Top Tips for Conducting DMR-QA Analyses

BOD

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Technical Manager
ERA – A Waters Company

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- Founded in 1977
- Golden, Colorado
- More than 7,000 laboratories
- More than 80 countries

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- Waste water
- Drinking water
- Soils
- Air & emissions
- Microbiology
- Radiochemistry
- Custom standards

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What is DMRQA

- DMRQA is an acronym which stands for Discharge Monitoring Report Quality Assurance
- It is a Proficiency Testing (PT) program required for facilities containing permits to discharge treated waters back into waterways.
- It is a once per year program designed to compliment the DMRs which treatment facilities submit to the states.
- Prior to discharging your effluent, the pollutants contained on your NPDES permit must be tested to ensure that these pollutants are below the maximum contaminant levels (MCLs) listed on your permit.
- Do I need to participate in this program and why?

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What is DMRQA

- The EPA needs to ensure that the data being reported on the DMRs is accurate. There are two main ways of determining this information.
- Lab Audits or PTs.
- DMRQA is a series of PT samples which contain the pollutants of interest listed on your permit.
- What analytes do I need to run?*
- The values of the contaminants are unknown to the testing laboratories. The PT samples must be tested by the same labs who perform the tests for the DMRs using the same methods and procedures used for the effluents. The labs then report back their findings. The test results are evaluated against a pre determined set of acceptance criteria.

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The DMRQA Process

- Receive the 308A letter from EPA.
- Return your address verification form.
- Order your samples from an accredited provider.
- Analyze the samples for the pollutants on your permit.
- Report data back to the PT provider by the close of the respective study.
- Receive your report back from the PT provider.
- Compile PT reports and send to your DMRQA Coordinator – Steve Roberts
- Perform corrective action if necessary.

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DMR-QA 36 Dates & Deadlines

- Opened Friday, March 18
- Closes Midnight, Friday, July 1
- PT providers send graded reports by July 29
- Contract labs forward PT provider graded reports to permittee by August 12
- Permittees send final report to DMR-QA coordinator by August 28
- Corrective Action reports due by October 21

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DMR-QA 36 Dates & Deadlines

- If running WP, report results by close of WP study.
  - WP study results are returned within 2 business days of the close of the study. (ERA is the only provider to have results in 2 days; due to the enormous size of the DMR-QA study, DMR-QA results will be available in less than 21 days)
- If you choose to use a WP study for DMR-QA, the study must close between January 1 and July 1.

	Opens	Closes	Results
WP 252	Jan 18	Mar 3	Mar 7
WP 253	Feb 15	Mar 31	Apr 4
WP 254	Mar 7	Apr 21	Apr 25
WP 255	Apr 11	May 26	May 30
WP 256	May 16	Jun 30	Jul 5
DMR-QA	Mar 18	Jul 1	Jul 29

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DMR-QA 36 Acceptance Limits

- Based upon EPA regression equations
- Find regression equations on the TNI website at www.nelac-institute.org
- 3 standard deviations/99% CI around an expected recovery
- Concentration dependent
- Expected recovery = assigned value * a + b
- Expected standard deviation = assigned value * c + d

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DMR-QA 36 Acceptance Limits

EPA Regression Equation for BOD

a - 0.6237; b - 0.7022; c - 0.0928; d – 0.6636

at 18 mg/L limits = 27.4 – 105%

at 230 mg/L limits = 34.0 – 91.0%

EPA Regression Equation for CBOD

a - 0.5648; b - 0.6665; c - 0.0965; d – 0.8253

at 18 mg/L limits = 17.5 – 103%

at 230 mg/L limits = 26.7 – 86.8%

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DMR-QA 36 Acceptance Limits

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Example Calculation MINIMUM BOD Value

Made at 18 mg/L

Expected Recovery = Value * a + b

18 * 0.6237 + 0.7022 = 11.93

1 Expected Standard Deviation (SD) = Value * c + d

18 * 0.0928 + 0.6636 = 2.334

3SD = 3 * 2.234 = 7.00

Limits = Expected Recovery ± 3SD = 11.93 – 7.00 = 4.93

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DMR-QA 36 Acceptance Limits

Example Calculation MAXIMUM BOD Value

Made at 230 mg/L

Expected Recovery = Value * a + b

230 * 0.6237 + 0.7022 = 144.15

1 Expected Standard Deviation (SD) = Value * c + d

230 * 0.0928 + 0.6636 = 22.01

3SD = 3 * 22.01 = 66.03

Limits = Expected Recovery ± 3SD = 144.15 + 66.03 = 210

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DMR-QA 36 Acceptance Limits

Working Concentration Ranges

BOD = 4.93 – 210 mg/L

CBOD = 3.15 – 200 mg/L

Total Residual Chlorine = 0.381 – 3.48 mg/L

Low Level Total Residual Chlorine = 5.00 – 310 µg/L

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DMR-QA 36 Acceptance Limits

Working Concentration Ranges

pH = 4.80 – 10.2 s.u.

NH_3-N = 0.599 – 23.7 mg/L

TSS = 12.3 – 110 mg/L

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Introduction to BOD

- Biochemical Oxygen Demand (BOD) is the amount of oxygen that bacteria take from water when they oxidize organic matter.
- Organic matter can be comprised of carbohydrates (cellulose, starch, sugar), proteins, petroleum hydrocarbons, and other materials.
- Organic matter can enter the water supply through natural sources or from pollution.
- Organic matter can be oxidized (combined with Oxygen) by burning, being digested in the bodies of animals and humans, or by biochemical action of bacteria.
- The significance of the oxidation of organic matter is that it produces carbon dioxide.

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The Significance of BOD

- Measurement of BOD is an important means for determining the degree of water pollution.
- It is the most important measurement made by the wastewater treatment plant.
- The measurement of BOD is made to determine the efficiency and effectiveness of sewage treatment.
- For example, it is common for the raw influent coming into a plant to be upwards of 300 mg BOD/L. If the measurement of BOD leaving the plant in the effluent is measure at 30 mg BOD/L, then the plant has been successful in removing 90% of the BOD.
- The Maximum Contaminant Levels (MCLs) of the effluent discharge are set to protect the wildlife in the waterways.

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The Significance of BOD

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- If the water being discharged from the plant into a waterway is too high in BOD, the bacteria living in that waterway will oxidize the organic matter, consuming oxygen from the waterway faster than it dissolves back in from the air.
- This will create a situation where oxygen levels become too low to sustain life in the fish in the waterways.
- This consequence is known as fish kill.

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The Measurement of BOD

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- Dilutions of the sample are made by placing various incremental portions of sample into BOD bottles and filling the bottles with dilution water.
- The dilution water will contain a known amount of dissolved oxygen. The dilution water will also contain inorganic nutrients and a pH buffer.
- The BOD bottles are completely filled, measured for initial dissolved oxygen levels, freed of air bubbles, sealed and allowed to stand for five days at a controlled temperature and in the dark.
- During this period, bacteria oxidize the organic matter using the dissolved oxygen in the water.
- The consumption of oxygen during the five days and sample volume is used to calculate BOD

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The Reliability of BOD

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- BOD is only partially reliable for measuring the organic matter in the water as it only measures the oxygen taken up by wastewater during the incubation period.
- There are many factors that affect the oxidation of the water by the bacteria.
- Bacteria grow during this period but generally very slowly so that the biological oxidation during the 5 days is never complete. Research has shown it is maybe 80% complete.
- Toxic substances in the water can inhibit or even prevent bacterial growth.
- The test can be affected by the initial dissolved oxygen levels in the water.
- Altitude and temperature changes also have an affect on the dissolved oxygen levels. Saturation decreases as altitude increases.

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The Reliability of BOD

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- The lower dissolved oxygen levels at higher altitudes limits the range for oxygen depletion during the test.
- Deionized water can contain somewhat high amounts of organic matter, which can affect the final results.
- Water distilled with an alkaline permanganate will more consistently product low organic matter. Remember that your blank water sample should show BOD levels less than 0.2 mg BOD/L. However, copper is an interferent and distilling in a copper still will cause problems.
- Quality of the seed needed for tests where the samples has no microorganisms (such as the GGA or DMRQA) will dramatically affect the biochemical activity.

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Method 5210B for DMRQA

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- Prepare your dilution water. Dilution water consists of phosphate buffer, magnesium sulfate, calcium chloride, and iron chloride. Bring the dilution water to $20 \pm 3^{o}C$. Saturate the dilution water with Dissolved Oxygen (DO). Ideally the dilution water should not be stored for more than 24 hours to prevent bacterial growth. Commercially available dilution water packets are acceptable.
- Prepare a glucose-glutamic acid (GGA) check sample to determine the quality of your test. This is done by doing a 2% dilution of a check standard consisting of 150 mg/L glucose and 150 mg/L Glutamic Acid.
- Dilute the DMRQA PT sample as per dilution instructions.
- Ensure that the pH of the diluted sample meets the requirements of your method.

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Method 5210B for DMRQA

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- If the pH is too low use a dilute solution of sodium hydroxide to adjust the pH. A 0.2N solution is recommended. ERA will provide this to you free of charge if you purchase our Demand sample. Just ask!!
- Ensure your BOD bottles are organic and chlorine free. Place an appropriate amount of sample into the BOD bottle. Fill your bottle mostly full with dilution water.
- Add an appropriate amount of seed to the sample. The DMRQA PT sample MUST be seeded. Then fill the BOD bottle to over full with dilution water. The method indicates to seed the dilution water. Please do not seed the dilution water. Seed each sample individually.
- Cap the bottle. Make sure there is dilution water on the neck of the bottle. Then put a protective material over the bottle top. (A plastic cap or aluminum foil will suffice).

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Method 5210B for DMRQA

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- The method recommends taking at least five dilutions, so that you have at least two dilutions which meet the method criteria.
- Prepare both a blank water check and a seed control check.
- Take an initial DO reading of the samples. The initial DO reading should be taken within 30 minutes.
- Place the samples into an incubator for 5 days ± 4 hours at a temperature of 20 ± 1°C.
- Remove the samples from the incubator and allow to cool.
- Read the final DO.
- Perform your calculation. Make sure you only use aliquots which meet the method requirements of a minimum depletion of 2.0 mg/L and a residual DO of 1.0 mg/L.

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Calculating BOD

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BOD, mg/L =

$$\frac{(D1 - D2) - (B1 - B2)f}{P}$$

Where

D1 = Initial DO of sample

D2 = DO of sample after incubation

P = decimal volumetric fraction of sample used

B1 = DO of seed control before incubation

B2 = DO of seed control after incubation

f = (volume of seed in sample)/(volume of seed in seed control)

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BOD – Tips and Tricks

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- There are many places for things to go wrong. The acceptance limits reflect this. Taking care to ensure your analysis is going correctly can solidify your analysis and leave you within the acceptance range.
- Dilute your sample properly. Adjust your pH. The diluted sample will have a pH of about 3.5-4. The test generally requires a pH of 6.5-7.5. Use dilute NaOH solution to adjust (0.2 N is recommended). More concentrated solutions will cause the pH to shoot up past the upper range.
- pH out of the range will distress the microorganisms and cause low results.
- Residual chlorine will distress or kill your microorganisms. Ensure all your glassware, water, and reagents used for the test are free from chlorine.

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BOD – Tips and Tricks

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- Improper incubation temperature will cause erroneous results. Your temperature needs to be 20 ± 1°C. Low temperatures will slow the microorganisms causing low results. High temperatures will speed up microorganisms causing high results.
- The samples you receive from your provider will not contain seed and thus need to be seeded prior to the analysis. The seed must be strong and consistent. Most plant raw will satisfy this need. Poly seeds are commercially available. The poly seed is generally not as strong and will require additional volume than the raw seed.
- Seed each bottle with the same amount of seed. Do not seed your dilution water, as different volumes of dilution water are used and will vary the amount of seed in each sample.

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BOD – Tips and Tricks

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- Run a seed control sample. Seed contains BOD. Ensure that your seed control values are subtracted out from your samples before performing final calculations.
- The BOD bottles are filled with nutrient (dilution) water. Nutrient water must be fresh to assure sufficient ammonia remains in the water. Nutrient water must be free of chlorine and organics.
- Check the quality of the nutrient water to ensure there is no BOD. Perform this check by incubating a bottle with just Nutrient water and a bottle with nutrient water plus seed. Your nutrient water should contain BOD at less than 0.2 mg/L.
- The dilutions performed on your sample are extremely important for proper testing. Do a series of dilutions to ensure that you have multiple samples meeting method requirements.

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BOD – Tips and Tricks

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- As per method 5210B, the incubation should result in a minimum DO depletion of 2.0 mg/L and a minimum residual DO of 1.0 mg/L. Use only samples that meet this requirement for performing calculations.
- The DMRQA BOD will be between 18 and 230 mg/L. Perform your dilutions to meet this range. Use your historical analyses to help determine the proper dilutions.
- When filling the BOD bottles full, make sure there is a small amount of nutrient water above the cap to ensure there is a water barrier. The cap of the bottle should be covered to prevent moisture loss. This will prevent any air from being introduced into the sample during incubation. Introducing air into the sample will add DO to your sample.

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BOD – Tips and Tricks

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- The initial DO readings should be between 7-9 mg/L DO. If the readings are greater, stir the sample to release DO.
- Incubate your sample for the exact amount of time listed in the method. 5 days ± 4 hours. Incubation outside of this time will affect the amount of DO depletion.
- The quality of your DO probe and the condition of your analyses will affect the quality of your measurements.
- The DO probe must be maintained. Clean the gold plate on the probe at least monthly and change the membrane at least weekly. Dirty membranes and gold plates will cause the probe to drift. Do a water check at the beginning and end of your run. This check should not show a DO difference of more than 0.15 mg/L. A drift greater than this will cause erroneous readings.

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DO Probes

- There are several different types of DO probes available. LDO, RDO, membrane.
- The DO probe must be maintained. For Membrane electrodes, clean the gold plate on the probe at least monthly and change the membrane at least weekly. Dirty membranes and gold plates will cause the probe to drift. Do a water check at the beginning and end of your run. This check should not show a DO difference of more than 0.15 mg/L. A drift greater than this will cause erroneous readings.
- Although very stable, slight drifts in LDO and RDO can cause large differences in numbers. Calibrate these electrodes each day.
- How do you know your DO probe is accurate. Check with a DO standard.

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Avoid Surprises

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- Run analyses as soon as possible
- Allow time for things to go wrong
- Establish a routine quality control process with the use of Certified Reference Materials

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Ohio Corrective Action

- Required for all “Not Acceptable” Results
- Do a Root Cause to try to determine what went wrong
- Fix the problem
- Run WP or Quick Turn sample
- Write a Corrective Action Report
- Send Report with Acceptable PT report to Steve Roberts by October 21

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Steve Roberts – Ohio DMRQA Coordinator

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QUESTIONS

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