

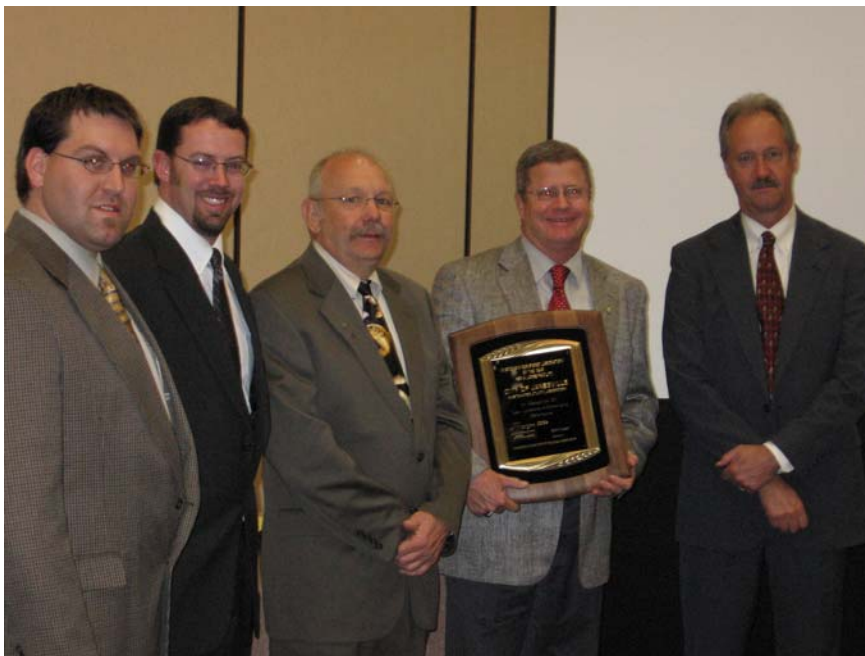
LABNOTES *Summer 2006*

...and the 2006 Wastewater Idols are...

By Camille G. Johnson

Two registered labs have recently been honored for their exceptional work. The winners of the 2006 LOY awards are the Village of Amherst Wastewater Treatment Plant (Small Registered Category) and the City of Janesville Wastewater Utility Laboratory (Large Registered Category). Both labs were honored on April 26, 2006 at the Natural Resources Board Meeting in Stevens Point, Wisconsin. The awards were presented by DNR Secretary Scott Hassett and Environmental Science Services Section Chief David Webb. During the award presentation Mr. Webb stated, *“These are the types of labs that can be a cornerstone or a first line of defense to protecting the environment, serving their communities, and helping the Department do its job - they put the science in sound science”*.

(Continued on next page)



From left, members of Janesville’s Wastewater Utility Laboratory are shown with DNR Secretary Scott Hassett (far right) after receiving the award for Lab of the Year Award (Large Facilities).

Also in this Issue:

- **Meetings & Training Opportunities.....3**
- **Program Administration..... 4**
 - Misunderstood NR 149
 - FY2007 Fees
 - Approved Methods for Landfill Analyses
 - LODS Req'd for SDWA
 - DO by Luminescence
 - EPA’s ATP website
- **Proficiency Testing..... 9**
 - Missing PT Letters
 - SDWA PT Reminders
- **Council Corner.....10**
- **Wastewater Focus..... 11**
 - Phosphorus& Calibration
 - Insufficient Depletion? Not Enough Solids?
 - BOD FAQs
 - Calculating with “<”
 - R U Seeding CBODs?
- **Waste Management.....14**
 - GEMS Newsletter
 - New SVOC list
 - GEMS on the Web
- **Cross Media Issues14**
 - Mercury & Sensitivity
- **General Interest.....15**
 - Latex Allergies & Labs

Labs of the Year, continued.

Lab work is a challenge for all labs, but some lab staff have to wear many hats and handle a variety of non-lab issues in addition to lab responsibilities. One such lab is found in the Village of Amherst located just east of Stevens Point. There, the sole operator, Lyle Lutz, strives to do his best each and every day. Lyle handles the operation of their treatment plant in addition to village issues while setting a very high priority on his lab analysis. In addition, he goes above and beyond the minimum requirements and really gives wastewater sample analysis his full attention. One of the nominators, DNR Area Engineer Joe Behlen, wrote about Amherst, *“The quality of workmanship stems from the knowledge of its trained staff and the ability to commit the necessary time to ensure testing and reporting accuracy”*.

At the awards ceremony David Webb said that, *“Mr. Lutz has an exceptionally positive attitude, superb knowledge and detailed records... for a small community lab with staff who handle many other village responsibilities it is really nice to see the high priority lab work is given.”* After accepting his award from DNR Secretary Scott Hassett, Mr. Lutz stated, “This is quite an honor for our small lab.” He went on to thank several DNR employees for the nomination and their help with lab and plant issues.

Farther south in Wisconsin, a larger wastewater facility found in Janesville is also achieving stellar results. Their lab staff include: Water Utility Director Dan Lynch, Wastewater Superintendent Dennis Egge, Chemist/Biologist Marc Zimmerman, and Laboratory Technician Brian Skaife. The lab was nominated for the award by Audit Chemist Greg Pils, who wrote, *“The laboratory has a mature quality assurance program that effectively evaluates the precision and accuracy of each set of test results against control limits...in many instances these control limits are much stricter than the norm...”* The Janesville plant has had an excellent track record for many years. They run quality control samples more often than required and strive to improve their operations in many ways.

Continued on next page.

LabNotes

Newsletter of the Laboratory Certification Program

LabNotes is published twice annually by the Wisconsin DNR Laboratory Certification and Registration Program. For information about distribution or to make suggestions for future articles, contact the editor.

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This publication is available in alternative format (large print, Braille, audio tape, etc.) upon request. Please call (608) 267-7633 for more information.

This document is available electronically at www.dnr.state.wi.us/org/es/science/lc.

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Lab of the Year winners, continued.

All the Janesville staff were on hand to receive the award from Mr. Hassett and Mr. Webb. During the presentation Mr. Webb said, *“The lab staff display exceptional technical knowledge and a high level of analytical curiosity. The lab is in a constant state of self-evaluation and improvement.”* Mr. Lynch spoke after accepting the plaque on behalf of Janesville. He credited his staff and their hard work for the achievement of the award. Lynch said, *“They want to find the answers to do the job right”*.

Congratulations to these two labs and all the other labs out there that strive to do their very best every day. Keep up the great work contributing to the sound science of our state!

We are now accepting nominations for the 2007 Lab of the Year award. Contact Camille Johnson at (715) 831-3272 or camille.johnson@dnr.state.wi.us for more information or a nomination form. ☺



Lyle Lutz (left), shows off the plaque for 2006 Lab of the Year Award earned by his wastewater treatment plant lab in the Village of Amherst. David Webb, Section Chief for the Laboratory Certification Program is pictured at right.

Training for Lab Analysts

Wastewater Lab - Advanced

August 29 & 30, 2006

Location: Delafield WWTP

To Register: Dan Tomaro (608) 770-5144

Wastewater Training Solutions

www.wastewatertrainingsolutions.com

www.dnr.state.wi.us/org/es/science/opcert/training.pdf



Exam Schedule & Meeting Opportunities

Operator Certification Exams

DNR will hold Wastewater, Drinking Water and Septage Operator Certification exams November 1, 2006 (*postmark deadline October 4, 2006*) in DNR Regions around the state. Check the Operator Certification web site for details, as they become available. Application packets will be mailed, about August 1, 2006, to all operators who have taken an exam in the last 18 months..

www.dnr.state.wi.us/org/es/science/opcert



2006 Conferences, Meetings

WLA 29th Annual Conference

The Wisconsin Lab Association will hold its Annual Fall Educational Conference September 16-17, 2006 in Madison at the Radisson. For more information, please contact Cindy Kallstrom (cKallstrom@Kerrygroup.com) or Dave Christel (DJChristel@landolakes.com).

www.wisconsinlabassociation.com



WWA 85th Annual Conference

The Wisconsin Water Association (formerly AWWA WS) 85th annual conference is scheduled for September 20 through 22, 2006 at the Kalahari Waterpark Resort, Wisconsin Dells. Register online at: <https://wih2oassoc.safesecureweb.com/registration.htm>.

<http://www.wiawwa.org>



WWOA 40th Annual Conference

The Wisconsin Wastewater Operators Association 40th annual conference is to be held October 3 through 6, 2006 at the Kalahari Resort in Wisconsin Dells. Check the WWOA web site for more details.

www.wwoa.org



WRWA 5th Operator Expo

The Wisconsin Rural Water Association will hold its 5th annual Operator Expo is to be held Thursday August 24, 2006 at state headquarters in Plover.

Check the WRWA web site for more details.

www.wrwa.org



Program Administration

NR 149 Questions

By Diane Drinkman, Audit Chemist

NR149 RAC Co-Leader

Since the Natural Resources Board authorized public hearings on the ch. NR 149, Wis. Adm. Code proposed rule revisions, the program has received numerous e-mails and phone calls asking how several sections would apply to everyday laboratory operations. Many laboratories had similar questions regarding the availability of training on several issues, from IDCs, to certification or registration for DO, pH and residual chlorine; from laboratory control samples to continuing calibration verification standards.

This article is not a formal response to comments received at the public hearings. We will provide answers to all the questions we received in an extended version of this article, which will be posted on the Laboratory Certification website: (www.dnr.state.wi.us/org/es/science/lc/). At a later date there will be a formal response to comments as part of the rule-making process.

The posted version will also detail how the tests BOD, Ammonia by ISE, Total Phosphorus and Non-filterable Residue (TSS) will be impacted. This article will concentrate on explaining: Analyst Training and IDCs; Enforcement; The 15-Minute Rule for Sample Preservation; Initial and Continuing Calibration Verification; and the Relationship between LCS, MS/MSD and QCS.

Analyst Training and IDCs [proposed s. NR149.36 (3)]

Analysts working in laboratories are exempt from performing an IDC if, in the year before the rule becomes effective, they have successfully analyzed a combination of 4 blinds, known standards, matrix spikes, reference samples or replicates with detectable concentration of analyte for each test (for ammonia this could be 2 matrix spikes, a reference sample and a duplicate). A laboratory would have to identify the analyses attributed to each analyst at the time of an audit, if requested. Once an analyst has performed an IDC for a method, another IDC is not required, unless the analyst stops working in the laboratory for more than a year or the laboratory changes instrument or instrument type.

An IDC is not part of the operator certification program, nor does it require outside training or verification, or purchase of additional proficiency

testing samples, blinds or other reference materials.

Do I have to perform an IDC? Not necessarily—the draft allows for an analyst to work under the supervision someone who has completed an IDC. It is not intended to mean “direct supervision” where both analysts are in the laboratory at the same time.

Enforcement [proposed s. NR149.10]

DNR follows a stepped enforcement process which typically starts with issuance of a Notice of Noncompliance (NON), or, if warranted, a Notice of Violation. Neither the current code (NR149.42) nor the draft code detail criteria for the preliminary steps of enforcement; the program would not ever be able to suspend, revoke or refer a laboratory to the Department of Justice for prosecution without following agency procedures. An improvement in this area is the elimination of automatic enforcement for non-drinking water proficiency testing failures (details are available in the PT portion of expanded article).

Sample Handling and the 15-Minute Rule [proposed s. NR149.46(3)]

Sample handling and preservation requirements are established by EPA, in 40 CFR Parts 136 and 141 for wastewater and drinking water respectively. Administrative codes, which must be as stringent as the federal regulations, require sample preservation immediately upon collection, with a few exceptions (i.e., metals in drinking water).

NR 219, Table F, footnote 2 states “All samples requiring preservation at $\leq 6^{\circ}\text{C}$ must be cooled immediately after collection, but not frozen.” When we try to determine what immediately means, we rely on the explanation used to define “analyze immediately”, since it is not logical to have a different definitions of “immediately” for sample preservation and sample analysis. Footnote 4 of Table F in NR 219 has strong suggestions about analyzing samples as soon as possible after collection. The note, referring to immediate analysis states: “The term ‘analyze immediately’ usually means within 15 minutes or less of sample collection.” Footnote 2 can then be translated into “All samples requiring preservation at $\leq 6^{\circ}\text{C}$ must be cooled within 15 minutes or less of sample collection, but not frozen.” A similar argument can be made for chemical preservation. We could strictly require preservation “IMMEDIATELY”, or allow a 15-minute window and still maintain that a sample was

preserved immediately.

Initial and Continuing Calibration Verification [proposed s. NR149.44(6) and (7)]

Initial Calibration Verification, (ICV), is performed whenever a calibration curve is established, using a standard from a source different than calibration standards. It isn't retesting the standards, but an independent means to verify the calibration's validity. Tests performed by instruments that follow the Nernst equation or other scientific law (DO, ISE, pH) are exempt from initial calibration verification. For those tests without a calibration step, such as solids, there obviously is no ICV. Laboratories have the option of substituting the analysis of quality control samples (QCS, or "blinds") for ICVs.

Continuing Calibration Verification (CCV) is performed on days when a full calibration is not carried out, using a standard from the same source as the initial calibration. This is referred to as the *Opening CCV*. You have been analyzing a "known standard" for some tests for years— this is the opening CCV. The *Closing CCV*, which ensures that your instrument has not drifted during analysis, is analyzed at the conclusion of the batch and very likely will encompass rereading same solution used for the opening CCV. The default acceptance criteria for CCVs ($\pm 10\%$ of the true value for inorganics and metals, $\pm 15\%$ for organics) has not changed from the current NR149.

Do I have to analyze *Closing CCVs*? No, a laboratory has the option to use the *Opening CCV* from the next batch of samples, provided that instrument conditions have not changed. The biggest risk is that one may have to qualify data from the previous analysis day if the opening CCV is not acceptable.

The Relationship Between Laboratory Control Samples, Matrix Spikes/Matrix Spike Duplicates, and Quality Control Samples [proposed s. NR 149.48(4), (5) and (8)]

A Laboratory Control Sample (LCS) is a sample of reagent water, spiked with a second source standard. Because LCSs are devoid of matrix interference, they are a better indication of a laboratory's ability to generate accurate data than matrix spikes. For tests that require a digestion or distillation, one Laboratory Control Sample (LCS) is processed with each set of samples digested together. When samples are analyzed directly, one LCS is required daily. If the

laboratory analyzes 7 or fewer samples for any quality system matrix in a week (wastewater influent and effluent are considered to be separate quality control matrices), a single LCS is all that is required each week. For BOD and CBOD, the LCS is GGA, as specified by the method.

Results of LCS are to be evaluated against acceptance criteria which will be established by the DNR, specified in an approved method, or from in-house limits.

Matrix Spikes and Matrix Spike Duplicates (MS/MSDs) are **only** required if specified in an analytical method, project plan or by client agreement. They are not required if your laboratory follows *Standard Methods* procedures, period. Many older EPA methods do not require their analyses either. Matrix spikes, when spiked with a second source standard, can be substituted for the LCS, provided that the laboratory evaluates their acceptance using the control limits for LCS.

Quality Control Samples (QCS) are the "blind standards" that laboratories have been analyzing for years. It is the intent of the program the QCS will only be required if a laboratory does not use a second source standard for ICV and LCS.

The program is committed to developing and making available guidance documents, sample benchsheets, forms, templates and other tools needed for implementation, and offering specific training to address the needs of the laboratories that participate in this program. For additional information or clarification of these or other requirements of the draft NR 149, please contact one of the following:

Diane Drinkman at (608) 264-8950 or

Diane.Drinkman@dnr.state.wi.us,

Brenda Howald at (608) 275-3328 or

Brenda.Howald@dnr.state.wi.us or

Alfredo Sotomayor at (608)266-9257 or

Alfredo.Sotomayor@dnr.state.wi.us



Fiscal Year 2007 Certification and Registration Fees

The Natural Resources Board on March 22 unanimously approved the department's laboratory certification and registration fee schedule for Fiscal Year 2007. The fee schedule was previously reviewed by the Certification Standards Review Council, who provided their unanimous support and recommended Board approval. The approved fee schedule will allow the Department to fund the laboratory certification and registration program at a level below its spending authority as established under Chapter 20.370(3)(fj), Wis. Stats.

Specifically, the cost per relative value unit (RVU) will increase from \$55.00 to \$58.00, an increase of only 5.5%. Certification renewal fees for the typical commercial laboratory (certified lab base fee + test categories 1-8, 10, 12, & 14-16) will be \$3,422.00. Registration fees for the typical municipal wastewater treatment laboratory (registered base fee + test categories 1-4) will be \$812.00.

The complete fee schedule is provided in the table below:


Laboratory Fees for FY 2007 (Sept.1, 2006 - Aug. 31, 2007)

Fee Item	FY 2007 Unit Price	Fee Item	FY 2007 Unit Price
Registered Base Fee	\$580.00	Category 10	\$232.00
Certified Base Fee	\$870.00	Category 11	\$232.00
Reciprocity Fee	\$1,740.00	Category 12	\$232.00
Initial Application Fee	\$348.00	Category 13	\$232.00
Revised Application Fee	\$174.00	Category 14	\$232.00
Category 1	\$58.00	Category 15	\$696.00
Category 2	\$58.00	Category 16	\$232.00
Category 3	\$58.00	Category 17	\$696.00
Category 4	\$58.00	Category 18	\$1160.00
Category 5	\$116.00	Category 18a (Nitrate Only)	\$116.00
Category 6	\$116.00	Category 18b (Nitrate & Fluoride)	\$232.00
Category 7	\$232.00	Category 19	\$232.00
Category 8	\$232.00	Category 20	\$1,508.00
Category 9	\$232.00	Category 21	\$232.00

Note: Application fees are effective July 1, 2006

Fees are calculated using the formula promulgated in s. NR 149.05, Wis. Admin. Code. This formula uses a relative value system to equitably distribute the cost of administering the program across all participating laboratories. Each fee item is assigned a relative value in Ch. NR 149, Table 2. The total number of available RVUs is the sum of the relative values of each fee item multiplied by the number of labs certified or registered for that fee item in the coming fiscal year. The cost per RVU is calculated by dividing the program's operating costs (not including projected travel costs for audits of out-of-state labs, for which these labs are billed directly), by the total number of available RVUs. The cost of each fee item is determined by multiplying its relative value by the cost per RVU.

Certification and registration renewal fees will appear on the environmental fee statements that will be mailed in late May. Payment will be due in full by June 30, 2006. Late fees will be assessed to laboratories that fail to pay renewal fees by this deadline.

Please contact Greg Pils at (608) 267-9564 or gregory.pils@dnr.state.wi.us if you have any questions about your fees. 

Approved Methods for Landfill Analyses under NR 507


By Camille Johnson

The recent revision (January 2006) of Chapter NR 507 Environmental Monitoring for Landfills (Register, January, 2006, No. 601) may affect the methods you are able to use for landfill related samples. NR 507 no longer allows for methods other than those included in the referenced versions of SW 846. Therefore, if your lab is doing landfill sample analysis under NR 507 you need to be sure you are using approved methods. The specific section of NR 507 is given below:

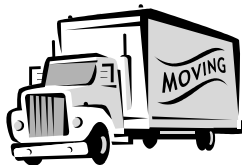
NR 507.17 (4) ANALYTICAL METHODS. Groundwater, lysimeter and leachate samples shall be handled and analyzed in accordance with the requirements of methods listed in "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication SW 846, third edition, November 1986, as amended by Updates I in July 1992, II in September 1994, IIA in August 1993, IIB in January 1995, III in December 1996 and IIIA in April 1998. The methods used shall be suitable for the matrix, type of analyte, expected level of analyte, regulatory limit, and potential interferences in the samples to be tested. Screening methods may not be used unless approved in writing by the department. Water supply samples shall be handled in accordance with s. NR 507.20. The department may approve alternative analytical methods under s. NR 149.12.

Note: The test methods are available at no cost at:


www.epa.gov/epaoswer/hazwaste/test/main.htm

For more information, please contact Camille Johnson at (715) 831-3272 or by email at Camille.Johnson@dnr.state.wi.us 

We've Moved (Again)!!!



In July 2001, LabCert Program staff were re-located to a state-leased building on the corner of Williamson and Blount Streets. The move was related to renovations being performed in the GEF2 building.

We've moved a little closer to home. We are now located on the 3rd floor of the GEF3 building. All of our phone numbers transferred with us, but to expedite mail delivery, you may wish to add "-SS/GEF3" after the name of the staff member you are corresponding with. 

LOD Requirements for Drinking Water Parameters

By Greg Pils

Labs applying for safe drinking water certification must achieve certain limits of detection for the parameters under application. LOD requirements are promulgated in s. NR 149.21, Wis. Adm. Code, which references the Maximum Contaminant Levels (MCLs) listed in 40 CFR part 141: http://www.access.gpo.gov/nara/cfr/waisidx_05/40cfr141_05.html

Volatile organic compound (VOC) LODs:

- 0.3 µg/L for vinyl chloride
- 0.5 µg/L for all other compounds.


Synthetic organic compound (SOC) and total trihalomethane (TTHM) LODs:

- As specified in 40 CFR part 141.24(h)(13)(ii) and (h)(18), OR
- 10% of the MCL, **whichever is greater.**

Inorganic chemical LODs:

- As specified in 40 CFR part 141.23(a)(4)(i) and 40 CFR part 141.89(a)(1)(iii) (*note that the limits published in these sections apply to composite samples only*), OR
- 10% of the MCL, **whichever is greater**

When the sections of 40 CFR part 141 cited above do not require an explicit detection limit for the parameter under application (for example, there are no explicit detection limit requirements for inorganic chemicals in non-composited samples) the department in most cases will require the lab to achieve a detection limit less than or equal to 10% of the parameter's MCL. In those cases where existing technology is not capable of achieving this level of sensitivity, the department may at its discretion accept an LOD greater than 10% of the parameter's MCL, as long as the LOD remains below the parameter's MCL.

Please contact Greg Pils at (608) 267-9564 or gregory.pils@dnr.state.wi.us; Rick Mealy at (608) 264-6006 or richard.mealy@dnr.state.wi.us; or your laboratory auditor if you have further questions about LOD requirements for safe drinking water certification. 

Dissolved Oxygen (DO) Using Luminescence Detection

By Greg Pils

Many of you have probably heard by now about a new technology that uses the property of luminescence to detect dissolved oxygen in aqueous matrices. We've received over the past several months a number of questions asking if this technology can be used to test samples for BOD for compliance with wastewater permits.

The immediate answer, unfortunately, is "no". Laboratories analyzing samples for compliance with NPDES permits are required under 40 CFR Part 136 to use only those test methods listed in that section, and none of the methods listed for BOD or dissolved oxygen use luminescence detection.

If a lab wishes to use a different analytical method (i.e. one that uses luminescence detection), they need to submit an Alternate Test Procedure (ATP) application to either the EPA Regional Administrator (for a limited use ATP) or the EPA Administrator (for a nationwide ATP). In either situation, the administrator reviews the ATP request and, if the alternate test method is determined to be equivalent or better than the methods in 40 CFR 136, it may be approved (The ATP application process is detailed and complex. For more information, visit www.epa.gov/ost/methods/EPA821B98002.pdf).

Unfortunately, the amount of time it takes for a new method to be either added to the list in 40 CFR 136 or approved as an ATP can be considerable – in some cases, years. EPA's Office of Water has told EPA's Regions that they might be able to grant "Interim approval" of such methods when either individual dischargers or labs, groups of dischargers or labs, or an instrument vendor requests approval of an ATP. However, there are some questions as to whether the language in 40 CFR 136 governing ATP approval provides EPA such broad authority. The central contention is that ATPs should be approved only to deal with matrix issues unique to a specific discharger when the methods listed in 40 CFR 136 are not able to provide adequate quantitation or qualitative analysis to determine compliance with permit limits. These concerns have been forwarded to EPA's Office of General Counsel for legal review, who to date has yet to offer their opinion.

To summarize: In the short term it does not appear that labs will be able to use luminescence technology to analyze wastewater samples for DO or BOD. This could change if EPA is able to grant interim approval of the method to interested labs and dischargers, but that is contingent upon receiving a favorable legal opinion from the Office of General Counsel. Interested labs and dischargers may still pursue their own ATP, but it may take a year or more to receive approval. Methods using luminescence detection will eventually be listed in 40 CFR 136, but most likely not in the near future.

Please contact Greg Pils at (608) 267-9564 or gregory.pils@dnr.state.wi.us if you have any questions. ☺

SDWA ATP website nears completion

Excerpted from: EPA's QA Newsletter

The Office of Ground Water and Drinking Water's (OGWDW) Alternate Test Procedure (ATP) Program is developing a website for posting approved and accepted Alternate Test Procedures for Drinking Water Compliance Monitoring Listed by Contaminant. Generally, analytical methods submitted fall into one of two categories, namely major modification and minor changes to approved method.

Major Modifications include analytical methods that make significant modifications to approved methods, or use a different technology than in the approved method, such as changing the chemistry of a method or the formulation of a microbiological product. These major modifications are referred to as alternate test procedures (ATPs). If EPA determines that an ATP is technically sound, the Agency will propose the analytical method for approval in a notice of proposed rulemaking to give the public an opportunity to comment. Assuming there are no outstanding issues after receiving public comment, EPA will publish a final rule adding the ATP in the Code of Federal Regulations (CFR).

Acceptable versions of approved methods have minor changes made that do not change the underlying science of a method (i.e., the changes are within the inherent flexibility of an approved method). The website will contain a compilation of approved ATPs, and acceptable versions that have been processed through the OGWDW's ATP Program. ☺

Proficiency Testing

Letters....We sent letters!

by Rick Mealy

Thanks to the assistance of Diane Drinkman, our data base contains current PT information for all laboratories in the program. For each laboratory, PT samples received were matched up with PT samples required. Subsequently, letters were sent out to all laboratories perceived to be "missing" one or more PT samples critical for an uneventful renewal of certification.

Ordinarily these letters are not sent out until the end of June, but sending them early just allows labs more time to obtain any PT samples that they might need. We certainly apologize for any inconvenience incurred. We hope, however, that you'll see this as a valuable opportunity to communicate one-on-one with us to ensure that the annual certification renewal process contains no unwanted surprises. ☺

Reminder: Drinking Water PT Samples are Method Specific

by Rick Mealy

Already we have had several cases where laboratories have successfully analyzed a PT sample, but reported a different method than the one for which they hold certification. These results DO NOT count and cannot be used to renew your certification.

We understand completely and have heard the arguments why this is not a favored practice many times...however, we must enforce the rule just as we do not allow PT results that are scored as "NOT Acceptable" because of transcription errors. If the error was made by the provider, and we receive documentation to that effect, we CAN accept your results.

When analyzing PTs for drinking water (category 18) be sure to review your certified "Scope of Accreditation" to ensure that the proper method is

used for analysis and cited on report forms.

We will NOT accept your results in any of the following cases:

- you report an unapproved method to the PT provider,
- you report a result for a method which you are not currently certified (based on the Status Update Form information)
- you report the incorrect method to the PT provider (*this is consistent with our policy to not accept results that are inadvertently reported in the incorrect units or a transcription error is made*).

☺

REMINDER: Renewal Deadlines

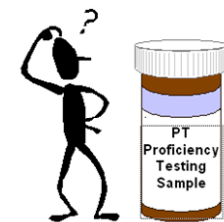
June 30 Fee statements must be paid by this date to avoid late payment charges.

August 31 Acceptable results must be received by the Department by midnight August 31, 2006.

September 1 Laboratories that did not submit acceptable reference sample results for each test for which they are required prior to September 1, 2006 are not renewed for those tests, must cease performing analyses for the analytes, and are required to subcontract the work to a certified laboratory.

Reapplication will be necessary.

Please direct questions about reference sample requirements to Rick Mealy, Laboratory Certification Chemist at (608) 264-6006 or richard.mealy@dnr.state.wi.us. ☺



Council Corner

By Paul Junio, Council Chair



What's this byline? Aren't we rid of this guy yet – after all, he wrote his good-bye article last time? Well, the Council Meeting in January was delayed due to a snowstorm, so I'm still the Council Chair at the time this article needed to be written. Long story short, you get some random notes from me:

WELA / NR149 Information session – The Wisconsin Environmental Laboratories Association held an information session on March 9. The session was envisioned as an opportunity to have the Department make a presentation to a broad range of affected parties, and then have a question and answer session. Attendance at the session (around 70 people) seems to indicate that it was a success. Thanks to WELA and to the DNR for the chance to discuss the proposed changes.


Metals lots from different vendors with same ultimate source – With the added emphasis on using a second source for standards in the proposed revision to NR149, I'd like to point out something that we've found in the past regarding secondary sources (as an aside, we've been using second sources on metals standards for a long time, and have been tracking different vendors and lots during that time). We've found that at least two different vendors are using the same ultimate stock for their products. This means that even though you might purchase a stock standard from two different vendors, if you track the lineage of the solution used to make each of them, you could find that they trace back to the same starting point. So, you could be in compliance with the requirements of the proposed changes, but not actually meet the intent (having two independent sources of a standard to verify that everyone has made it properly).

VOC Standard issues due to chemical inavailability – Similar to the issue where the production of 85% n-Hexane has stopped, we've heard a rumor that certain VOC compounds may become unavailable due to import issues. The following comes from one of our vendors:

Certain ozone depleting substances have been banned from import into the United States and we are having increasing difficulty obtaining some of the compounds necessary to manufacture Analytical Reference Materials that contain these compounds. I do not have a comprehensive list of these compounds, but I do know that the following compounds are becoming increasingly difficult for [vendor name] to purchase:


Bromomethane
Bromochloroacetonitrile
Dibromofluoromethane
Chloroethane
Vinyl chloride

If and when our supplies are depleted, we would no longer be able to supply Analytical Reference Materials containing these compounds. I believe that other manufacturers of Analytical Reference Materials are dealing with the same issue.

Has anyone else heard anything like this? The lab business just keeps getting more and more interesting! 

New Council member Appointments

Paul Junio (Commercial Lab Rep.), George Bowman (State Lab of Hygiene Rep) and Marcia Kuehl (Demonstrated Interest in LabCert rep.) have all completed their 2nd 3-year term and now rotate off the Council. All of us in the LabCert Program want to thank them for their hard work and dedication to the Program.

As new members are appointed, we'll let people know. 

Representation	Name	Phone# / e-mail	Term	Expires
Commercial Laboratory	---TBA---		1	07/09
State Laboratory of Hygiene	---TBA---		1	07/09
Small Municipal Wastewater Plant	Randy Herwig (Chair)	(608) 592-3247 rherwig@wppisys.org	2	07/07
Large Municipal Wastewater Plant	Kurt Knuth (Vice Chair)	(608)222-1201 Ext. 293 kurtk@madsewer.org	2	07/09
Industrial Laboratory	Steve Jossart	(920)438-2898 steve.jossart@GAPAC.com	1	07/08
Public Water Utility	Katie Edgington (Secretary)	(608) 755-3115 edgingtonk@ci.janesville.wi.us	2	07/08
Demonstrated Interest in Lab Certification	---TBA---		1	07/09

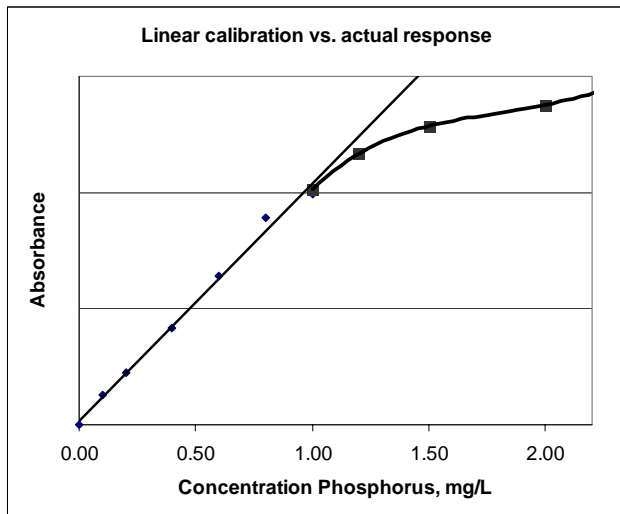
Wastewater Forum

Total Phosphorus:

working within your calibration range

by Brenda Howald

Why is it best to have the concentrations of digested samples between your lowest and highest calibration standards? Imagine the color of each calibration standard corresponds to a location along a 10-foot measuring tape. Your standards mark off the measuring tape divisions that convert the intensity of the sample's blue color into concentration in mg/L phosphorus. You haven't clearly defined any relationship between absorbance (color) and concentration above the concentration for the top standard. Determining sample concentrations above the top of your standards is like trying to accurately measure a 15 foot distance using the 10 foot tape measure that has been anchored to the ground. You are only able make accurate measurements within the range of your calibration standards. Spectrophotometers that use a set of calibration standards to give direct readout of sample concentrations assume that the line created by the calibration can be extended beyond the highest calibration standard to any concentration level. Unfortunately, this isn't true for phosphorus as the responses drop off above the linear portion of the calibration, which is shown in the graph below.



The linear relationship between absorbance and phosphorus concentration starts to change somewhere around 1 mg/L. The point where this happens may be higher or lower in your laboratory because it depends on the equipment and wavelength used. The graphed data comes from the Darlington Wastewater Treatment Plant. You can determine how high you

can calibrate while maintaining a straight line by adding a series of standards at and above 1 mg/L to your calibration curve. If you space them 0.2 mg/L apart you should get a good idea of exactly where things are no longer linear. How can you tell? The correlation coefficient (R) for your linear regression will start dropping as you add each higher standard concentration to your linear regression. When $R < 0.995$, you no longer have a valid calibration curve and you have likely exceeded the linear range for the test. You can also plot the standards on a graph to help visualize where the relationship starts to change.

Limiting the concentration of digested samples to the calibration range can be troublesome when a laboratory spikes a sample that has a concentration near the high end of the calibration. This will typically give spiked sample concentrations that are above the top end of the calibration. If a concentration above the calibration range is used and the level was above the linear portion of the calibration curve you would get low biased spike recoveries. To get accurate results the sample would need to be diluted to bring the total concentration within the calibration range.

A laboratory can also run into trouble working near the lower end of the calibration. If you are diluting your samples to avoid going over the top of your calibration you have to be careful not to dilute them too much. It's good to have sample readings near the middle of your calibration curve but it's especially important to have them higher than your lowest calibration standard. The accuracy and precision of the analysis decreases at lower concentrations, especially near the limit of quantitation, and you do not want to be exaggerating the effect by multiplying it with a dilution factor. Diluted samples with results below the lowest calibration standard should be reanalyzed using a larger sample volume. ☺

Unsure what to do when you can't get enough DO depletion or filtered solids??

by Brenda Howald

Most operators encounter this issue when they have infiltration from a rain event or the plant has undergone an upgrade and now the sample results are lower than expected. The first step to address this issue is to increase sample volume to increase the DO


depletion or filtered solids. The largest required sample volume for BOD is 300 ml and 500 ml for TSS when you are reporting results for a WPDES discharge permit. If you use these volumes and still don't meet the required depletion or capture enough solids, you do not need to make any other volume changes, but, you do need to report a less than "<" value.

To determine the correct < value to use you substitute the required minimum result for the actual sample depletion or weight of solids captured in the calculation. This is called the reporting limit since it is calculated using a minimum value set in the method.

For BOD: $\frac{300 \times 2 \text{ mg/L}}{\text{sample volume used}}$ (required minimum)

For TSS: $\frac{1,000 \times 1 \text{ mg}}{\text{sample volume used}}$ (required minimum)
or $\frac{1,000,000 \times 0.0010 \text{ gm}}{\text{sample volume used}}$ (required minimum)

What happens when I use 300 ml for BOD and I still don't get a 2 mg/L depletion? If you don't get enough depletion you just have to report a "<" with a value calculated using 2 mg/L for the depletion and the largest sample volume used. If my effluent is always < 2mg/L and I use 300ml of sample do I need to set up any other bottles for that sample? Yes, the method requires you to set up a series of dilutions. The second bottle should be at a volume below 300 ml. This allows you to cover a wider sample concentration range which could be important if your effluent is above the reporting limit. Do I also report a less than "<" when all of my influent dilutions are below 2 mg/L. Yes, you would use the largest influent sample volume prepared in the above calculation. The calculated reporting limit would be much higher for influent samples since the volumes used are much smaller.

When you filter the maximum required volume of 500 ml for suspended solids and don't capture the 1 mg of solids your reporting limit will be < 2 mg/L. You can filter more than 500 ml of sample if you want, but you do not need to increase your volume to capture more solids. However, if you still do not capture 1 mg of solids with a larger volume, you will need to recalculate the reporting limit using the larger volume. 

Frequently Asked Questions (FAQ) about BOD Analysis

By George Bowman and Rick Mealy

Can I throw out a dilution if it is anomalous?

What does Standard Method say?

- 18th, 19th and 20th are mute on the point
- 21st Edition provides the following guidance:

"...Identify samples in test reports when serial dilutions show more than 30% between high and low values. Exceptions occur for highly treated wastewaters and natural waters having BODs less than 20 mg/L."

Here is what we recommend:

- DO NOT discard dilutions without evaluating the data
- Identify problem dilutions and try to determine cause (e.g., "chucks", high solids)
- If you discard the a dilution, you must qualify results and be prepared to defend your actions.

How should I report my result if the smallest sample volume over-depletes (e.g., <1 mg/L residual DO)?

What does Standard Method say?

- 18th, 19th and 20th don't say much
- 21st Edition provides the following guidance:

"When all dilutions result in a residual DO of < 1.0 mg/L, select the bottle having the lowest DO concentration (greatest dilution) and report:"

$$> \frac{(DO_I - DO_F) - [\text{seed correction}] \times 300}{\text{Smallest sample volume used}}$$

*Ex: 100 mL volume, DO_I=8.5 mg/L, DO_F=<1 mg/L
BOD = 8.5-1.0 X 300/100 = >22.5 mg/L*

- We believe older editions of Standard Methods imply results should be reported as a "greater than" (>) value based on common sense.
- DO NOT report "over depleted" on your DMR. You have enough information to say the result is greater than a certain value.

Note: Find other BOD FAQs on the LabCert website:

www.dnr.state.wi.us/org/es/science/lc/whatsnew.htm



Calculating With "Less-Thans"

by Tom Mugan

A number of measures of pollution that the Department requires permittees to report on a monitoring form involve a calculated result. A question that is commonly asked is; "How do I use a non-detect in the calculation?"

Examples of reporting that involve calculations include:

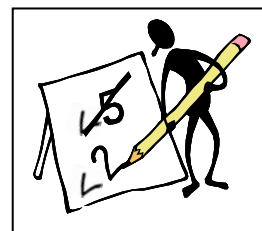
- Organic nitrogen (kjeldahl nitrogen minus ammonia)
- Nitrate plus nitrite
- Amenable cyanide
- Total PAHs
- Total PCBs
- Weekly or monthly average discharge
- Mass discharge

Here are tips for reporting:

- Report each result above the limit of detection (LOD) as a numerical result. If there are spaces on the monitoring form for the LOD and LOQ, report those values.
- Report all individual non-detects as < (less than) the value of the LOD (For example, if the result is a non-detect at an LOD of 10 µg/L, report the result as < 10 µg/L.). If there are spaces on the monitoring form for the LOD and LOQ, report those values.
- To use a non-detect in a calculation, substitute 0 (zero) for the value and then perform the calculation as normal. For example:
 - To report the monthly average of 2 detected results and 2 non-detects, total the two detected results, divide by 4 and report the numerical result.
 - Report the monthly average of 4 non-detects as 0.
 - To report the mass discharge for a day when the test result is a non-detect report 0, since 0 times any rate of flow is 0. If there are spaces on the monitoring form for the LOD and LOQ, determine the mass-based LOD and LOQ using the LOD and LOQ concentrations and the flow for the day [concentration (mg/L) X flow (MGD) X 8.34 = mass (pounds per day)].

- To report results of a calculation for total concentrations, such as total PCBs or total PAHs:
 - If all of the individual concentrations are non-detect, report 0. In the spaces for the LOD and LOQ, if the LODs and LODs are different for each congener, report the highest LOD and LOQ.
 - If one or more of the individual concentrations are detects, sum the numerical values and report the result. In the spaces for the LOD and LOQ, if the LODs and LODs are different for each congener, report the highest LOD and LOQ.

Do not report negative values. For example, if the measured value for ammonia is greater than the measured value for total Kjeldahl nitrogen (TKN), attempt to find out if there was some reporting error. If you cannot find a documented error, report 0. ☹



Food for Thought – Are you seeding CBOD samples?

by John Condron

Some laboratories are required to test for the Carbonaceous Biochemical Oxygen Demand (CBOD)₅ test for effluent samples on their WPDES permit.

2-chloro-6-(trichloro methyl) pyridine (TCMP) is designed to inhibit nitrifying bacteria. However, it is believed that TCMP might also inhibit *non-nitrifying* bacteria. If the nitrification inhibitor is inhibiting more bacteria than just the nitrifying bacteria, then the (CBOD)₅ results would be biased low. If this is true, then seeding the effluent CBOD sample should solve this problem.

The 21st edition (which is not approved for WPDES yet) of **Standard Methods for the Examination of Water and Wastewater** recommends that all inhibited samples be seeded. ☹

Waste Management



Reminder: Use New SVOC List

Facilities and labs are reminded that the revisions to the NR 500 series became effective on February 1, 2006. Facilities are expected to substitute the new NR 507 Appendix 4 list of Semi-Volatile Organic Compounds (SVOCs) for the base/neutral and acid extractable compounds. For additional information about the new SVOC list and how it was developed, please see the Spring 2005 GEMS Newsletter: <http://dnr.wi.gov/org/aw/wm/publications/monitoring/newsltr-03-05.pdf>.

For additional information see Wisconsin Administrative Code Chapter NR 507:

<http://www.legis.state.wi.us/rsb/code/nr/nr507.pdf>

If you have questions, please contact the Hydrogeologist for the DNR Region the facility is located in, per

<http://dnr.wi.gov/org/aw/wm/monitor/emtStaff.htm>



GEMS on the Web!

The GEMS subteam is proud to announce that the GEMS on the web (GOTW)

(<http://dnr.wi.gov/org/aw/wm/monitor/gemsweb/>) search and retrieval tool is now available Department's Waste & Materials Management web page: <http://dnr.wi.gov/org/aw/wm/>. You can find it on the left tool bar in the expanded Environmental Monitoring menu under the heading "Landfills."

Working on the project since late 2002, a team of hydrogeologists, IT support staff and programmers completed the Facility Search option on January 12, 2006.

With GOTW you can search/retrieve the following:

- A specific facility by license
- Facility name, owner, location
- Facilities in a geographic area
- Facility monitoring contact(s)
(knowledgeable about the site's monitoring)

- Points at a facility by owner or geographic area
- Well/Point construction information for a site or by owner or geographic area
- Sample dates/results for an entire site – a "data dump"
- Sample dates/results for a point
- All results for a single parameter at a point



Cross Media Issues

Mercury Test Sensitivity



By Tom Mugan

Labs performing mercury testing to determine effluent or river background levels for the permit program should use a test method with the lowest possible quantitation levels.

The water quality criterion for mercury is 1.3 nanograms per liter (ng/L). Because river background levels commonly exceed this criterion value, the limits placed on effluent discharges by the Department of Natural Resources generally equal the criterion of 1.3 ng/L. To be able to determine if mercury in a water sample meets water quality standards, results must be quantified at or below that level.

The approved method with the lowest quantitation level is EPA Method 1631, Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. EPA has established the minimum quantitation level (ML) for Method 1631 at 0.5 ng/L. Labs capable of the necessary low-level testing have submitted evidence of their capabilities to the Laboratory Certification Program. You may find a listing of those labs in a guidance document for generating low-level mercury results at:

http://www.dnr.state.wi.us/org/water/wm/ww/mercury/clean_hands.pdf

Labs may use less sensitive methods to test permit samples of waste streams with higher mercury levels. The selected method for a given sample type must be predicted to quantify mercury levels for all samples of that type.



General Interest



Latex in the Workplace—NOT!!!

by Lorraine D. Edwards, Senior Chemist
University of Wisconsin, State Laboratory of Hygiene

Many of us think nothing of picking up a gallon of paint at our local, home-improvement center for a weekend of painting. If you are allergic to latex, however, this type of weekend project could prove to be life threatening. In recent years, concerns associated with exposure to latex have spread from the elementary classroom and dental office, to the local hospital emergency room. Latex, which comes from the milky white sap from the Brazilian rubber tree, is found in thousands of common household items including paint, balloons, garden hoses, shoe soles, rubber bands, and elastic in clothing. Latex is relatively inexpensive to manufacture and because it is an extremely effective barrier against bacteria and viruses, latex is routinely used in products such as surgical gloves and condoms to stop the spread of infectious diseases. The use of latex rubber products, especially gloves, in laboratories is of particular concern due to the potential for chronic exposure by the employee. Health-care professionals believe that anyone could potentially develop an allergy to latex given repetitive exposure (Dr. Todd Mahr, Gunderson Lutheran, La Crosse, WI, personal communication). Symptoms of latex sensitivity typically begin with hives or itchy welts that can appear on any part of the body. In severe cases, blisters may even appear. Hay fever-like symptoms including nasal stuffiness, sneezing, runny nose and itching of the nose, eyes or inside of mouth and throat are indicative of more long-term or chronic exposure. In serious situations, anaphylaxis can occur and lead to blocked airways, swelling of the throat and a drop in blood pressure. Immediate, emergency medical attention is critical. For the protection of all laboratory workers and staff, every effort to reduce the amount of latex should be made. The following changes should be considered:

- 1) Remove all latex gloves from the building and exchange for non-latex, type gloves (e.g., nitrile).
- 2) Change all latex rubber tubing to alternative materials (e.g., Tygon™, C-Flex™, etc.). Incidentally, C-Flex™ tubing is a superior alternative to the latex tubing commonly used in BOD testing.
- 3) Exchange rubber stoppers, anti-fatigue mats and other types of laboratory equipment (e.g., eye dropper and pipette bulbs) for non-latex varieties such as silicone.

Finally, be aware of employees that may already have latex allergies or may become sensitive to wearing latex gloves. Encourage staff to wear Medical Alert Identification if necessary. Some people are so sensitized to latex that they risk an immune response through the simple inhalation of air carrying the latex allergen. Airborne allergens, due to the presence of balloons, the cornstarch powder that comes off latex gloves can be extremely serious and in rare cases, deadly.

If you would like additional information about latex in the laboratory, contact Lori at (608) 224-6281, or via e-mail at: edwardsld@mail.slh.wisc.edu



Other Latex Allergy references:

- www.aafp.org/afp/980101ap/reddy.html
- www.thegoldweb.com/lam/management.htm
- www.allergycapital.com.au/Pages/latex.html
- www.nurselearn.com/lesson_plan_latex.html
- www.lib.uiowa.edu/hardin/md/latex.html
- www.latexallergy.ndo.co.uk/





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Important Dates:

- 6/30/06: Fee payments due
(or subject to late fee)
- 7/1/06: FY07 Fee schedule takes
effect
- 8/31/06: All PTs and fee
payments must be
received to be renewed
- 9/1/06: FY07 Certification period
begins

