

How Do I Report ... THIS?



Rick Mealy
DNR-Regional Certification Coordinator



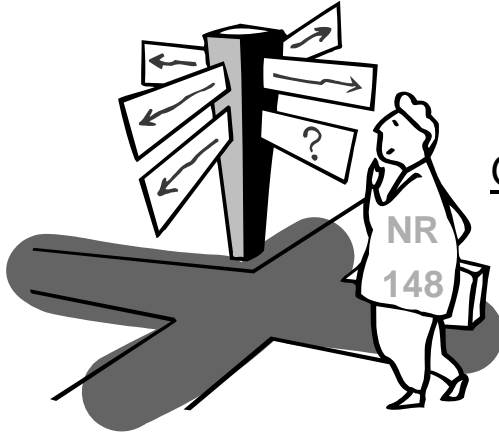
Bridging the Information Gap



Code & Guidance

The Code as a data reporting resource...

... a wastewater lab's perspective



Guidance Available

- "Helpful Hints" archive
- "LabNotes" publication

Bottom Line: *We can generalize to some extent, but can't anticipate all possible scenarios*

Close Encounters of the Reporting Kind

These are the things to fear when it comes time to report results

TSS

poor replicates
too little residue
too much residue
solids "sloughing"

BOD

poor replicates
over-depletion
under-depletion
toxicity

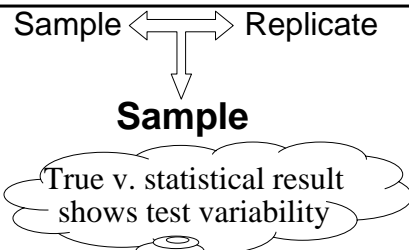
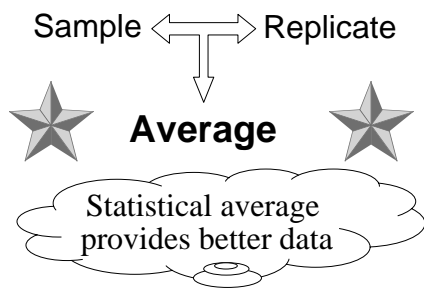
TP & NH3

poor replicates
over-calibration
dilute until < LOD
contamination

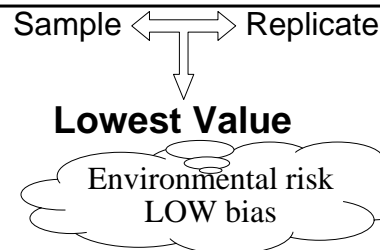
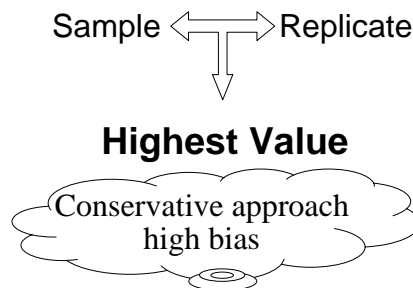
General Practices

Reporting Replicates

Defensible Options



NOT Defensible Options



Dealing with “< LOD” Values

In those instances where either the sample or the replicate (*or both*) are determined to be below the LOD, you will not have a valid measure of precision.

Sample BOD = 2.8 Range is NOT 2.8, 0.8, or anything else.
 Replicate BOD = < 2 It cannot be calculated because we do not know what the actual replicate value is.

Sample NH₃ = < 0.04 Range is NOT 0 (zero), or anything else.
 Replicate NH₃ = < 0.04

- Provides another rationale for knowing what the LOD is.
- If replicates are frequently below the LOD, a better measure of precision is obtained through analysis of replicate spikes.
 Substitute a replicate for a duplicate spike (at same level).

Significant Figures

of significant figures to report

| | <u>1</u> | <u>2</u> | <u>3</u> |
|------------|---------------------------|--------------|------------|
| BOD | 2 - 9.99 ppm | 10-99.99 ppm | >99.99 ppm |
| TSS | 2.1 - 9.99 ppm | 10-99.99 ppm | >99.99 ppm |
| Ammonia | 0.1 - 1.0 ppm | > 1.0 ppm | ----- |
| Phosphorus | 0.1 - 1.0 ppm | 1 -99.99 ppm | > 100 ppm |

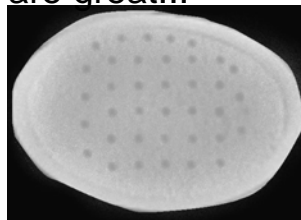
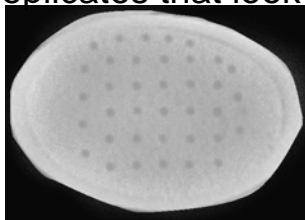
| | | | |
|------------|-------------------|--------------------|----------------------|
| BOD | 1.8 = 2 | 21.4 = 21 | |
| & TSS | 9.4 = 9 | 99.44 = 99 | 117.4 = 117 |
| | 9.8 = 10 | 99.99 = 100 | 1267 = 1270 |
| Ammonia | 0.47 = 0.5 | 4.72 = 4.7 | 21432 = 21400 |
| & T. Phos. | 0.75 = 0.8 | 85.4 = 85 | |

TSS

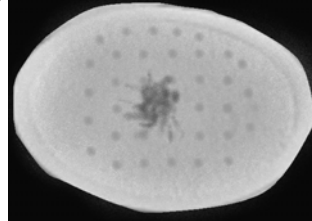
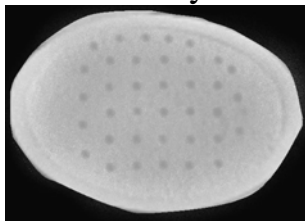
Reporting

TSS Replicate Anomalies

Replicates that look like this are great...

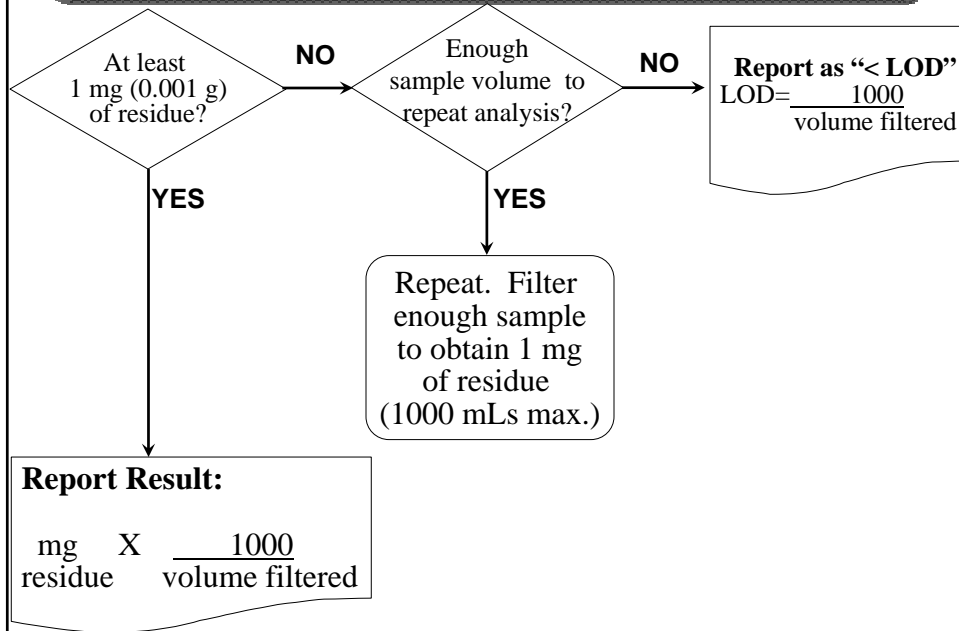


...but what do you do when they that look like this?



Paste the filters (or a copy) to a corrective action form.
Consider this to be an outlier result.
Comment on DMR.

TSS Reporting FlowChart



B.O.D.

Reporting

BOD: Excess Depletion

High dilution; over deplete

| <u>Sample</u> | <u># mLs</u> | <u>DO_i</u> | <u>DO_f</u> | <u>ΔDO</u> | <u>BOD</u> | <u>Report</u> |
|---------------|--------------|-----------------------|-----------------------|------------|------------|---------------|
| 005 | 10 | 8.44 | 0.92 | 7.52 | 226 | ? |
| 005 | 15 | 8.40 | 0.00 | 8.40 | 168 | |

The 168 is probably a low number - COULD have used more O₂ (if available)

The 226 may also be biased low - Readings below 1.00 mg/L are less accurate

Take a conservative approach

Maximum volume; over deplete

| <u>Sample</u> | <u># mLs</u> | <u>DO_i</u> | <u>DO_f</u> | <u>ΔDO</u> | <u>BOD</u> | <u>Report</u> |
|---------------|--------------|-----------------------|-----------------------|------------|------------|---------------|
| 006 | 300 | 8.33 | 0.40 | 7.93 | 7.9 | ? |
| 006 | 250 | 8.31 | 0.90 | 7.41 | 8.9 | |

Both values probably biased low - Readings below 1.00 mg/L are less accurate

Take a conservative approach

BOD: Insufficient Depletion

Over-diluted; under deplete

| <u>Sample</u> | <u># mLs</u> | <u>DO_i</u> | <u>DO_f</u> | <u>ΔDO</u> | <u>BOD</u> | <u>Report</u> |
|---------------|--------------|-----------------------|-----------------------|------------|------------|---------------|
| 007 | 1 | 8.44 | 8.10 | 0.34 | 102 | ? |
| 007 | 5 | 8.40 | 6.83 | 1.57 | 94.2 | |

Result must be < 120 - If the least diluted sample met depletion reqs. -->120 mg/L

Clearly the BOD is at least 94, do not want this averaged as a zero

Reporting either 94 or average of the two (98) is an approximation

Report what you can substantiate (more sample; greater depletion)

Under 300 mLs; under deplete

| <u>Sample</u> | <u># mLs</u> | <u>DO_i</u> | <u>DO_f</u> | <u>ΔDO</u> | <u>BOD</u> | <u>Report</u> |
|---------------|--------------|-----------------------|-----------------------|------------|------------|---------------|
| 008 | 200 | 8.33 | 6.52 | 1.81 | 2.7 | ? |
| 008 | 100 | 8.31 | 6.60 | 1.71 | 5.1 | |

200 mL dilution would be < 3 (LOD is 3)

If you ignore 200 mL dilution, result would be "< 6"

Reporting "> 5" is best case scenario when dealing with averages

BOD: Excess & Insufficient Depletion

1 over depletes

| <u>Sample</u> | <u># mLs</u> | <u>DO_i</u> | <u>DO_f</u> | <u>ΔDO</u> | <u>BOD</u> | <u>Report</u> |
|---------------|--------------|-----------------------|-----------------------|------------|------------|---------------|
| 009 | 1 | 7.44 | 4.57 | 2.87 | 861 | ? |
| 009 | 5 | 7.43 | 0.10 | 7.33 | 440 | |

The difference between the results cause concern

There is certainly more than 440 ppm; supporting a result of "> 440"

Could report 861 and qualify results

1 under depletes; 1 over depletes

| <u>Sample</u> | <u># mLs</u> | <u>DO_i</u> | <u>DO_f</u> | <u>ΔDO</u> | <u>BOD</u> | <u>Report</u> |
|---------------|--------------|-----------------------|-----------------------|------------|------------|---------------|
| 010 | 5 | 7.81 | 6.84 | 0.97 | 58.2 | ? |
| 010 | 25 | 7.72 | 0.09 | 7.63 | 91.4 | |

An upper boundary would be "< 120" 5 ml: if depletion=2, bod=120 ppm

A lower boundary would be "> 81" 25 ml: if residual=1, bod = 80.6

Greater volume leads to higher result; > 91

Toxicity-Some facts

- ↳ Typically results in UNDER-reporting the BOD of a waste
- ↳ Pattern is a decrease in BOD as the sample volume increases (increase in BOD as sample dilution increases)
- ↳ Nitrification LOOKS LIKE toxicity
- ↳ If samples are high in ammonia (e.g., lagoons in spring) and nitrification is going on, you will see the opposite effect.
- ↳ Even pH adjustments can result in this effect
- ↳ Failure to mix sample b/w dilutions can LOOK LIKE toxicity
- ↳ Pipetting technique
- ↳ Difficult to diagnose without at least three dilutions
- ↳ NOT expected from a purely domestic/municipal system

Toxicity?

| Sample mLs | Depletion (mg/L) | BOD mg/L | Report? |
|---------------|---------------------|-------------|--------------|
| 25 | 7.2 | 86.4 | 41.6 ? |
| 50 | 5.1 | 30.6 | 86.4 ? |
| 100 | 2.6 | 7.8 | 41.6 _____ ? |

Actual effluent data

| mLs | depleted | BOD |
|-----|----------|------|
| 100 | 5.1 | 15.3 |
| 200 | 6.7 | 10.1 |
| 300 | 7.6 | 7.6 |

> 15
~~11~~

Actual influent data

| mLs | depleted | BOD |
|-----|----------|-----|
| 6 | 3.8 | 190 |
| 8 | 4.5 | 169 |
| 10 | 5.2 | 156 |

> 190
~~172~~

- ➔ Best answer: report ">" plus the highest BOD
- ➔ MUST qualify these results as exhibiting "toxicity"
- ➔ Should repeat w/ additional dilutions (e.g., 5, 10 mLs)

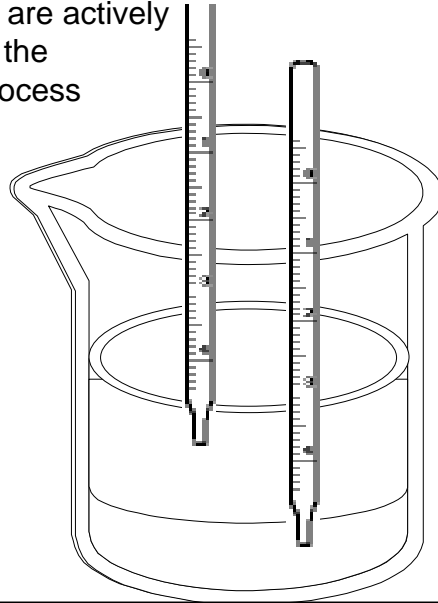
Toxicity - Are you sure?

- ↳ Use at least 3 dilutions (Difficult to diagnose without at least 3)
- ↳ Any industry? If not, it's doubtful that you're dealing with toxicity (NOT expected from a purely domestic/municipal system)
- ↳ Check records to see if an industry discharged something [unusually] toxic
- ↳ Look at your bugs for signs of stress
- ↳ How dramatic is the change with dilution?
- ↳ Use "quick pour" approach vs. careful (*lots-of-time-for-solids-to-settle*) technique to arrive at a specific volume.
- ↳ Do not use "Mohr" or serological pipets. Never use a single pipet filling for more than one dilution.
- ↳ Keep the sample stirring between (and during) dilutions.

Sub-sampling

During pipetting, solids are actively settling during the entire transfer process

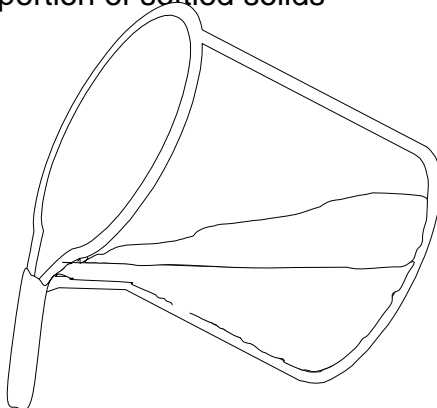
- Ensure that the position of the pipet tip isn't causing a selective sub-sampling of supernatant or settled solids.
- Sample must be well-mixed during the entire time it takes to fill the pipet.
- Macro-bore pipets are required.



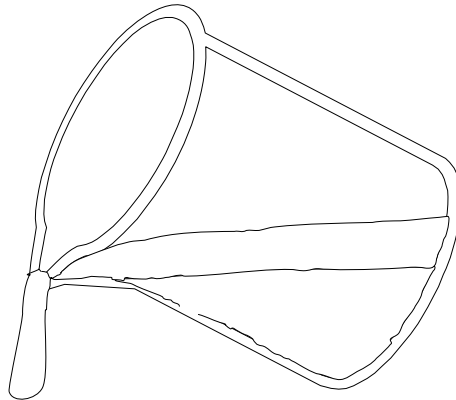
Sub-sampling

When pouring, solids are also actively settling during the entire transfer process

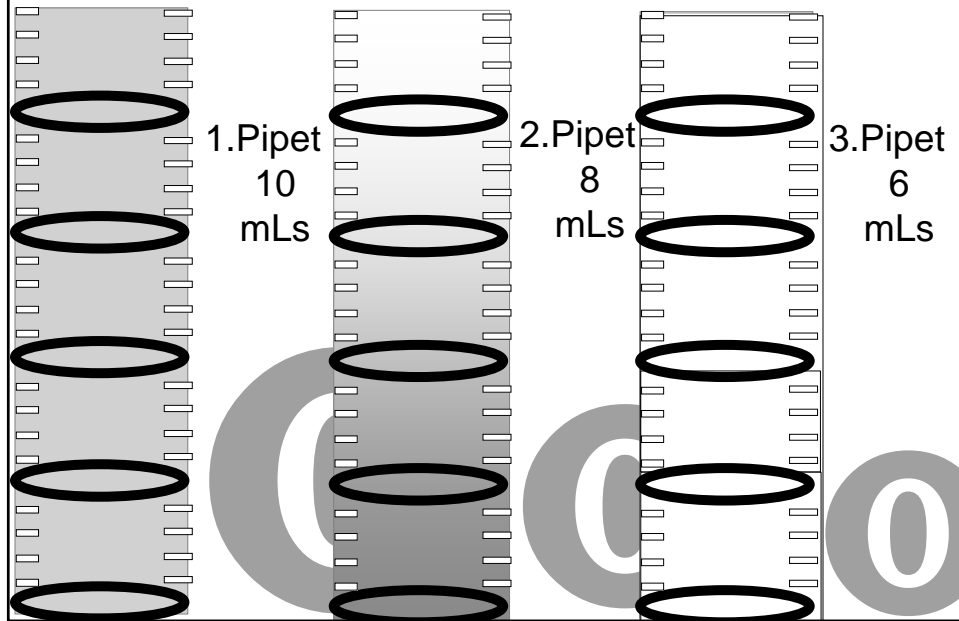
Pouring **quickly** favors an aliquot containing a significant portion of settled solids



Pouring **slowly** favors an aliquot containing a significant portion of diluted supernatant



Serological Pipet Concerns



TP & NH₃
Reporting

Calibration Range and Reporting

Excessive dilution of a sample can make reporting difficult...

Calibration maximum = 1.0 ppm
Calibration minimum = 0.1 ppm
LOD = 0.05 ppm
Sample Diluted 10x
Sample reads = 0.045 ppm

What should you report? >0.45ppm? 0.45? <1.0? < 0.5?

> 0.45ppm? Since you diluted it, it must be there. Accuracy is not as good at low levels so a conservative approach would call this “greater than”.

0.45 ppm? Since you diluted it, it must be there. Take the instrument result and multiply it by 10

<1.0? The value is certainly <[low standard X 10].

< 0.5? I can say with confidence it's <[LOD multiplied by 10].

Diluted result below LOD

What DO you know?

The raw result (0.045) is less than the LOD (0.05).

What DON'T you know?

Whether the raw result (0.045) is due to sample...or background
How the raw result (0.045) relates to method blank concentration

What should you do in this situation?

- If possible, repeat any sample with less dilution.
- Any result below the LOD must be reported as “<”
- In a diluted sample, the LOD must be raised by the DF
- If unsure of dilution required, try a “quick & dirty” test

Calibration Range and Reporting

What effect does the calibration range have on reporting results?

Calibration maximum = 1.0 ppm
Calibration minimum = 0.1 ppm
LOD = 0.05 ppm
Sample NOT Diluted (1x)
Sample reads = 1.36 ppm as P

What should you report? 1.4 ppm >1.4 ppm? >1.0 ppm?

- 1.4 ppm?** A rationale might be that the color was darker than that of the high standard and it isn't significantly above the calibration range.
- > 1.4 ppm?** A rationale might be that results are biased low due to non-linearity of the curve.
- > 1.0 ppm?** Since you only established a calibration up to 1.0 ppm, that limits your ability to report beyond that level.

Result over-calibration

What DO you know?

The raw result (1.36) significantly exceeds the calibration range.
Phosphorus is non-linear above 1 ppm.

What DON'T you know?

The accuracy of results even slightly over the high standard.

What should you do in this situation?


- If possible, repeat sample at a higher dilution.
- Any result above the highest calibration standard must be reported as ">" + the value of the highest standard.

Qualifying Data

Qualifying Data - Blanks

Situation: Your BOD blank depletions have been unacceptable for the past week. You traced the problem to a new bottle of “Cowboy Bob’s” distilled water.

 ~~BOD blank failed.~~

 2/10/02 to 2/17/02 - BOD blank depleted more than is allowed (0.2 mg/L).
Blank depletions ranged 0.6 to 1.1 mg/L.
Traced to new bottle of water.

Qualifying Data - Known Standards

Situation: Your BOD glucose-glutamic acid (GGA) exceeded acceptance criteria. You used a new lot of GGA standard the next day and results were fine.

~~☒ GGA exceeded acceptance criteria.~~

☒ 2/7/02 - GGA analyzed this day (235 mg/L) exceeded criteria (198 ± 30.5). Repeated GGA with new lot on 2/12/02. Result was 202 mg/L.

Qualifying Data - Replicates


Situation: Your effluent TSS replicate on 2/17/02 exceeded upper control limit.


~~☒ Replicate failed for TSS.~~

☒ 2/17/02 - Replicate range (5.5 mg/L) for TSS on effluent exceeded upper control limit (1.9 mg/L). Replicates are done weekly, so data since 2/10/02 are affected. Heavy rains caused TSS levels to be 3 times typical levels. Did another replicate next day and it passed.

Qualifying Data - Spikes

Situation: Your phosphorus effluent spike on 2/17/02 exceeded control limits.

 ~~Phosphorus spike exceeded control limit~~

 2/17/02 - Spike for phosphorus on final effluent (35%) exceeded criteria (79-128%). Final is spiked every two weeks, so data back to 2/3/02 is affected. High phosphorus this day (1.2 mg/L) and the spike amount was too low (0.1 mg/L). I raised the spike amount to 0.5 mg/L, made up a spike the next day and it passed.

Qualifying Data - Final Words

- There is a significant level of QC required in testing, and thus - statistically speaking- you are going to exceed something each month.
- Even a lab doing only BOD and TSS 3x/week can generate up to 24-30 QC samples/ month.
- Add in ammonia & phosphorus, and the number increases to 76-95/month
- Consequently, it's almost an expectation that something will be qualified each month.
- With qualifiers, "less" is not more.

Resources

Your Regional Auditor
Your Basin Engineer (or Specialist)
Regional Water Experts

Lab Certification Contacts

Regional Certification Coord.

Rick Mealy

(608) 264-6006

mealyr@dnr.state.wi.us

LabCert Section Chief

David Webb

(608) 266-0245

webbd@dnr.state.wi.us