ORGANIZATION						
40 CFR Part 136 Approved ¹						
Pollutant	EMSL-CIN ²		EDL (µg/L)	USGS ³		ASTM ⁴
	ML (µg/L)	MDL (µg/L)		Method	EDL (µg/L)	
chrysene	10	2.5 0.18	5 1	GCMS 625 "Benzofluorene and Acids" HPLC/UV 610 "Polynuclear Aromatic Hydrocarbons" GCMS 1625 "Benzofluorene Organic Compounds by Isotope Dilution"	GCMS 0-3118 "Benzofluorene Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry" HPLC/UV 0-3113 "Polynuclear Aromatic Hydrocarbons (PNA), Total Recoverable, High Performance Liquid Chromatography"	
acenaphthylene	10	2.5 2.2	5	GCMS 625 "Benzofluorene and Acids" HPLC/UV 610 "Polynuclear Aromatic Hydrocarbons" GCMS 1625 "Benzofluorene Organic Compounds by Isotope Dilution"	GCMS 0-3118 "Benzofluorene Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
anthracene	10	1.8 0.09	5 1	GCMS 625 "Benzofluorene and Acids" HPLC/UV 610 "Polynuclear Aromatic Hydrocarbons" GCMS 1625 "Benzofluorene Organic Compounds by Isotope Dilution"	GCMS 0-3118 "Benzofluorene Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry" HPLC/UV 0-3113 "Polynuclear Aromatic Hydrocarbons (PNA), Total Recoverable, High Performance Liquid Chromatography"	
benzo (ghi) perylene	20	4.1 0.078	5 1	GCMS 625 "Benzofluorene and Acids" HPLC/UV 610 "Polynuclear Aromatic Hydrocarbons" GCMS 1625 "Benzofluorene Organic Compounds by Isotope Dilution"	GCMS 0-3118 "Benzofluorene Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry" HPLC/UV 0-3113 "Polynuclear Aromatic Hydrocarbons (PNA), Total Recoverable, High Performance Liquid Chromatography"	
fluorene	10	1.8 0.21	5	GCMS 625 "Benzofluorene and Acids" HPLC/UV 610 "Polynuclear Aromatic Hydrocarbons" GCMS 1625 "Benzofluorene Organic Compounds by Isotope Dilution"	GCMS 0-3118 "Benzofluorene Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
phenanthrene	10	5.4 0.04	5 1	GCMS 625 "Benzofluorene and Acids" HPLC/UV 610 "Polynuclear Aromatic Hydrocarbons" GCMS 1625 "Benzofluorene Organic Compounds by Isotope Dilution"	GCMS 0-3118 "Benzofluorene Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry" GCMS 0-3116 "Benzofluorene Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
dibenzo (a,h) anthracene	20	2.5 0.039	5 1	GCMS 625 "Benzofluorene and Acids" HPLC/UV 610 "Polynuclear Aromatic Hydrocarbons" GCMS 1625 "Benzofluorene Organic Compounds by Isotope Dilution"	GCMS 0-3118 "Benzofluorene Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry" HPLC/UV 0-3113 "Polynuclear Aromatic Hydrocarbons (PNA), Total Recoverable, High Performance Liquid Chromatography"	
indeno (1,2,3-cd) pyrene	20	2.7 0.061	5	GCMS 625 "Benzofluorene and Acids" HPLC/UV 610 "Polynuclear Aromatic Hydrocarbons" GCMS 1625 "Benzofluorene Organic Compounds by Isotope Dilution"	GCMS 0-3118 "Benzofluorene Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	

ACHIEVABLE DETECTION LEVELS (Continued)

Pollutant	ORGANIZATION					
	40 CFR Part 136 Approved ¹					
	EPA		Method	USGS ²		ASTM ³
	MDL (ug/L)	MDL (ug/L)		MDL (ug/L)	Method	
pyrene	10	1.8 0.27	GCMS 825 "Base/Neutrals and Acids" HPLC/UV 810 "Polynuclear Aromatic Hydrocarbons" GCMS 1625 "Semivolatile Organic Compounds by Isotope Dilution"	5 1	GCMS 0-3118 "Base/Neutrals Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry" HPLC/UV 0-3113 "Polynuclear Aromatic Hydrocarbons (PNA), Total Recoverable, High Performance Liquid Chromatography"	
tetrachloroethylene	10	0.03 4.1	GCMS 801 "Purgeable Hydrocarbons" GCMS 834 "Purgeables" GCMS 1634 "Volatile Organic Compounds by Isotope Dilution"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	1 GCEC 03073 "Test Method for Low Molecular Weight Monosubstituted Hydrocarbons in Water"
toluene	10	6.0 0.2	GCMS 834 "Purgeables" GCMS 802 "Purgeable Hydrocarbons" GCMS 1634 "Volatile Organic Compounds by Isotope Dilution"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
trichloroethylene	0.1	0.12 1.8	GCMS 801 "Purgeable Hydrocarbons" GCMS 834 "Purgeables"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
1,2-trans-dichloroethylene	0.1	0.1 1.6	GCMS 801 "Purgeable Hydrocarbons" GCMS 825 "Base/Neutrals and Acids"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
2,4-dichlorophenol	10	0.28 2.7	GCMS 804 "Phenols" GCMS 825 "Base/Neutrals and Acids" GCMS 1625 "Semivolatile Organic Compounds by Isotope Dilution"	1	GCMS 0-3117 "Acid Extraction Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	1 GCED 02580 "Test Methods for Phenols in Water by Gas Liquid Chromatography"
1,2-dichloropropane	0.1	0.04 6.0	GCMS 801 "Purgeable Hydrocarbons" GCMS 834 "Purgeables"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
1,3-dichloropropane	1	0.24	GCMS 801 "Purgeable Hydrocarbons"			
2,4-dimethylphenol	10	0.32 2.7	GCMS 804 "Phenols" GCMS 825 "Base/Neutrals and Acids" GCMS 1625 "Semivolatile Organic Compounds by Isotope Dilution"	1	GCMS 0-3117 "Acid Extraction Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
2,4-dinitrotoluene	10	0.02 5.7	GCMS 809 "Nitroaromatics and Isobutene" GCMS 825 "Base/Neutrals and Acids" GCMS 1625 "Semivolatile Organic Compounds by Isotope Dilution"	5	GCMS 0-3118 "Base/Neutrals Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
2,6-dinitrotoluene	10	0.01 1.8	GCMS 809 "Nitroaromatics and Isobutene" GCMS 825 "Base/Neutrals and Acids" GCMS 1625 "Semivolatile Organic Compounds by Isotope Dilution"	5	GCMS 0-3118 "Base/Neutrals Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
1,2-dichloroethane	1	0.1	GCMS 801 "Purgeable Hydrocarbons"			

ACHIEVABLE DETECTION LEVELS (Continued)

		ORGANIZATION					
		40 CFR Part 136 Approved ¹					
		EPA		EMSL-CIN ²	USGS ³	ASTM ⁴	
Pollutant	EDL (ppb)	EDL (ppb)	Method	EDL (ppb)	Method	EDL (ppb)	Method
ethylbenzene	10	7.3 9.3	GCMS 624 "Purge-and-Trap" GCMS 601 "Purge-and-Trap" GCMS 1624 "Volatile Organic Compounds by Isotope Dilution"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
fluoranthene	10	2.2 9.2	GCMS 625 "Base/Natural and Acidic" HPLC/DV 910 "Thermally Stable Hydrocarbons" GCMS 1625 "Semi-volatile Organic Compounds by Isotope Dilution"	5 1	GCMS 0-3116 "Base/Natural Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry" HPLC/DV 0-3113 "Polynuclear Aromatic Hydrocarbons (PNA), Total Recoverable, High-Performance Liquid Chromatography"		
4-chlorophenyl phenyl ether	10	2.8 4.3	GCMS 611 GCMS 625 "Base/Natural and Acidic" GCMS 1625 "Semi-volatile Organic Compounds by Isotope Dilution"	5	GCMS 0-3116 "Base/Natural Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
4-bromophenyl phenyl ether	20	2.3 1.2	GCMS 611 GCMS 625 "Base/Natural and Acidic" GCMS 1625 "Semi-volatile Organic Compounds by Isotope Dilution"	5	GCMS 0-3116 "Base/Natural Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
bis (2-chloroethoxy) ether	10	0.8 5.7	GCMS 611 GCMS 625 "Base/Natural and Acidic" GCMS 1625 "Semi-volatile Organic Compounds by Isotope Dilution"	5	GCMS 0-3116 "Base/Natural Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
bis (2-chloroethoxy) methane	10	0.8 5.3	GCMS 611 GCMS 625 "Base/Natural and Acidic" GCMS 1625 "Semi-volatile Organic Compounds by Isotope Dilution"	5	GCMS 0-3116 "Base/Natural Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
methylene chloride	10	0.25 2.8	GCMS 601 "Purgeable Hydrocarbons" GCMS 624 "Purge-and-Trap" GCMS 1624 "Volatile Organic Compounds by Isotope Dilution"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
methyl chloride	0.2 ¹	0.08	GCMS 601 "Purgeable Hydrocarbons"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
methyl bromide	0.2 ¹	1.18	GCMS 601 "Purgeable Hydrocarbons"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"		
dichlorodifluoromethane	0.2 ¹	1.81	GCMS 601 "Purgeable Hydrocarbons"				
bromobenzene	10	0.20 4.2	GCMS 601 "Purgeable Hydrocarbons" GCMS 624 "Purge-and-Trap" GCMS 1624 "Volatile Organic Compounds by Isotope Dilution"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	1	GC/E C 029/73 "Test Method for Low Molecular Weight Halogenated Hydrocarbons in Water"
chlorobromomethane	0.2 ¹	0.19 0.3	GCMS 601 "Purgeable Hydrocarbons" GCMS 624 "Purge-and-Trap"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	1	GC/E C 029/73 "Test Method for Low Molecular Weight Halogenated Hydrocarbons in Water"

ACHIEVABLE DETECTION LEVELS

Continued)

Pollutant	ORGANIZATION					
	40 CFR Part 136 Approved ¹					
	EPA		Method	USEPA ²		ASTM ³
	EDL (ppb)	EDL (ppb)		EDL (ppb)	EDL (ppb)	
chlorodibromomethane	0.2	0.05 2.1	GC/MS 801 "Purgeable Hydrocarbons" GCMS 824 "Purgeables"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	1
hexachlorobutadiene	10	0.24 0.6	GC/MS 812 "Chlorinated Hydrocarbons" GCMS 825 "Base/Neutrals and Acids" GCMS 1625 "Semivolatile Organic Compounds by Isotope Dilution"	5	GCMS 0-3116 "Base/Neutrals of Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
hexachlorocyclopentadiene	10	0.40	GC/MS 812 "Chlorinated Hydrocarbons" GCMS 1625 "Semivolatile Organic Compounds by Isotope Dilution"	5	GCMS 0-3116 "Base/Neutrals of Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	1-10 ppb
isophorone	10	5.7 2.2	GC/MS 806 "Microconstituents and Isophorone" GCMS 825 "Base/Neutrals and Acids" GCMS 1625 "Semivolatile Organic Compounds by Isotope Dilution"	5	GCMS 0-3116 "Base/Neutrals of Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
naphthalene	10	1.8 1.0	GCMS 825 "Base/Neutrals and Acids" HPLC/UV 610 "Polynuclear Aromatic Hydrocarbons" GCMS 1625 "Semivolatile Organic Compounds by Isotope Dilution"	5 1	GCMS 0-3116 "Base/Neutrals of Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry" HPLC/UV 0-3113 "Polynuclear Aromatic Hydrocarbons (PNAH), Total Recoverable, High-Performance Liquid Chromatography"	
nitrobenzene	10	3.8 1.8	GC/MS 806 "Microconstituents and Isophorone" GCMS 825 "Base/Neutrals and Acids" GCMS 1625 "Semivolatile Organic Compounds by Isotope Dilution"	5	GCMS 0-3116 "Base/Neutrals of Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
2-nitrophenol	20	0.45 2.6	GC/MS 804 "Phenols" GCMS 825 "Base/Neutrals and Acids" GCMS 1625 "Semivolatile Organic Compounds by Isotope Dilution"	1	GCMS 0-3117 "Acid Extraction Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
4-nitrophenol	50	2.8 2.4	GC/MS 804 "Phenols" GCMS 825 "Base/Neutrals and Acids" GCMS 1625 "Semivolatile Organic Compounds by Isotope Dilution"	1	GCMS 0-3117 "Acid Extraction Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
2,4-dinitrophenol	50	12.0 42	GC/MS 804 "Phenols" GCMS 825 "Base/Neutrals and Acids" GCMS 1625 "Semivolatile Organic Compounds by Isotope Dilution"	1	GCMS 0-3117 "Acid Extraction Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
vinyl chloride	10	0.18	GC/MS 801 "Purgeable Hydrocarbons" GCMS 1624 "Volatile Organic Compounds by Isotope Dilution"	3	GCMS 0-3115 "Purgeable Organic Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	
xylene	0.01	0.001 1.0	GC/MS 825 "Base/Neutrals and Acids" GCMS 825 "Base/Neutrals and Acids"	0-01	GCMS 0-3104 "Organochlorine and Organophosphorus Compounds, Total Recoverable and Dissolved, Gas Chromatography/Mass Spectrometry"	

ACHIEVABLE DETECTION LEVELS (Continued)

Pollutant	ORGANIZATION					
	40 CFR Part 136 Approved ¹					
	EMSL-CIN ²		USGS ³		ASTM ⁴	
	MDL (ug/L)	MDL (ug/L)	MDL (ug/L)	Method	MDL (ug/L)	Method
dieldrin	0.005 ⁵	0.002 2.5	0.01	GC/EC 808 "Organochlorine Pesticides and PCBs" GCMS 825 "Benzofurans and Acids"	10 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"
chlordane	0.05 ⁵	0.014	0.05	GC/EC 808 "Organochlorine Pesticides and PCBs"	50-1000 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"
4, 4'-DDT	0.05 ⁵	0.012 4.7	0.01	GC/EC 808 "Organochlorine Pesticides and PCBs" GCMS 825 "Benzofurans and Acids"	10 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"
4, 4'-DDE	0.01 ⁵	0.004 5.0	0.01	GC/EC 808 "Organochlorine Pesticides and PCBs" GCMS 825 "Benzofurans and Acids"	10 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"
4, 4'-DDD	0.01 ⁵	0.011 2.0	0.01	GC/EC 808 "Organochlorine Pesticides and PCBs" GCMS 825 "Benzofurans and Acids"	10 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"
alpha-endosulfan	0.05 ⁵	0.014	0.01	GC/EC 808 "Organochlorine Pesticides and PCBs"	10 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"
beta-endosulfan	0.01 ⁵	0.004	0.01	GC/EC 808 "Organochlorine Pesticides and PCBs"	10 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"
endosulfan sulfate	0.1 ⁵	0.005 5.0				
endrin	0.02 ⁵	0.005 5.0	0.01	GC/EC 808 "Organochlorine Pesticides and PCBs" GCMS 825 "Benzofurans and Acids"	10 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"
endrin aldehyde	0.05 ⁵	0.022				
heptachlor	0.01 ⁵	0.003 1.0	0.01	GC/EC 808 "Organochlorine Pesticides and PCBs" GCMS 825 "Benzofurans and Acids"	10 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"
heptachlor epoxide	0.1 ⁵	0.003 2.2	0.01	GC/EC 808 "Organochlorine Pesticides and PCBs" GCMS 825 "Benzofurans and Acids"	10 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"
alpha-BHC	0.01 ⁵	0.003			10 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"
beta-BHC	0.01 ⁵	0.005 5.0			10 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"
gamma-BHC	0.01 ⁵	0.005	0.01	GC/EC 808 "Organochlorine Pesticides and PCBs" GCMS 825 "Benzofurans and Acids"	10 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"
delta-BHC	0.01 ⁵	0.005 5.0			10 ng/L	GC/EC D3086 "Test Method for Organochlorine Pesticides in Water"

ACHIEVABLE DETECTION LEVELS (Continued)

Pollutant	ORGANIZATION					
	40 CFR Part 136 Approved ¹					
	EMSL-CIN ²		USGS ²		ASTM ²	
	MDL (ug/L)	MLL (ug/L)	Method	EDL (ug/L)	Method	EDL (ug/L)
PCB-1242	0.1	0.001	GCEC 608 "Organochlorine Pesticides and PCBs" GCMS 629 "Benzothiazole and Acids"	0.01	GCEC 0-3104 "Organochlorine and Organophosphorus Compound, Total Recoverable and Dissolved, Gas Chromatography"	1
PCB-1254	100	20	GCEC 608 "Organochlorine Pesticides and PCBs" GCMS 629 "Benzothiazole and Acids"	0.01	GCEC 0-3104 "Organochlorine and Organophosphorus Compound, Total Recoverable and Dissolved, Gas Chromatography"	1
PCB-1221	100	20	GCEC 608 "Organochlorine Pesticides and PCBs" GCMS 629 "Benzothiazole and Acids"	0.01	GCEC 0-3104 "Organochlorine and Organophosphorus Compound, Total Recoverable and Dissolved, Gas Chromatography"	1
PCB-1232	nd	nd	GCEC 608 "Organochlorine Pesticides and PCBs" GCMS 629 "Benzothiazole and Acids"	0.01	GCEC 0-3104 "Organochlorine and Organophosphorus Compound, Total Recoverable and Dissolved, Gas Chromatography"	1
PCB-1248	nd	nd	GCEC 608 "Organochlorine Pesticides and PCBs" GCMS 629 "Benzothiazole and Acids"	0.01	GCEC 0-3104 "Organochlorine and Organophosphorus Compound, Total Recoverable and Dissolved, Gas Chromatography"	1
PCB-1260	nd	nd	GCEC 608 "Organochlorine Pesticides and PCBs" GCMS 629 "Benzothiazole and Acids"	0.01	GCEC 0-3104 "Organochlorine and Organophosphorus Compound, Total Recoverable and Dissolved, Gas Chromatography"	1
PCB-1018	nd	nd	GCEC 608 "Organochlorine Pesticides and PCBs" GCMS 629 "Benzothiazole and Acids"	0.01	GCEC 0-3104 "Organochlorine and Organophosphorus Compound, Total Recoverable and Dissolved, Gas Chromatography"	1
Toxaphene	1	0.01	GCEC 608 "Organochlorine Pesticides and PCBs"	0.01	GCEC 0-3104 "Organochlorine and Organophosphorus Compound, Total Recoverable and Dissolved, Gas Chromatography"	50-1000 ng
2,3,7,8-tetrachlorodibenzo-dioxin (TCDD)	0.005	0.002	GCMS 612 "2,3,7,8-Tetrachlorodibenzo-dioxin"	5	GCMS 0-3119 "Benzothiazole Extractable Compounds, Total Recoverable, Gas Chromatography/Mass Spectrometry"	

¹ This chart represents only those methods approved under the NPDES program. 40 CFR Part 136 lists other methods that are not NPDES approved, but may be used for comparison. [This list is attached for reference].

² A description of the methods and other supporting information may be found in Appendices A through D of 40 CFR Part 136. Underlined methods, MDLs and MLLs signify the method with the lowest detection levels for the corresponding pollutant.

ACHIEVABLE DETECTION LEVELS-ABBREVIATIONS¹

ORGANIZATION: The custodial organization responsible for the method codes are:

ASTM American Society for Testing Materials

EMSL-CIN EPA Environmental Monitoring and Support Laboratory in Cincinnati, Ohio

USGS U.S. Geological Survey Techniques of Water Resources Investigations

METHOD APPARATUS: As derived from the METHOD. The following codes are used:

CVAA Cold vapor atomic absorption spectrometry

FLAA Flame atomic absorption spectrometry

GCEC Gas chromatography with electron capture detector

GCFID Gas chromatography with flame ionization detector

GCHRMS Gas chromatography with high resolution mass spectrometry

GCHSD Gas chromatography with halogen-specific detector (Hall, O.I., microcoulometric, electrolytic conductivity)

GCMS Gas chromatography/mass spectrometry

GCPID Gas chromatography with nitrogen-photoionization detector

HPLC High performance liquid chromatography

HPLCUV HPLC with an ultra-violet detector

METHOD TITLES: Where a method number is assigned in the table, the full title of the method is given here.

601 "Purgeable Halocarbons," EPA EMSL-Cin

602 "Purgeable Aromatics," EPA EMSL-Cin

603 "Acrolein and Acrylonitrile," EPA EMSL-Cin

604 "Determination of Pentachlorophenol Salt in Wastewater," EPA EMSL Cin

605 "Benzidines," EPA EMSL-Cin

606 "Phthalate Ester," EPA EMSL-Cin

607 "Nitrosoamines," EPA EMSL-Cin

608 "Organochlorine Pesticides and PCBs," EPA EMSL-Cin

609 "Nitroaromatics and Isophorone," EPA EMSL-Cin

610 "Polynuclear Aromatic Hydrocarbons," EPA EMSL-Cin

¹The information in this appendix is based on data and definitions described in EPA/600/4-92-010.

ACHIEVABLE DETECTION LEVELS

(Continued)

3.Methods may be found in "Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments" U.S. Dept. of the Interior, U.S. Geological Survey, Open-file Report 85-495.

4.Annual Book of ASTM Standards Volume 11.02, ASTM, Philadelphia, PA. 1991. Publication Code Number 01-110291-16.

5.Interim MLs are denoted by "" are represented here as 3.18 times the lowest MDL achievable using an EPA approved method.

ACHIEVABLE DETECTION LEVELS-ABBREVIATIONS
(Continued)

611	"Haloether," EPA EMSL-Cin
612	"Chlorinated Hydrocarbons," EPA EMSL-Cin
613	"2,3,7,8-Tetrachlorodibenzo- <i>p</i> -Dioxin," EPA EMSL-Cin
624	"Purgeables," EPA EMSL-Cin
625	"Determination of Pentachlorophenol Salt in Wastewater," EPA EMSL-Cin
1613	"Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution," EPA OWRS,ITD
1624	"Volatile Organic Compounds by Isotope Dilution GCMS," EPA OWRS, ITD
1625	"Semivolatile Organic Compounds by Isotope Dilution GCMS," EPA OWRS, ITD
D2580	"Test Method for Phenols in Water by Gas-Liquid Chromatography," Annual Book of ASTM Standards, Section 11, ASTM
D3000	"Test Method for Organichlorine Pesticides in Water," Annual Book of ASTM Standards, Section 11, ASTM
D3371	"Test Methods for Nitriles in Aqueous Solution by Gas-Liquid Chromatography," Annual Book of ASTM Standards, Section 11, ASTM
D3534	"Test Method for Polychlorinated Biphenyls (PCBs) in Water," Annual Book of ASTM Standards, Section 11, ASTM
D3973	"Test Method for Low-Molecular Weight Halogenated Hydrocarbons in Water," Annual Book of ASTM Standards, Section 11, ASTM
METHOD SUFFIX	The suffix to the METHOD. The suffix is specific to the sample fraction, matrix, and level. Suffixes are defined as follows:
O-3104	"Organochlorine and Organophosphorus Compounds, Total Recoverable and Dissolved, Gas Chromatographic," Methods for the Determination of Organic Substances in Water and Fluvial Sediments, United States Geological Survey (USGS)
O-3113	"Polynuclear Aromatic Hydrocarbons (PNA), Total Recoverable, High-Performance Liquid Chromatographic," Methods for the Determination of Organic Substances in Water and Fluvial Sediments, USGS
O-3115	"Purgeable Organic Compounds, Total Recoverable, Gas Chromatographic/Mass Spectrometric," Purge and Trap, Methods for the Determination of Organic Substances in Water and Fluvial Sediments, USGS
O-3117	"Acid Extraction Compounds, Total Recoverable, Gas Chromatographic/Mass Spectrometric," Methods for the Determination of Organic Substances in Water and Fluvial Sediments, USGS

ACHIEVABLE DETECTION LEVELS-ABBREVIATIONS
(Continued)

**O-3118 "Base/Neutral Extractable Compounds, Total Recoverable, Gas
Chromatographic/Mass Spectrometric," Methods for the Determination of
Organic Substances in Water and Fluvial Sediments, USGS**

ACHIEVABLE DETECTION LEVELS-ABBREVIATIONS
(Continued)

METHOD SUFFIX

The suffix to the METHOD. The suffix is specific to the sample fraction, matrix, and level. Suffixes are defined as follows:

<u>Suffix</u>	<u>Frac</u>	<u>Matrix</u>	<u>Level</u>
AW	Acid	Water	
BN	Base/neutral		
BNW	Base/neutral	Water	
CHS	Combined	Solid	High
W		Water	

The following codes are used:

EDL	Estimated detection limit
MDL	Method detection limit (49 <u>FR</u> 43234 (Appendix B))
ML	Minimum Level - used in EPA OWRS Industrial Technology Division programs; definition of the minimum level that must give recognizable mass spectra and acceptable calibration points (see footnote 2 on Table 2 of Method 1624, Revision B (49 <u>FR</u> 43234)).

APPENDIX B

GUIDANCE FOR PERMIT WRITERS AND THE PERMITTEE ON THE DEVELOPMENT AND REVIEW OF DISCHARGE-SPECIFIC METHOD DETECTION LIMITS

CHAPTER 1 — WHY ARE DISCHARGE-SPECIFIC MDLS NECESSARY?

1.1 UNDERSTANDING EPA'S STRATEGY

The continuing implementation of EPA's National Pollutant Discharge Elimination System (NPDES) program has resulted in the development of water quality-based effluent limitations (WQBELs) which are below analytical detection levels. EPA's October 20, 1992 document, *National Strategy on the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection Levels* ("the strategy") addresses the issuance of permits that have limits set below the detection levels of current analytical chemistry technology. EPA believes that the implementation of this strategy will result, to the greatest extent possible, in the protection of water quality.

As part of this strategy, EPA has specified that the value in the NPDES permit should be expressed as the calculated WQBELs regardless of the ability to measure to the level of the WQBELs. Permit limits that are expressed as calculated WQBELs are consistent with the requirements found in 40 Code of Federal Regulations (CFR) 122.44(d) which indicate that limits be protective of water quality standards.

The purpose of this guidance is to clarify the provisions in 40 CFR Part 136, Appendix B, for developing site-specific Method Detection Limits (MDLs). Specifically, this guidance addresses those circumstances when the analytical methods do not provide permittees with the capability to measure to levels as low as the WQBEL when determining compliance. For example, a permittee's analytical laboratory may be able to achieve an MDL of only 1.0 mg/L for the analyte of interest in the permittee's discharge due to interferences; however, the MDL provided in an analytical method in 40 CFR Part 136 may be 0.02 mg/L, and the monthly average and daily maximum WQBELs may be 0.0005 mg/L and 0.001 mg/L, respectively. In this situation, compliance cannot be

assured because the analyses provided by the laboratory do not reach the level of the WQBELs. Simply detecting to a level of 1.0 mg/L, or even to the MDL of 0.02 mg/L does not demonstrate compliance with the WQBELs. EPA recognizes that in some cases, permittee laboratories may fail to reach low, but achievable, quantitation levels. Other times, even when quantifying to the lowest levels possible, permittee laboratories may be unable to reach the level of the effluent limitations.

To address this problem, EPA's strategy specifies that in cases where limits are below quantifiable levels, an interim Minimum Level (ML) should be established. The ML is a term that originated in the EPA 1600 Series methods, and is defined as the concentration in a sample that is equivalent to the concentration of the lowest calibration standard analyzed by a specific analytical procedure, assuming that all the method-specified sample weights, volumes, and processing steps have been followed. Because the majority of EPA methods for wastewater analysis do not contain method-specified MLs, EPA has developed an approach for calculating an interim ML for use in permit compliance. That approach often requires the calculation of a discharge-specific MDL.

The interim ML is designed to be used as a quantitation level that facilities must meet in analyzing samples and reporting results. The ML is not to be confused with the basis for determining permit compliance, which is the WQBEL. The ML's role in compliance evaluations is not a direct relationship; rather, it is the threshold for recording the analytical data which will then be summarized and reported on Discharge Monitoring Reports (DMRs). The values reported on the DMRs will be used for determining compliance.

1.2 UNDERSTANDING DISCHARGE-SPECIFIC MDLS

The MDL is defined in 40 CFR Part 136, Appendix E, as "the minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero as determined by a specific laboratory method" (40 CFR Part 136). As specified in 40 CFR Part 136, the MDL may be determined in reagent (blank) water because reagent water is available to all laboratories. The MDL also may be determined in the wastewater of interest, provided that the analyte concentration is adjusted to be within 1-5 times the estimated detection limit.

In this strategy, EPA has established a procedure for estimating the interim ML of an analyte from a discharge-specific MDL. Those procedures are described in Chapter 3 of this guidance.

EPA acknowledges that in a wastewater discharge matrix, permittees may not be able to accurately quantify to the level of the MDL determined in reagent water on all occasions; therefore, EPA addressed this concern through the use of a conversion factor when developing the compliance threshold. This multiplier is 3.18 times the MDL. The calculated ML is then rounded to the nearest multiple of 1, 2, 5, 10, 20, 50, 100, 200, 500, etc., as provided in Section IV of this guidance. When following appropriate analytical procedures and incorporating appropriate quality assurance and quality control practices, most permittees should be able to attain the interim MLs, contained in EPA's strategy, in their discharge-specific matrix.

In some cases however, laboratories may be unable to meet the EPA-specified MDLs, due to matrix interferences. In other cases, inappropriate laboratory techniques and poor adherence to laboratory and quality control procedures will result in permittees failing to meet EPA-specified MDLs. EPA believes that

in cases where true matrix interference can be demonstrated, a discharge-specific MDL is justified as the basis for establishing a site-specific ML. EPA does not believe that laboratory error or the use of an inappropriate analytical method should be used as a basis for seeking discharge-specific MDLs. Therefore, it is important to distinguish the cause of the failure to achieve EPA-specified MDLs so that the strategy will work as planned.

Matrix interferences occur when constituents in a sample other than those being measured cause deviations of the analytical test results. Matrix interferences generally occur as a result of three situations: (1) a substance is similar to the analyte being measured and cannot be distinguished from the analyte, thus producing a higher measured value; (2) a substance reacts with the analyte being measured and produces a lower measured value; and (3) a substance reacts with chemical reagents used in the analysis, and causes a higher or lower measured value.

The evaluation of potential matrix interferences requires both modest investments in analytical testing and data evaluation by the permittee, and a slight increase in the level of oversight performed by the permitting authority. Thus, the determination that a discharge-specific MDL needs to be established should be based on technical goals consistent with the EPA strategy. This guide is designed to help permit writers in making this determination by providing guidelines and procedures under which facilities must conduct studies and, if appropriate, develop discharge-specific MDLs. EPA believes that such guidelines will help meet the goals of the strategy, while precluding the development of discharge-specific MDLs without technical justification.

CHAPTER 2 — HOW DO PERMITTEES DEMONSTRATE THAT DISCHARGE-SPECIFIC MDLS ARE WARRANTED?

Prior to proceeding with the discharge-specific MDL development process, the need for discharge-specific MDLs must be demonstrated. Through this demonstration process, the permitting authority can identify those facilities that warrant discharge-specific MDLs due to matrix interferences. In this process, it is the permittee's responsibility to request discharge-specific MDLs and demonstrate that such an MDL is warranted. It is the permit writer's responsibility to evaluate the adequacy of permittee submittals and determine whether discharge-specific MDLs should be granted based on the submitted information.

EPA provided flexibility for dealing with matrix interferences when it promulgated the analytical methods for the measurement of pollutants in 40 CFR Part 136 (49 FR 43234). The major flexibility options are found in the Preamble, including a mechanism for obtaining approval of an alternate test procedure on a nationwide or discharge-specific basis (40 CFR Parts 136.4 and 136.5). The alternate test procedure process was intended to encourage the development of new analytical methods by instrument manufacturers, permittees, and individual laboratories. However, such new methods may not be used for compliance monitoring purposes without completing the approval process.

The allowance for flexibility in the promulgated methods is intended to give analysts a number of options for resolving analytical problems unique to specific waste waters. The Preamble to the publication of the 600 and 1600 Series Methods in 40 CFR Part 136 on October 26, 1984 contains a lengthy discussion of the need for and allowances for flexibility in these methods. The Response to Comments section also includes a discussion that reads, in part:

"Analysts may also use their discretion in selecting cleanup procedures. EPA has also relaxed the strict protocol for

sample extract concentration . . . Accordingly, within the scope of the GC, HPLC, and GC/MS test procedures, analysts are permitted some discretion in selection of concentration techniques."

In addition, the 600 and 1600 Series Methods for organic pollutants contain a statement to the effect that the analyst is permitted to modify the method to "improve separations or lower the costs of analyses" provided that the results are not less precise or less accurate than the results obtained using the unmodified method. As a result, analysts may use their discretion in selecting packed or open tubular columns, operating temperatures, carrier gas or solvent flow rates, and type of detector, as well as cleanup procedures and extract concentration procedures, within guidelines outlined in each method and in the Preamble to the regulation.

EPA recognizes that there may be a few intractable sample matrices that do not yield to extensive analytical efforts. In this case, the analyst must document for EPA the steps taken by the analyst, the solutions found, and the instances in which a given matrix did not yield to known analytical techniques. EPA does not wish to learn that "the sample couldn't be analyzed" and that an analyst made no attempt to reduce the matrix interferences. EPA will view the lack of an attempt to overcome matrix interferences as in direct conflict with the spirit of flexibility permitted by the regulation and the methods.

EPA has set forth guidelines by which permittees may request discharge-specific MDLs, therefore, permit writers can evaluate discharge-specific MDL requests in a consistent and thorough manner. The suggested roles of the permittee and permit writer in this process are discussed below. To provide more information to both the permittee and the permit writer in determining how to demonstrate that discharge-specific MDLs are appropriate, example solutions to matrix interference problems, and case histories of industry claims of matrix interferences have been provided. The

examples are taken directly from *Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring*, June 1993 (EPA 821-B-93-001) (Monitoring Guidance). Copies of this document may be obtained from the Office of Water, Engineering and Analysis Division, Office of Science and Technology, 401 M St., SW, Washington, DC 20460.

2.1 PERMITTEE'S ROLE

To demonstrate that discharge-specific MDLs are warranted, each permittee must:

- Demonstrate that the permittee's laboratory is capable of achieving the EPA-specified MDL in reagent (blank) water; that is, the permittee should test spiked reagent water to illustrate that the EPA-specified MDL can be met by the analytical laboratory;
- Demonstrate that a reasonable attempt to resolve the matrix interference has been made using the approaches suggested in the Monitoring Guidance; and
- Demonstrate that the EPA-specified MDL cannot be achieved in the permittee's effluent.

These demonstrations require that the permittee's role be primarily one of analytical testing, because qualitative assessments of laboratory capabilities and matrix problems are not sufficient. Thus, an analytical testing program must be implemented by the permittee and must consist of the following:

- Testing of spiked reagent water to illustrate that the EPA-specified MDL can be met;
- Testing of effluent discharge to demonstrate that matrix interferences occur and that the EPA-specified MDL for reagent water cannot be met in the effluent; and
- Testing of the approaches suggested in the Monitoring Guidance, and testing of other analytical approaches to demonstrate that matrix interferences cannot be overcome.

For each analyte for which discharge-specific MDLs are requested, permittees should conduct testing of samples of spiked reagent water and samples of effluent discharge. The permittee may not assume that matrix interferences for one analyte are necessarily an interference for another analyte. The number of samples and replicates that are required for this demonstration may differ based on the permittee's situation.

In many cases, the permittee may employ a commercial laboratory for its compliance monitoring analyses. In these instances, the role of the permittee is to: 1) establish the testing program outlined above, 2) have the testing program implemented by the laboratory, 3) collect all the relevant information from the laboratory, and 4) use it to demonstrate to EPA that a discharge-specific MDL is warranted. When a commercial laboratory is employed for such a testing program, it is imperative that the same laboratory that was used to demonstrate that the EPA-specified MDL can be achieved in reagent water also be used to demonstrate that the EPA-specified MDL cannot be achieved in the permittee's effluent. Ideally, both demonstrations also should involve the same analytical instrumentation and personnel. EPA recognizes that this may not always be practical in a commercial laboratory setting. However, EPA expects that where this is not practical, the instruments and personnel used for both demonstrations will have equivalent capabilities. For instance, it would not be appropriate to use a more sensitive instrument for the reagent water testing and a less sensitive instrument for the effluent testing.

Ultimately, the permittee must demonstrate to the permit writer's satisfaction that a discharge-specific MDL is warranted; also, this demonstration must be supported by specific analytical data. The following checklist of laboratory data, which is required to support a claim that a permittee has been unable to measure pollutants due to matrix interferences, was taken from

the Monitoring Guidance; however, this checklist, shown in Exhibit 2-1, has been modified to also include data related to the analysis of metals.

2.2 PERMIT WRITER'S ROLE

The permit writer's role in the process of demonstrating that a discharge-specific MDL is warranted can be summarized into three specific functions:

- Recognizing situations in which discharge-specific MDL development may be necessary;
- Specifying prerequisite requirements and time frames for permittees to submit demonstrations of the need for discharge-specific MDLs; and
- Evaluating the adequacy and accuracy of permittee demonstrations of the need for discharge-specific MDLs.

A discussion of these roles follows.

At some point in the permitting process, the permit writer may recognize that reported analytical data do not achieve the EPA-specified MDLs. This may occur prior to drafting the permit as a result of reviewing DMR or other data. It is also possible that the permit writer may be well into the permit development stage prior to noting that, based on data such as that submitted in a permit application form, the interim MLs specified in EPA's strategy will not be met. A permittee's inability to meet the EPA-specified interim MLs may be the result of one of two situations: (1) the laboratory simply is not measuring to the lowest level of sensitivity, namely the EPA-specified interim ML; or (2) matrix interferences or laboratory error result in the laboratory not measuring to the EPA-specified interim ML. Permit writers have few options outside of requiring a permittee to both re-analyze for parameters of concern, and then resubmit data that meets the EPA-specified interim ML (to distinguish between these two situations). Because parameter-specific analyses may be

**EXHIBIT 2-1: CHECKLIST OF LABORATORY DATA TO DEMONSTRATE
MATRIX INTERFERENCE**

Type of Laboratory Data	Examples
Method number of the base method used for the measurement.	<ul style="list-style-type: none"> • Method number from 40 CFR Part 136 • Changes made to the EPA method should be described, including supporting data that demonstrates equivalent performance
Detailed narrative discussing the problems with the analysis, corrective actions taken, and the changes made to the base method identified above.	<ul style="list-style-type: none"> • Permittee must require analytical chemist to thoroughly document problems encountered and solutions attempted
Summary level report or data reporting forms giving the pollutants for which analyses were conducted and the concentrations detected. For the pollutants that were not detected, the detection limits or estimated detection limits, must be provided.	<ul style="list-style-type: none"> • Results should be provided for each field sample analyzed, including all dilutions and reanalyses • The means for estimating detection limits must be provided • If flags are used in the laboratory report, the definitions must be provided with the data
Summary of all quality control results required by the base method, including but not limited to the examples shown.	<ul style="list-style-type: none"> • Instrument tuning • Calibration • Calibration verification • Initial precision and recovery • Ongoing precision and recovery • QC check standard • Matrix spike, matrix spike duplicate results • Surrogate recoveries • Labeled compound recoveries for isotope dilution methods • Blank results • Serial dilutions • Method of standard additions, if applied • Interference check standards • Quality control charts and limits

**EXHIBIT 2-1: CHECKLIST OF LABORATORY DATA TO DEMONSTRATE
MATRIX INTERFERENCE (continued)**

Type of Laboratory Data	Examples
Raw data that allow an independent reviewer to validate each determination and calculation performed by the laboratory, including but not limited to the examples shown.	<ul style="list-style-type: none"> • Sample numbers or other identifiers • Extraction/digestion dates • Analysis dates and times • Sequence of analyses and run logs • Sample volume • Extract volume prior to and after each cleanup step • Final extract volume prior to injection • Digestion volume • Titration volume • Percent solids or percent moisture • Dilution data • Instruments and operating conditions • GC/MS, GC, AA, and ICP operating conditions • Chromatograms, ion current profiles, bar graph spectra, library search results • Quantitation reports, data system outputs, and other data used to link raw data to results reported • AA and ICP peak profiles and raw data • Direct instrument readouts • Laboratory bench sheets, logbook pages
Example calculations that allow the data reviewer to determine how the laboratory used the raw data to arrive at the final results.	<ul style="list-style-type: none"> • Examples of both detected and nondetected compounds • Show all adjustments for sample volume, dry weight, etc.
For GC/MS and other instruments involving data systems, the permittee should be prepared to submit raw data on magnetic disk upon request by EPA.	
Names, titles, addresses, and telephone numbers of the analysts who performed the analyses, and the quality assurance officer who will verify the analyses.	
Summary of steps taken to overcome matrix interferences	<ul style="list-style-type: none"> • References to sections in the Monitoring Guidance • Details of other approaches used to overcome interferences

costly and often point to the need to develop discharge-specific MDLs, it may be more reasonable for the permitting authority to require the permittee to conduct analytical testing as part of discharge-specific MDL demonstrations (discussed below).

Ultimately, the review of these demonstrations may result in additional burdens being placed on permittees and permitting staff. Thus, when it becomes evident that discharge-specific MDLs may be needed, it is to the permitting authority's advantage to have a well-planned program in place that stipulates the permittee's role in the process of demonstrating the need for a discharge-specific MDL. For example, establishing prerequisite standard procedures for permittees in a short guide may help to initially explain the demonstration process, and therefore, may help to avoid a deficient submittal that could result in resource expenditures by both permittees during revisions and permit writers during reevaluation. Another idea is to require the submittal of data in a simple format that can be easily reviewed. Some additional considerations to help ensure the completeness and accuracy of submittals include prerequisite requirements for the following:

- The simultaneous submittal of all necessary data,
- A statement indicating that the laboratory in which analyses for this demonstration package were performed is the same as the laboratory that will be used in subsequent testing;
- A statement indicating that the samples used during the demonstration process are representative of the discharge;
- A statement indicating that all data that were generated as part of this demonstration are being submitted;
- Specification of the laboratory method(s) used; and
- Reference to the sections of the Monitoring Guidance that were applied in attempts to overcome matrix interference problems.

As previously indicated, the permittee's responsibilities will primarily entail analytical testing. Permit writers should consider prescribing the desired amount of analytical testing to help avoid deficient submittals. Four approaches suitable for different analytical testing requirements are described in Exhibit 2-2.

EXHIBIT 2-2: DECISION MAKING PROCESS FOR REQUIRING TESTING

Analytical Requirement	Variables
Perform a single analysis each of one aliquot of reagent water and one aliquot of effluent discharge	<ul style="list-style-type: none"> • Laboratory performance not questionable • Matrix interference very likely
Perform analyses of several replicates of reagent water and a single sample of effluent discharge	<ul style="list-style-type: none"> • Laboratory performance questionable • Matrix interference very likely
Perform analyses of a single sample of reagent water and several samples of effluent discharge	<ul style="list-style-type: none"> • Laboratory performance not questionable • Matrix interference questionable
Perform analyses of several replicates of reagent water and several aliquots each of the different samples of effluent discharge	<ul style="list-style-type: none"> • Laboratory performance questionable • Matrix interference questionable

The permit writer can determine if a potential matrix interference exists by comparing the MDL determined in reagent water to the MDL determined in the permittee's discharge. If the MDL in the discharge is greater than twice the MDL in reagent water, then a potential matrix interference exists.

In comparing the MDLs determined in reagent water and in the permittee's discharge, the permit writer should evaluate data that reflect the quality of the laboratory as well as the MDLs currently achieved by the permittee. Information available in making an assessment of this type can be obtained through review of:

- **Inspection reports:** Inspection reports such as compliance evaluation inspections and performance audit inspections (PAIs) may point to laboratory performance problems. PAIs also may provide overviews of procedural problems with individual parameters which may include matrix interference problems or in some cases, may show that an analytical method less sensitive than needed is currently being used. Information on quality assurance and quality control (QA/QC) measures also may point to performance problems.
- **DMR QA program data:** The DMR QA program was established to periodically evaluate the quality of data submitted on DMRs by requiring laboratories to perform analyses on samples containing unknown quantities of analytes. At least annually, these unknown samples are sent to permittees. The resulting DMR QA program data

may provide trends showing problems in the analyses for particular parameters.

- **DNR and permit application form data:** This data indicates permittee laboratory performance. Past DNR data that are at concentrations above the EPA-specified interim ML may have been questioned by the enforcement or permitting staff. As a result, matrix interference concerns may have been previously addressed. Data from the DNR and application form may show trends where particular parameters are above EPA-specified interim MLs while others are not. This may point to matrix interference.
- **Laboratory certification programs:** Many states have laboratory certification programs that require that all analyses for parameters of concern be certified. These programs vary widely. Some may involve laboratory inspection programs and more frequent DNR QA requirements, while others do not. However, some information may be gained from records of these programs.

If the permittee has employed a number of laboratories for testing in the recent past, these sort of historical records may be less valuable. Permit writers may find it useful to consult with personnel from the state laboratory or the EPA Regional laboratory who may have experience with the analysis of the permittee's effluent or with the methods in question.

Once the permittee has completed analytical testing in accordance with the permit writer's instructions, the request to develop a discharge-specific MDL must be submitted for review and approval. At this point, the permit writer must review these requests for completeness and accuracy. Here, the permit writer's primary responsibility is ensuring that matrix interferences are the true cause of a laboratory's inability to reach the quantifiable level. This evaluation requires a certain level of expertise in laboratory data evaluation because it involves a thorough review of analytical data sheets. Again, consultations with state and EPA Regional laboratory personnel may be useful.

EPA highly encourages permit writers to be proactive in providing permittees with support and guidelines in the conduct of this demonstration process. Chapter 3 of this document provides a discussion on how the discharge-specific MLs are developed. Permit writers should consider establishing procedures in which demonstrations are approved prior to permittees being authorized to proceed with discharge-specific MDL development. Ultimately, such procedures will help minimize resource burdens on both permit writers and permittees.

2.3 EXAMPLES OF SOLUTIONS TO MATRIX PROBLEMS

Some example solutions to matrix problems are described below. These examples are taken from *Guidance on Evaluation, Resolution, and Documentation*

of Analytical Problems Associated with Compliance Monitoring (Monitoring Guidance). Other solutions addressing specific parameters and using laboratory techniques of interest, may be found by conducting literature searches. The examples provided here are intended to help the analyst understand how to develop solutions to matrix problems by utilizing the flexibility provided by the EPA methods. Any modifications made to EPA methods within the scope of the allowed flexibility *must be tested* by performing the initial demonstration of capabilities (the "start up" tests) and by meeting the performance specifications described in the 40 CFR Part 136 methods prior to using the modified method for compliance monitoring.

The issue of increased laboratory costs for resolving matrix interference problems is also addressed in the document cited above. Some estimated incremental costs associated with cleanup techniques and other approaches are provided, ranging from no increased costs (associated with the use of GC with selective detector in place of GC/MS), to as much as \$500 per sample (associated with the use of isotope dilution GC/MS in Methods 1624 and 1625). However, costs may vary, depending on the laboratory, the number of samples, laboratory capacity, and other factors.

Examples of solutions to matrix interferences in samples containing volatile organic pollutants:

- *Use of selective GC detectors.* The CWA 304(h) methods for volatiles include EPA methods 601, 602, 603, 624, and 1624. When effluent limits are in the 10 µg/L or greater range, the selective GC detectors allow detection levels well below those achieved by mass spectrometers. The specificity provided by electrolytic conductivity detector and by the photoionization detector allow detection of the halogenated and aromatic analytes, respectively, in complex matrices.
- *Concentrated samples: micro-extraction and gas chromatography with selective detectors.* The selective GC detectors in Methods 601 and 602 provide sensitivity that is 10 to 100 times greater than that required to detect the analytes of interest. Some of this sensitivity can be used to substitute micro-extraction in place of purge-and-trap. The advantage of micro-extraction is that the pH of the water can be adjusted to attempt to keep the interferences in solution while the analytes of interest are extracted.
- *Sample dilution.* Methods 601 and 602 can achieve method detection limits of less than 1 µg/L for many volatile analytes. The added sensitivity of selective GC detectors can be used to overcome matrix problems by diluting the sample by a factor of 10 to 100. Even with such dilutions, the pollutants can be detected at the levels required, and the effects of interferences can be reduced or eliminated.
- *Isotope dilution.* Method 1624 employs stable isotopically labeled analogs of the pollutants as internal standards in the analysis. The use of these labeled compounds frequently permits the pollutant to be determined in the presence of interferences. This is due to the unique spectrum of the labeled compound which can be located in the presence of these interferences. The pollutant's spectrum, can then be located by reference to the labeled compound.

Examples of solutions to matrix interferences in samples containing semivolatile organic pollutants include:

- *Use of selective GC detectors.* EPA methods 604 through 612 employ gas chromatography with selective detectors and high performance liquid chromatography with an ultraviolet (UV) detector to detect pollutants in the presence of interferences. As with volatiles, the added sensitivity of the selective detectors permits the sample to be diluted by a factor of 10 to 100 while allowing detection of the analytes at the effluent limits specified in most permits.
- *Use of pH change.* A very powerful means of separating the pollutants of interest from interferences is to adjust the pH of the sample to keep the interferences in solution while allowing the pollutants to be extracted in an organic solvent. For example, neutral pollutants can be extracted at either low or high pH.
- *Gel permeation (size exclusion) chromatography.* This technique is described in Revision C of Method 1625. The same technique is used in the Superfund Contract Laboratory Program (CLP) methods and SW-846 methods, and has been shown to be effective for removing lipids and high molecular weight interferences that can degrade GC and mass spectrometer performance.
- *Use of adsorbents florisil, alumina, and silica gel.* These adsorbents are effective in separating neutral species from polar interferences. For polar analytes of interest, the adsorbent must be evaluated to determine if the analyte will be recovered. The level of activation of the adsorbent plays a major role in this recovery process.
- *Isotope dilution.* Method 1625 permits determination of pollutants in the presence of interferences in semivolatile samples in the same way described for volatiles. In addition, the ranges of recoveries of the labeled analogs permitted in the method allow for quantitation of the pollutant when interferences reduce the efficiency of the extraction.

If any of these techniques are applied to the analysis of waste water samples under the allowance for flexibility in 40 CFR Part 136 methods, their use must be supported by performing the initial demonstration of capabilities using these modifications. This demonstration must take place before the modified method is applied to the analysis of samples, and must meet the performance specifications of the original method.

2.4 CASE HISTORIES OF CLAIMS OF MATRIX INTERFERENCES

The case histories presented below were adapted from the *Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring* (Monitoring Guidance). These case histories demonstrate cases in which the permittees and/or the contract laboratories were using incorrect analytical methods, did not follow the required procedures in 40 CFR Part 136, did not submit data necessary to document that the methods were being followed, or did not submit documentation regarding the nature of interferences and the attempts (if any) to resolve these interferences. These case histories are included here to provide examples of

the type of response that permit writers may receive from dischargers who claim that they are unable to meet permit limits due to interferences. The identities of the dischargers and the analytical laboratories are not disclosed.

Case History 1 - The information submitted by the analytical laboratory revealed inconsistencies with the stated analytical methods. The discharger allowed the laboratory to use either methods alternate to 40 CFR Part 136, or to use modifications to methods 624 and 625. Alternate methods are allowed under 40 CFR Parts 136.4 and 136.5, provided that the facility submits the alternate methods to EPA's Environmental Monitoring and Support Laboratory in Cincinnati, Ohio (EMSL-Ci) for approval. Otherwise, alternate methods are not allowed. No reference to alternate methods approved by EMSL-Ci was found.

If methods 624 and 625 were modified as allowed under 40 CFR Part 136, these modifications were not documented and equivalence was not demonstrated. Modifications that were made by the laboratory to these methods included:

- Combining acid and base/neutral fractions;
- Using a fused silica capillary column for the analysis; of acid and base/neutral fractions;
- Employing alternate internal standards;
- Employing alternate surrogates;
- Achieving higher detection limits;
- Using fewer matrix spike compounds; and
- Using matrix spike amounts inconsistent with regulatory compliance, background, or method-specified levels.

EPA recognizes that the use of multiple internal standards and a fused capillary column for the base/neutral/acid fraction represent improvements; however it does not believe that combining fractions, higher detection limits, alternate matrix spike compounds, and matrix spike amounts which are inconsistent with background or regulatory compliance levels represent improvements. On the contrary, these changes degrade method performance, and are therefore in violation of both the spirit and letter of the flexibility permitted in the 600/1600 Series 40 CFR Part 136 organic methods.

The detection limits reported for the semivolatiles were, for the most part, twice the MLs given in method 1631 and were approximately 10-20 times the MDLs given in Method 625. No explanation for the increased detection levels was given, nor could the limits be derived in any meaningful fashion from the data provided. The laboratory made no attempt to clean up the samples using pH change, gel permeation chromatography, or the other techniques in the 600/1600 Series methods or the draft Monitoring Guidance that had been provided to the permittee.

Case History 2 - The permittee provided insufficient information for a detailed review of the analytical results. The discharger in this case history submitted samples to a contract laboratory for analyses by a GC/MS method which failed to produce useful results. The discharger and/or the laboratory attributed the problems to large concentrations of acetone in the discharge. However, this problem could not be confirmed from the information provided. The discharger's analytical laboratory proposed an approach to overcome the interference problems. This solution was to employ Methods 601 and 602 for the volatiles analysis. Because these methods are both more sensitive and more selective than a GC/MS method, the analytes regulated should be measurable in the presence of a large concentration of acetone. The discharger chose to ignore the laboratory's proposal and submitted a claim of matrix interference. EPA believes that the approach suggested by the laboratory is workable and appropriate, and should have been attempted. Furthermore, the documentation of the laboratory results should include the material listed in Exhibit 2-1, Checklist of Laboratory Data.

Case History 3 - The permittee submitted letters and reports from several contract laboratories, with only some of the data specified in Exhibit 2-1, Checklist of Laboratory Data. Data items that were submitted included instrument tunes, run chronologies, chromatogram, calibration data, calibration verification data, results for blanks, quantitation reports for samples, and matrix spike data runs against the QC limits for Methods 624 and 625. Missing were the initial precision and recovery (IPR) data that demonstrate method equivalence.

The semivolatile matrix spike data were puzzling. The results of the unspiked samples indicated that some of the acids and base/neutrals were not detected, yet the results for the spiked samples showed large concentrations of some of these analytes that were not spiked into the samples. The volatiles matrix spike had been diluted by a factor of 200 and spiked after dilution. Diluting and spiking will not show matrix interferences, and thus these data are of no value in evaluating the undiluted sample results.

Case History 4 - The permittee submitted summary reports from the analytical laboratory. None of the materials submitted contained the information required, as listed in Exhibit 2-1, Checklist of Laboratory Data, and none of the materials contained explanations of the nature of the interferences found or descriptions of attempts to overcome the interferences.

Undoubtedly, permit writers have or will encounter situations not described in these case histories. However, the similarity among these cases

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that will likely apply to other situations is the lack of documentation provided by the permittees when making claims of matrix interferences or other analytical difficulties. The information necessary to evaluate such claims is outlined in the checklist in Exhibit 2-1, and includes the information that is necessary to demonstrate that a matrix interference is present and to demonstrate the performance of any method modifications made under the allowance for flexibility in 40 CFR Part 136.

CHAPTER 3 - HOW ARE DISCHARGE-SPECIFIC MDLs DEVELOPED?

Once the permittee has demonstrated to the permit writer's satisfaction that a discharge-specific MDL is warranted, the process of developing discharge-specific MDLs begins. In this process, it is the permittee's responsibility to develop a technically-based discharge-specific MDL and use this to determine an appropriate interim ML. As in the demonstration of whether the permittee warrants a discharge-specific MDL, the permit writer's role is one of oversight. The permit writer must evaluate the adequacy of the permittee submittals and determine whether or not the discharge-specific MDL developed by the permittee is appropriate and should be granted. Information contained in this document does not differ from that given in 40 CFR Part 136, and is intended to provide guidance on the applicability of the regulation to the development of discharge-specific MDLs when matrix interferences are a problem.

3.1 THE PERMITTEE'S ROLE

EPA has set forth a procedure for the development of discharge-specific MDLs in Appendix B to 40 CFR Part 136. This procedure can be used with a wide variety of sample types ranging from reagent water containing an analyte to wastewater containing an analyte. However, in the development of a discharge-specific MDL, the matrix must be wastewater. The MDL procedure was designed for applicability to a broad variety of physical and chemical methods, and as such, the procedure is device- and instrument-independent. However, the calculated MDL value is essentially a "snapshot" of laboratory capability at the time that the MDL was determined. Therefore, it is imperative that discharge-specific MDLs be developed in each laboratory in which the permittee's samples will be analyzed for the analytes in question. Given the cost of developing discharge-specific MDLs, it may be to the permittee's advantage to limit the number of laboratories that are employed for routine analyses.

Permittees who wish to develop discharge-specific MDLs must follow the procedures set forth in Appendix B to 40 CFR Part 136. A summary of the discharge-specific MDL development process is provided below:

- *Step 1: Make an initial estimate of the detection limit;*
- *Step 2: Prepare a laboratory standard in the discharge-specific matrix that contains an acceptable concentration of the analyte;*
- *Step 3: Take a minimum of seven aliquots of the discharge sample and process these sample aliquots through the entire analytical method, recording the measurements;*

- **Step 4:** Calculate the variance and the standard deviation of the replicate measurements;
- **Step 5:** Calculate the MDL; and
- **Step 6:** Verify the reasonableness of the estimated detection limit and the subsequent MDL determination.

Step 1 involves making an initial estimate of the detection limit using the permittee's best judgement. One of the four following techniques set forth in Appendix B to 40 CFR Part 136 must be used when formulating an initial estimate:

- Determine the concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5;
- Determine the concentration equivalent to three times the standard deviation of replicate instrumental measurements of the analyte in reagent (blank) water;
- Locate the region of the standard curve where there is a significant change in sensitivity (i.e., a break in the slope of the standard curve); and
- Utilize the instrumental limitations.

In **Step 2**, a wastewater discharge sample should be obtained and analyzed to determine if the analyte is in the recommended range of 1 to 5 times the estimated detection limit. If so, it can be used for developing an MDL. If not, and the measured level of analyte is less than this recommended range, a known amount of analyte should be added to bring the level of analyte to the recommended range of between one and five times the estimated detection limit. On the other hand, if the measured level of analyte is greater than five times the estimated detection limit, there are two options. The first option is to obtain, if possible, another wastewater discharge sample with a lower level of analyte. The other option is to use the sample as is, as long as the analyte level does not exceed ten times the EPA-specified MDL. When the measured level of analyte is between 5 and 10 times the estimated detection level, it is important to realize that the resulting discharge-specific MDL may not be truly reflective of lower analyte concentrations. This is because the variance of the analytical method is a function of concentration.

Step 3 involves analyzing a minimum of seven aliquots of the wastewater discharge sample. This is the core of the discharge-specific MDL development process. Strict adherence to procedures and well-kept records are essential.

If a blank measurement is required by the analytical method to calculate the measured level of analyte (e.g., for a spectrophotometric method involving a color change), then a separate blank is analyzed for each sample aliquot.

Each blank measurement should be subtracted from the respective sample measurement to obtain the final result. These blank-subtracted results are then used to calculate the MDL. (Note: This blank subtraction only applies to those 40 CFR Part 136 methods that explicitly require it. It does not apply to those methods that require the preparation of a method blank concurrent with the sample preparation (i.e., it does not apply to the 600 or 1600 Series EPA methods)).

Before performing all seven analyses, it may be economically and technically desirable to evaluate the estimated MDL before analyzing all seven aliquots. To ensure that the MDL estimate is appropriate, it is necessary to determine that a lower concentration of analyte will not result in a significantly lower discharge-specific MDL. To do this, two aliquots of the wastewater discharge sample should be processed through the entire method, including the blank measurements described above. If the measurements indicate that the sample is in a desirable range for determining the MDL, the five additional aliquots can be analyzed and all seven measurements can then be used to calculate the MDL. If the measurements indicate the sample is not in the correct range, the MDL should be re-estimated, a new wastewater discharge sample should be obtained as described in Step 2, and Step 3 should be repeated.

In Step 4, the variance (S^2) and the standard deviation (S) of the replicate measurements taken in Step 3 are calculated as follows:

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

and

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

where $X_1 \dots X_n$ are the analytical results in the final method reporting units obtained from the n sample aliquots and \sum is the sum of the values X_1 to X_n .

Note that the calculation of S^2 uses $n-1$ degrees of freedom.

Step 5 involves the calculation of the MDL using the equation:

$$MDL = t_{(n-1, 1-\alpha/2)} (S)$$

where $t_{(n-1), 0.99}$ = the Student's *t* value appropriate for a 99% confidence level and *n*-1 degrees of freedom.

Step 6 is the iterative procedure in 40 CFR Part 136 that must be used to verify the reasonableness of the MDL. It is also the step that is most often overlooked. The calculated MDL value is compared to the estimated detection limit determined in Step 1. If the spiking level used was not within a factor of five of the calculated MDL, then the calculated MDL value is not valid. The reason for this test is that while the absolute variability in an analytical measurement increases with increasing concentration, the relative variability embodied in the standard deviation decreases with increasing concentration. Thus, samples spiked at the very high concentration may result in a very low MDL value that is not representative of the capabilities of the analytical procedure at the lower limit of its sensitivity.

In addition, the procedures in Appendix B 40 CFR Part 136 contain instructions for an optional iterative procedure to evaluate the reasonableness of multiple MDL determinations. Given the cost concerns that exist in discharge-specific MDL determinations, this optional procedure is not discussed here.

Once the permittee has developed a discharge-specific MDL for each analyte, this MDL is translated into a calculated interim ML by multiplying the discharge-specific MDL by a factor of 3.18. The calculated interim ML is rounded to 0.1, 0.2, 0.5, 1, 2, 0.5, 1, 2, 5, 10, 20, 50, etc. to produce the final interim ML. Rounding simplifies both the calibration of analytical instruments and the reporting of results on the DMR.

There are no precise rules to apply to the level of effort that must be expended in this procedure. However, it is the permittee's responsibility to gather the appropriate data that will substantiate the discharge-specific MDL. In developing the discharge-specific MDL, it is the permittee's responsibility to ensure that the proper procedures have been followed, that adequate data have been collected, and that sufficient documentation is provided to justify the discharge-specific MDL.

3.2 PERMIT WRITER'S ROLE

The permit writer's role in the discharge-specific MDL development is one of oversight and evaluation. To fulfill this role, the permit writer must fully understand the discharge-specific MDL development requirements and the process by which the MDLs are used to generate the interim MLs. It also

requires that the permit writer either possess or obtain the technical expertise required to evaluate the supporting data, determine the adequacy of assumptions, and interpret the data results. As noted in Chapter 2, during this evaluation, the permit writer may wish to consult with others, including personnel from state and EPA Regional laboratories.

It is imperative that the data provided by the permittee for evaluation allow the permit writer to reach the same conclusions and develop the same discharge-specific MDL. As such, the permit writer should be prepared to take the data submitted by the permittee and calculate a discharge-specific MDL for verification purposes.

As part of this process, the permit writer may be expected by the permittee to act as a technical resource in understanding procedures for discharge-specific MDL development. Additionally, the review of these requests may result in burdens being placed on permittees and permitting staff. As discussed previously under Section 2.2, it may be advantageous for the permitting authority to have a set program that involves roles and responsibilities, and procedures for implementation. Establishing standard procedures for permittees similar to those outlined in Section 3.1 may be useful, as would the use of a standard report format/outline or standard summary form. Exhibit 3-1 provides one example of such a standard format. Other suggestions that may ease the burden on the permittee and permit writer have been highlighted in Section 2.2.

EXHIBIT 3-1: DISCHARGE-SPECIFIC MDL DEVELOPMENT WORKSHEET

DISCHARGE-SPECIFIC MDL DEVELOPMENT WORKSHEET

Facility Name: _____ Date: _____

Facility Address: _____

Permit Number: _____

Pollutant: _____

Sample Matrix: _____

Initial Estimate of MDL Based on: (Check one)

- ___ a. Concentration value that corresponds to an instrument signal/noise in the range of 2.5 to 5
- ___ b. Concentration equivalent to three times the standard deviation of replicate instrumental measurements of the analyte in reagent water
- ___ c. The 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. The instrumental limitations, which are described below.

ANALYTICAL TEST RESULTS

<u>Replicate</u>	<u>Result</u>	<u>Blank *</u>	<u>Difference*</u>
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

Concentration Units _____

* Note that results for the blank and the blank-subtracted result (difference) only apply to those 40 CFR Part 136 methods that explicitly require a blank correction.

s^2 = _____

Spiking Level _____

S = _____

t = _____

Use $n-1$ degrees of freedom for S^2 and t . A minimum of 7 replicates are required.

MDL = _____

APPENDIX C

RECOMMENDED NPDES PERMIT WRITING BOILERPLATE LANGUAGE

RECOMMENDED PERMIT WRITING BOILERPLATE LANGUAGE

This appendix provides recommended boilerplate language to use when including WQBELs in permits. The example used represents a hypothetical situation in which the discharger's permit contains a WQBEL for mercury. In addition, the example only addresses this specific limit and the portions of the permit that are directly related. This example is not intended to represent an entire permit, nor is it intended to be a recommendation to establish a limit for mercury.

RECOMMENDED PERMIT WRITING BOILERPLATE LANGUAGE

A. EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS

1. During the period beginning on the effective date of this permit and lasting through the expiration date, the Permittee is authorized to discharge from outfall(s) serial number(s) 001: noncontact cooling water, boiler blowdown, and treated process water to the Merrie River.

Such discharge shall be limited and monitored by the Permittee as specified below:

<u>EFFLUENT CHARACTERISTICS</u>	<u>DISCHARGE LIMITATIONS</u>				<u>MONITORING REQUIREMENTS</u>	
	(lbs/day)		Other Units (Specify)		Measurement	Sample
	Monthly	Daily	Monthly	Daily	Frequency	Type
	Average	Maximum	Average	Maximum		
Flow (MGD)	N/A	N/A	Report	Report	Continuous	Recorder
Mercury, Total (1)	0.0084	0.025	0.1 µg/L	0.3 µg/L	1/week	Grab

(1) The water quality-based effluent limitations for this parameter are not quantifiable using EPA approved analytical methods. Thus, EPA has set forth a reporting threshold to measure the highest, acceptable quantification level for this parameter. This reporting threshold does not authorize the discharge of total mercury in excess of the WQBELs. For more information, see special condition A in this permit.

RECOMMENDED PERMIT WRITING BOILERPLATE LANGUAGE (Continued)

A. Conditions Applicable to WQBELs Below Detection Levels

1. For purposes of reporting, the Permittee shall use the reporting threshold equivalent to the ML. The ML is defined as the concentration in a sample equivalent to the concentration of the lowest calibration standard analyzed in a specific analytical procedure assuming that all the method-specified sample weights, volumes, and processing steps have been followed. As such, the permittee must conduct analyses in accordance with the method specified below and must utilize a standard equivalent to the concentration of the ML specified below:

<u>Parameter</u>	<u>Analytical Method</u>	<u>ML and Lowest Calibration Concentration</u>
Mercury	245.2	0.2 µg/L

2. For purposes of reporting on the discharge monitoring report, actual analytical results should be reported whenever possible. All analytical values at or above the ML shall be reported as the measured value. When results can not be quantified, values below the ML shall be reported as "0".
3. In the "Comment Section" of the DMR, the permittee shall report the lowest calibration standard used, the ML achieved, and the number of times non-detectable results were reported as "0".

APPENDIX D

RECOMMENDED PERMITTEE PROCEDURES FOR REPORTING

PERMITTEE PROCEDURES FOR REPORTING

RECOMMENDED PERMITTEE PROCEDURES FOR REPORTING

When reporting analytical data on Discharge Monitoring Report (DMR) forms, permittees should follow the instructions set forth in the EPA Office of Water publication entitled *NPDES Self-Monitoring System User Guide*, March 1985. Reporting procedures also have been summarized in the general instructions given on the DMR report form. These instructions are provided below.

DMR General Instructions

1. If form has been partially completed by preprinting, disregard instructions below pertaining to preprinted information.
2. Enter "PERMITTEE NAME/MAILING ADDRESS" (and facility name/location, if different). Enter "PERMIT NUMBER," and "DISCHARGE NUMBER" where indicated. (A separate form is required for each discharge.)
3. Enter beginning and ending dates for "MONITORING PERIOD" covered by form where indicated.
4. Enter each "PARAMETER" as specified in monitoring requirements of permit.
5. Enter "SAMPLE MEASUREMENT" data for each parameter under "QUANTITY AND "QUALITY" in units specified in the permit. "AVERAGE" is normally arithmetic average (geometric average for bacterial parameters) of all sample measurements for each parameter obtained during "MONITORING PERIOD." "MAXIMUM" and "MINIMUM" are normally extreme high and low measurements obtained during "MONITORING PERIOD." (NOTE to municipals with secondary treatment requirement, enter 30-day average of sample measurements under "AVERAGE" and enter maximum 7-day average of sample measurements obtained during monitoring period under "MAXIMUM.")
6. Enter "PERMIT REQUIREMENT" for each parameter under "QUANTITY" and "QUALITY" as specified in permit.
7. Under "NO. EX" enter the number of sample measurements during monitoring period that exceed the maximum and/or 7-day or monthly average (and/or are lower than the minimum) permit requirement for each parameter. If none, enter "0."
8. Enter "FREQUENCY OF ANALYSIS" both as "SAMPLE MEASUREMENT" (actual frequency of sampling and analysis used during monitoring period) and as "PERMIT REQUIREMENT" specified in

PERMITTEE PROCEDURES FOR REPORTING

permit (e.g. enter "CONT." for continuous monitoring; "1/7" for one day per week. "1/30" for one day per month; "1/90" for one day per quarter, etc.)

9. Enter "SAMPLE TYPE" both as "SAMPLE MEASUREMENT" (actual sample type used during monitoring period) and as "PERMIT REQUIREMENT" (e.g. enter "GRAB" for individual sample; "24HC" for 24-hour composite; "N/A" for continuous monitoring, etc.).
10. WHERE VIOLATIONS OF PERMIT REQUIREMENTS ARE REPORTED, ATTACH A BRIEF EXPLANATION TO DESCRIBE CAUSE AND CORRECTIVE ACTIONS TAKEN. REFERENCE EACH VIOLATION BY DATE.
11. If no discharge occurs during the monitoring period, enter "NO DISCHARGE" across form in place of data entry.
12. Enter "NAME/TITLE OF PRINCIPAL EXECUTIVE OFFICER" with "SIGNATURE OF PRINCIPAL EXECUTIVE OFFICER OR AUTHORIZED AGENT." Also enter "TELEPHONE NUMBER" and "DATE" at bottom of form.
13. Mail the signed discharge monitoring report to the Office(s) in accordance with the date(s) specified in the permit. Retain a copy for your records.
14. More detailed instructions for use of this DMR form may be obtained from the Office(s) specified in the permit.

In accordance with EPA's *National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantification Levels*, the following guidance should be followed when reporting analytical data below detectable levels:

- Substitute "0" as the value for analytical test results below the ML;
- Use "0," for results below the ML when determining the average and maximum values in accordance with the DMR instructions;
- Record the determined average and maximum values in accordance with DMR instructions; and
- Record in the comment section of the DMR, the lowest calibration standard used, and the ML achieved, and the number of times non-detectable results were reported as zero.

PERMITTEE PROCEDURES FOR REPORTING

This appendix provides two sets of example data to demonstrate how MLs are determined and how average concentrations and loadings should be calculated when the permit limits are at or below the detection/quantification level. Using these same example data, determinations of exceedances also have been provided. These data have been summarized on example DMRs included near the end of this appendix.

Using the ML as a Reporting Threshold

This example presents hypothetical permit conditions in Table 1 on the next page, in which WQBELs are below analytical detection limits. For each pollutant, the values to report on the DMR will depend on the ML; thus, it is important to correctly identify the ML. Table 1 depicts the following situations:

- For pyrene, an ML is specified in the approved method. The permittee must achieve this ML in its analyses and must base its reporting calculations on this ML.
- For dieldrin, no ML is specified in the approved method. The permittee has therefore calculated an interim ML equal to 3.18 times the MDL (and then rounded to an appropriate calibration dilution). The permittee must achieve this ML in its analyses and must base reporting calculations on this ML.
- For benzene, an ML, is specified in the analytical method, but the facility is unable to achieve the ML because of matrix interference. Due to problems with matrix interference, the permittee has developed a discharge-specific MDL, and correspondingly, an ML equal to 3.18 times the discharge-specific MDL. In this case the facility has previously demonstrated to the permitting authority that a discharge-specific ML was warranted. Note that the benzene example is expanded to demonstrate the calculation of monthly averages and the compliance evaluation.

Calculating Monthly Average Concentrations Using Example Analytical Data

A set of hypothetical data is provided in Table 2, to which all procedures refer. These data are fictional and are intended to serve as an example only. The example represents a situation where water quality-based permit limits are required for benzene; however, it also is applicable to any other pollutant. Both the

Table 1
Determining the ML

Pollutant	Method ¹ (µg/L)	MDL (µg/L)	Method Specified ML (µg/L)	Interim ML ¹ (µg/L)	Discharge Specific ML ² (µg/L)	Permit Limits			
						Daily Max. (µg/L)	Month. Avg. (µg/L)	Daily Max. (lb/d)	Month. Avg. (lb/d)
Pyrene	1625	1.9 ³	10	NA	NA	5	5	0.42	0.42
Dieldrin	608	0.002	None	1	NA	0.1 ng/L	0.1 ng/L	8.3 x 10 ⁻⁶	8.3 x 10 ⁻⁶
Benzene	1624	4.4 ³	10	NA	20	10	10	0.83	0.83

NA - Not Applicable

¹Specified in Permit

²Specified in Permit and previously approved by permitting authority following a demonstration of a discharge specific MDL (from which an interim ML was derived) such as described in Appendix B.

³Because Methods 1625 and 1624 employ the concept of an ML, a single laboratory MDL determination (such as appears in the 600 series methods) was not published in Method 1625.

Table 2
Example Monthly Laboratory Analytical Data-Concentrations

Parameter: Benzene			
EPA Method: 1624			
ML: 20 µg/L			
Date	Result (µg/L)	Date	Result (µg/L)
9/1/93	< 20	12/2/93	< 20
9/3/93	< 20	12/5/93	< 20
9/6/93	< 20	12/9/93	< 20
9/10/93	< 20	12/12/93	< 20
9/13/93	< 20	12/15/93	< 20
9/17/93	< 20	12/18/93	< 20
9/20/93	< 20	12/21/93	20
9/24/93	< 20	12/22/93	20
9/27/93	< 20	12/23/93	< 20
		12/25/93	< 20
		12/28/93	< 20
		12/31/93	< 20
10/1/93	< 20	1/3/94	< 20
10/5/93	< 20	1/5/94	< 20
10/8/93	20	1/9/94	< 20
10/12/93	30	1/12/94	< 20
10/15/93	30	1/15/94	< 20
10/19/93	40	1/19/94	< 20
10/22/93	30	1/22/94	< 20
10/23/93	20	1/25/94	30
10/26/93	< 20	1/28/94	30
10/29/93	< 20		
11/1/93	< 20	2/1/94	30
11/4/93	< 20	2/2/94	50
11/7/93	< 20	2/4/94	40
11/11/93	< 20	2/7/94	30
11/14/93	< 20	2/10/94	< 20
11/18/93	< 20	2/14/94	< 20
11/21/93	30	2/17/94	< 20
11/25/93	40	2/20/94	< 20
11/28/93	< 20	2/24/94	< 20
		2/27/94	< 20

PERMITTEE PROCEDURES FOR REPORTING

daily maximum and monthly average limits are below the ML, which in this case, is a discharge-specific ML. The steps for calculating a monthly average concentration for reporting purposes and compliance evaluations follow.

1. Determine the number of samples analyzed during the month for a given parameter.

Using the example data provided in Table D-2, the number of samples analyzed were:

September = 9	December = 12
October = 10	January = 9
November = 9	February = 10

2. Determine the number of results that were found to be below the ML (nondetectable).

Using the example data provided in Table D-2, the number of results below the ML were:

September = 9	December = 10
October = 4	January = 7
November = 7	February = 6

3. Calculate the monthly average concentrations, substituting zero for the results below the ML (nondetectable).

Average Concentration = $\frac{\text{Sum of all results}}{\text{Number of samples taken during the month}}$

Using the data shown in Table D-2, the monthly average concentrations for benzene are calculated as follows:

$$\text{September } \frac{(9)(0)}{9} = 0.0 \mu\text{g/L}$$

$$\text{October } \frac{(4)(0) + (3)(30) + (2)(20) + (1)(40)}{10} = 17 \mu\text{g/L}$$

$$\text{November } \frac{(7)(0) + (1)(30) + (1)(40)}{9} = 7.8 \mu\text{g/L}$$

PERMITTEE PROCEDURES FOR REPORTING

$$\text{December } \frac{(10)(0) + 2(20)}{12} = 3.3 \mu\text{g/L}$$

$$\text{January } \frac{(7)(0) + 2(30)}{9} = 6.7 \mu\text{g/L}$$

$$\text{February } \frac{(6)(0) + 2(30) + (1)(40) + (1)(50)}{10} = 15 \mu\text{g/L}$$

Calculating Monthly Average Loadings Using Analytical Data

1. Calculate the monthly average loadings, substituting zero for the results below the ML (nondetectable). Using the same six months of data shown in Table 2, the loadings for benzene are calculated as shown in Table 3. The conversion factor from concentration in $\mu\text{g/L}$ to loading in lb/day is 0.00834. While loading limits for benzene are uncommon, these calculations are transferrable to any pollutant. Monthly average loading is calculated as follows:

$$\begin{aligned} \text{Monthly Average Loading} &= \frac{\text{sum of [(each result in } \mu\text{g/L) (flow in MGD) (0.00834 (lb)/(gal)(}\mu\text{g)}\{)]}}{\text{Number of samples taken during the month}} \end{aligned}$$

Table 3 illustrates the calculation that converts the pollutant concentration data in $\mu\text{g/L}$ into a loading in lb/day. Using these converted values, the monthly average loadings for benzene are calculated as follows:

$$\text{September } \frac{(9)(0)}{11} = 0 \text{ lb/d}$$

$$\begin{aligned} \text{October } &\frac{(4)(0) + 1.70 + 2.53 + 2.53 + 3.27 + 2.50 + 1.68}{10} \\ &= 1.42 \text{ lb/d} \end{aligned}$$

$$\text{November } \frac{(7)(0) + 2.6 + 3.4}{9} = 0.67 \text{ lb/d}$$

$$\text{December } \frac{(10)(0) + 1.67 + 1.68}{12} = 0.28 \text{ lb/d}$$

PERMITTEE PROCEDURES FOR REPORTING

$$\text{January} \quad \frac{(7)(0) + 2.5 + 2.5}{9.0} = 0.56 \text{ lb/d}$$

$$\text{February} \quad \frac{(6)(0) + 2.48 + 4.09 + 3.30 + 2.52}{10} = 1.24 \text{ lb/d}$$

Table 3
Example Monthly Analytical Data - Loadings

Parameter: Benzene					
EPA Method: 1624					
ML: 20 µg/L					
Date	Result (µg/L)	No. to use in calculations (µg/L)	Flow (MGD)	Quantity x conversion = (lb/d)	
9/1/93	< 20	0	10.1	0.00834	0
9/3/93	< 20	0	10.4	0.00834	0
9/6/93	< 20	0	9.9	0.00834	0
9/10/93	< 20	0	9.8	0.00834	0
9/13/93	< 20	0	10.1	0.00834	0
9/17/93	< 20	0	10.2	0.00834	0
9/20/93	< 20	0	10.3	0.00834	0
9/24/93	< 20	0	10.2	0.00834	0
9/27/93	< 20	0	10.1	0.00834	0
10/1/93	< 20	0	9.7	0.00834	0
10/5/93	< 20	0	10.4	0.00834	0
10/8/93	20	20	10.1	0.00834	1.70
10/12/93	30	30	10.1	0.00834	2.51
10/15/93	30	30	10.2	0.00834	2.51
10/19/93	40	40	9.8	0.00834	3.27
10/22/93	30	30	10.0	0.00834	2.50
10/23/93	20	20	10.1	0.00834	1.68
10/26/93	< 20	0	10.0	0.00834	0
10/29/93	< 20	0	10.2	0.00834	0
11/1/93	< 20	0	9.9	0.00834	0
11/4/93	< 20	0	10.0	0.00834	0
11/7/93	< 20	0	10.2	0.00834	0
11/11/93	< 20	0	10.0	0.00834	0
11/14/93	< 20	0	10.4	0.00834	0
11/18/93	< 20	0	10.2	0.00834	0
11/21/93	30	30	10.4	0.00834	2.6
11/25/93	40	40	10.2	0.00834	3.4
11/28/93	< 20	0	10.0	0.00834	0

Table 3
Example Monthly Analytical Data - Loadings (Continued)

Parameter: Benzene					
EPA Method: 1624					
ML: 20 µg/L					
Date	Result (µg/L)	No. to use in calculations (µg/L)	Flow (MGD)	x conversion	Quantity = (lb/d)
12/2/93	< 20	0	9.8	0.00834	0
12/5/93	< 20	0	9.8	0.00834	0
12/9/93	< 20	0	9.7	0.00834	0
12/12/93	< 20	0	9.8	0.00834	0
12/15/93	< 20	0	9.8	0.00834	0
12/18/93	< 20	0	10.0	0.00834	0
12/21/93	20	20	10.0	0.00834	1.67
12/22/93	20	20	10.1	0.00834	1.68
12/23/93	< 20	0	10.0	0.00834	0
12/25/93	< 20	0	9.9	0.00834	0
12/28/93	< 20	0	9.8	0.00834	0
12/31/93	< 20	0	9.7	0.00834	0
1/3/94	< 20	0	9.7	0.00834	0
1/5/94	< 20	0	9.8	0.00834	0
1/9/94	< 20	0	9.8	0.00834	0
1/12/94	< 20	0	9.9	0.00834	0
1/15/94	< 20	0	10.1	0.00834	0
1/19/94	< 20	0	10.0	0.00834	0
1/22/94	< 20	0	9.9	0.00834	0
1/25/94	30	30	10.0	0.00834	2.5
1/28/94	30	30	10.0	0.00834	2.5
2/1/94	30	30	9.9	0.00834	2.48
2/2/94	50	50	9.8	0.00834	4.09
2/4/94	40	40	9.9	0.00834	3.30
2/7/94	30	30	10.0	0.00834	2.52
2/10/94	< 20	0	10.1	0.00834	0
2/14/94	< 20	0	10.2	0.00834	0
2/17/94	< 20	0	10.2	0.00834	0
2/20/94	< 20	0	10.0	0.00834	0
2/24/94	< 20	0	10.1	0.00834	0
2/27/94	< 20	0	9.9	0.00834	0

PERMITTEE PROCEDURES FOR REPORTING

Determining Exceedances

Using the example data provided in Tables 2 and 3 and comparing these data to the WQBELs in Table 4 below, the following compliance determinations can be made. Notice that in this example, both the daily maximum and the monthly average are equal and are below the ML.

Table 4
Water Quality-Based Effluent
Limitations for Benzene

	Concentration ($\mu\text{g/L}$)	Loading (lbs/day)
Daily maximum	10	0.83
Monthly average	10	0.83

The number of exceedances reported on the DMR refer to the number of sample measurements during a monitoring period that exceed the maximum permit limit requirement for each parameter. When an NPDES permit contains limits for both the concentration and the loading for a parameter, it is possible to violate both limits with one sample measurement. However, this is reported as one exceedance.

Table 5 summarizes the exceedances to be reported on the DMR forms on the following pages. Of note is the fact that for this example, the daily maximum is exceeded whenever a result greater than the ML occurs. However, if more than one sample is analyzed on a particular day (i.e. multiple grab samples are collected) then the daily maximum is calculated as the average of samples within the 24 hour period. As a result, a concentration found above the ML would not necessarily result in an exceedance of the daily maximum limit.

Sample completed DMRs follow this discussion. The daily maximum concentrations, calculated monthly averages, and loadings are presented along with the number of exceedances. As per instructions in the beginning of this appendix, the lowest calibration standard and the ML achieved is also noted in the comments section. Since this is a fictional example, it does not include attachments explaining the exceedances. In reality, the permittee should attach a brief explanation to describe the cause and corrective actions taken, with each violation referenced by date.

Table 5
Exceedances of Benzene Limits

Date	Daily Max. Conc. Potentially Exceeding the Limit (µg/L)	Daily Max. Loadings Potentially Exceeding the Limit (lb/d)	Mo. Avg. Conc. (µg/L)	Mo. Avg. Loadings (lb/d)
September				
9/1/93- 9/30/93	0	0	0	0
Number of Exceedances of Daily Max: 0				
October				
10/8/93	20	1.70	-	-
10/12/93	30	2.53	-	-
10/15/93	30	2.53	-	-
10/19/93	40	3.27	-	-
10/22/93	30	2.50	-	-
10/23/93	20	1.68	-	-
10/1/93- 10/31/93	-	-	17	1.42
Number of Exceedances of Daily Max: 6				
November				
11/21/93	30	2.6	-	-
11/25/93	40	3.4	-	-
11/1/93- 11/30/93	-	-	7.8	0.67
Number of Exceedances of Daily Max: 2				
December				
12/21/93	20	1.67	-	-
12/22/93	20	1.68	-	-
12/1/93- 12/31/93	-	-	3.3	0.28
Number of Exceedances of Daily Max: 2				

Table 5
Exceedances of Benzene Limits (Continued)

Date	Daily Max. Conc. Potentially Exceeding the Limit ($\mu\text{g/L}$)	Daily Max. Loadings Potentially Exceeding the Limit (lb/d)	Mo. Avg. Conc. ($\mu\text{g/L}$)	Mo. Avg. Loadings (lb/d)
January				
1/25/94	30	2.5	-	-
1/28/94	30	2.5	-	-
1/1/94- 1/31/94	-	-	6.7	0.56
Number of Exceedances of Daily Max: 2				
February				
2/1/94	30	2.48	-	-
2/2/94	50	4.09	-	-
2/4/94	40	3.30	-	-
2/7/94	30	2.52	-	-
2/1/94- 2/28/94	-	-	15	1.24
Number of Exceedances of Daily Max: 4				

NATIONAL POLLUTANT DISCHARGE REPORT (NPDES)

DISCHARGE MONITORING REPORT (DMR)

DISCHARGE NUMBER
001

PERMIT NUMBER
15000001

MONITORING PERIOD
YEAR NO DAY
93 9 30
TO
YEAR NO DAY
93 9 30

Form Approved
OMB No 2040-0004
Approval expires 10-31-94

NOTE: Read instructions before completing this form

PLANTER NAME/ADDRESS (include
Firm, Name, or other identifier)
NAME
Wells River Manufacturing
ADDRESS
1 North Main Road
Mooseville
LOCATION
Mills County

PARAMETER (22-23)		AVERAGE (10-13)		MAXIMUM (10-13)		UNITS		QUALITY OR CONCENTRATION (10-13)		UNITS		MAXIMUM (10-13)		AVERAGE (10-13)		HOURS		PERMIT NUMBER		OFFICE OR AUTHORIZED AGENT		AREA CODE		YEAR		NO		DATE		
Flow	10.1	10.4	MCD	16/d	0	0	mg/L	0	2/wk	Grab	N/A	CONT.	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
Benzene	0	0	16/d	0	0	mg/L	0	2/wk	Grab	N/A	CONT.	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	
PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT	MEASUREMENT	PERMIT

Non detectable results reported 1 hour out
of 100 samples analyzed

PERMITTEE NAME/ADDRESS (Include
Facility Name/Location if different)

NAME Messie River Manufacturing

ADDRESS 1 Messie River Road

Mercerville USA 12111

FACILITY

LOCATION Messie County

NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM (NPDES)
DISCHARGE MONITORING REPORT (DMR)

(2-16)

(17-19)

V50002001

PERMIT NUMBER

001

DISCHARGE NUMBER

Form Approved.

OMB No 2040-0004

Approval expires 10-31-04

MONITORING PERIOD

FROM YEAR 93 MO 11 DAY 1 TO YEAR 93 MO 11 DAY 30
(2-17) (2-18) (2-19) (2-20) (2-21) (2-22) (2-23)

NOTE: Read instructions before completing this form

PARAMETER (32-33)		(3 Cont Only) QUANTITY OR LOADING (46-51)			(4 Cont Only) QUALITY OR CONCENTRATION (52-57)			NO. OF ANALYSES (58-59)	FREQUENCY OF ANALYSIS (60-61)	SAMPLE TYPE (62-63)
		AVERAGE (46-47)	MAXIMUM (48-49)	UNITS (50-51)	MINIMUM (52-53)	AVERAGE (54-55)	MAXIMUM (56-57)			
Flow	SAMPLE MEASUREMENT	10.1	10.4	MCD					CONT	N/A
	PERMIT REQUIREMENT									
Benzene	SAMPLE MEASUREMENT	0.67	3.4	lb/d		7.8	40	2	2/wk	Grab
	PERMIT REQUIREMENT									
	SAMPLE MEASUREMENT									
	PERMIT REQUIREMENT									
	SAMPLE MEASUREMENT									
	PERMIT REQUIREMENT									
	SAMPLE MEASUREMENT									
	PERMIT REQUIREMENT									
	SAMPLE MEASUREMENT									
	PERMIT REQUIREMENT									
	SAMPLE MEASUREMENT									
	PERMIT REQUIREMENT									

NAME/TITLE PRINCIPAL EXECUTIVE OFFICER

[Signature]
TYPED OR PRINTED

I, [Signature], under penalty of law that I have personally examined and on basis of the information submitted herein and based on the results of these examinations, certify that the information provided on this report is true and correct to the best of my knowledge and belief. I am aware that there are civil and criminal penalties for submitting false information, including the possibility of fine and imprisonment, or both, and I am aware that I am subject to the penalties of perjury.

[Signature]
SIGNATURE OF PRINCIPAL EXECUTIVE
OFFICER OR AUTHORIZED AGENT

TELEPHONE

DATE

AREA CODE 555 NUMBER 5555 YEAR 93 MO 12 DAY 2

CONSENT AND CERTIFICATION OF ANY VIOLATIONS (Section 306(b)(7)(C))

Consent and certification of any violations - 10/11/11
All = 20 µg/L

Unacceptable results reported as 1210 7 times out of 7 total samples analyzed.

Facility Name (or shop # if owned)
NAME Merric River Manufacturing
ADDRESS 1 Merric River Road
Merrillville USA 12111

ADDRESS 1 Merrie River Road
Mecullville USA 1211

LOCATION Merile County

**NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM (NPDES)
DISCHARGE MONITORING REPORT (DMR)**
(2-16) (17-19)

1250000001
PERMIT NUMBER

001
DISCHARGE NUMBER

MONITORING PERIOD

FROM

YEAR	MO	DAY
94	1	1

 TO

YEAR	MO	DAY
94	1	31

Form Approved.
OMB No 2040-0004
Approval expires 10-31-94

NOTE: Read instructions before completing this form

[illegible]

~~NAME~~ ~~WILLIAM~~ ~~EDWARD~~ ~~RECAUTIV~~ ~~OFFICER~~

[illegible]

Eric S. Luce
SIGNATURE OF PRINCIPAL EXECUTIVE
OFFICER OR AUTHORIZED AGENT

TELEPHONE

DATE

(261)	555	-	74	2	2
AREA	NUMBER		YEAR	MO	DAY

1. WILLIAM AND JOHN WILLIAMS

1. General 2. Particular 3. Conclusion 4. Signature 5. Date

1. n. detectable results reported as zero 7 times
.. of 9 total samples analyzed.

Alc 20 g/L

COMPLIANCE EVALUATION

The permittee must periodically submit a discharge monitoring report (DMR) to the permitting authority for its review to determine whether there are violations of NPDES permit requirements. Any violation of a NPDES permit is a violation of the Clean Water Act for which the permittee is liable. EPA uses a policy of enforcement discretion in deciding on a response to a violation. Compliance history, type, frequency, and magnitude of the violation are some of the factors considered in deciding what an appropriate enforcement action should be. Enforcement actions can be informal (e.g., phone call) or formal (e.g., issue an Administrative Order). EPA's Enforcement Management System (1989) and Guidance for Preparation of Quarterly and Semi-Annual Noncompliance Reports provides recommendations for evaluating noncompliance and determining appropriate enforcement responses.

Benzene Example

The recommendations in the "National Guidance for Permitting, Monitoring, and Enforcement of Water Quality-based Effluent Limitations Set Below Analytical Detection" were applied to evaluate compliance in the benzene example. Non-detect values were reported as 0 on the DMR, and 0 represented those values in the calculation of monthly averages. The ML is identified and the number of non-detect values for that month are identified in the comment section of the DMR. Based on all the information included in this Appendix, example appropriate enforcement responses are discussed below. These are meant to be illustrative, not prescriptive. The permitting authority has discretion in determining an appropriate response.

September

Compliance status: Facility is in compliance with daily maximum and monthly average limits.

Violations: none

Enforcement response: none

October

Compliance status: Facility is non-compliant.

Violations: 6 exceedances of daily maximum limit; monthly average limit exceeded.

Enforcement response: exceeds the violation review action

criteria (VRAC) outlined in the EMS which requires these violations to be reviewed by a professional. Due to dramatic difference between Sept. and Oct., the permitting authority called the facility to inform them of the violation and see if there is an explanation. No explanation was provided so a letter was sent (under section 308 of the Clean Water) requiring the facility to provide additional monitoring data or other information (any change in process) to determine the increase in the discharge of benzene.

Any limit violation suspected by the permitting authority to have the potential to cause a water quality or health problem exceeds can be considered significant noncompliance (SNC) and reported on the quarterly noncompliance report (QNCR).

November

Compliance status: Facility is non-compliant.

Violations: 2 exceedances of daily maximum limit

Enforcement response: no additional action taken this month

December

Compliance status: Facility is non-compliant.

Violations: 2 exceedances of daily maximum limit

Enforcement response: no additional action taken this month

January

Compliance status: Facility is non-compliant.

Violations: 2 exceedances of daily maximum limit

Enforcement response: DMR data and additional data collected by 308 letter indicate a chronic problem with this facility meeting its limits for benzene. Notice of violation sent to the facility.

February

Compliance status: Facility is non-complaint.

Violations: 4 exceedances of daily maximum limit; monthly average limit exceeded.

Enforcement response: 4 or more violations of daily maximum exceed the VRAC so the violations are professionally reviewed. Also, this is the second month within 6 months that the monthly average was exceeded so a professional review of those violations is required.

The monthly average violations were evaluated to see if they should be reported on the QNCR. They should be reported on the QNCR if the monthly average limit violation is greater than or equal to the product of the technical review criteria (TRC) times the effluent limit, and occurs 2 months within a 6 month period. Benzene is an organic pollutant and is therefore classified as a Group II pollutant with a TRC = 1.2.

First month of violation was October: $17 \geq (1.2 \times 10)$
 $17 \geq 12$

Second month of violation was February: $15 \geq 12$

This facility is in significant non-compliance (SNC) because benzene discharged from this facility exceeded the product of TRC times the monthly average limit 2 months in a 6 month period. There are also chronic exceedances of the daily maximum limit. This facility is listed on the QNCR and an Administrative Order is issued.

APPENDIX E

RECOMMENDED PERMIT WRITER PROCEDURES FOR CALCULATING WATER QUALITY-BASED EFFLUENT LIMITS AT INTERNAL WASTESTREAMS

**RECOMMENDED PERMIT WRITER PROCEDURES FOR CALCULATING WATER
QUALITY-BASED EFFLUENT LIMITS AT INTERNAL WASTESTREAMS**

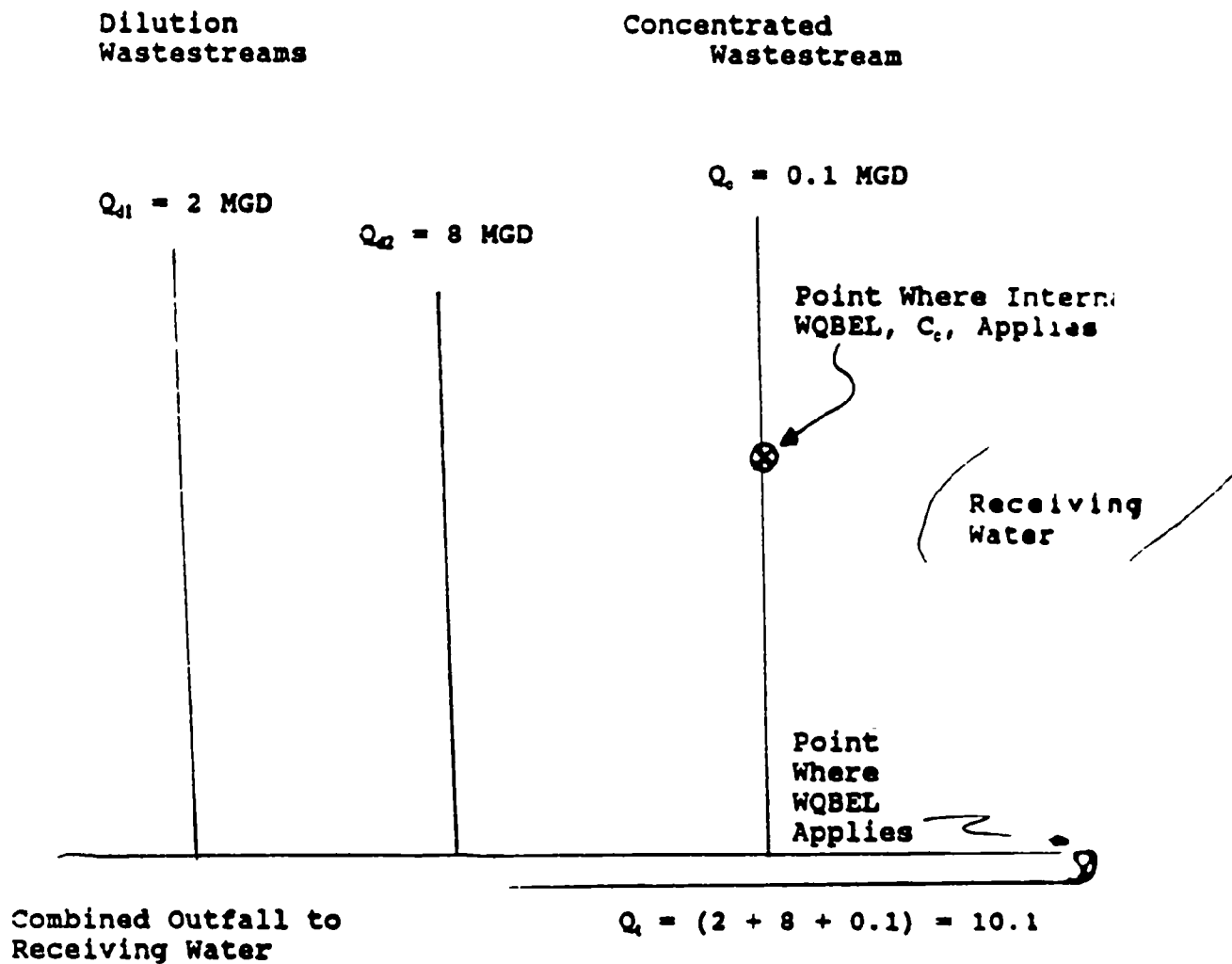
With the continuing imposition of WQBELs in permits, many facilities are noting the feasibility in combining discharges into one outfall prior to discharge. One advantage of this practice is that combining wastestreams minimizes costs associated with sample collection and analyses at multiple outfalls. Combined wastestreams may also provide greater dilution for specific pollutants, thus, the WQBELs are more easily met. However, in some cases, dilution of a given wastestream with other wastewaters may result in matrix interferences and/or concentrations of pollutants below detectable levels. Where a wastestream is diluted by other wastewaters, EPA recommends that the permit writer consider establishing a WQBEL for the individual wastestream. The following approach sets forth several steps for the calculation of a WQBEL at an internal outfall.

- STEP 1: Locate an accessible sampling point of the concentrated wastestream, C. If not immediately accessible, the permit writer may require the construction of an accessible monitoring point pursuant to 40 CFR 122.45(h).
- STEP 2: Determine the long term average flow at the internal sampling point (Q_c)
- STEP 3: Determine the long term average flow of all dilution wastestreams (Sum of Q_d)
- STEP 4: Assuming that the dilution wastestream is contributing no tangible amount of the pollutant, calculate the concentration at the internal sampling point (C_c) which must be met in accordance with the following formula:

$$C_c = \frac{WQBEL * Q_d}{Q_c}$$

An example of this calculation is provided on the following page.

RECOMMENDED PERMIT WRITER PROCEDURES FOR CALCULATING WATER
QUALITY-BASED EFFLUENT LIMITS AT INTERNAL WASTESTREAMS
Continued



$$C_c = \frac{\text{WQBEL} \times Q}{Q_c}$$

$$C_c = \frac{0.0002 \text{ mg/l} \times 10.1 \text{ MGD}}{0.1 \text{ MGD}}$$

$$C_c = 0.02 \text{ mg/l}$$