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Strategic Pre-emptive Strikes: Revisiting BOD Analysis

The 411 on BOD LOD

Defining "depletion"

Dear Rock & Gonzo
I have a question for you.
With the following results from a cBOD *run, how would the result be written down? Our samples make the requirement of at least 2 ppm, but once we subtract the seed correction factor it is under the 2ppm criterion.*
Thanks!
Scooter

Sample Size: 275 ml (*Dilution factor: 1.09*)
Initial DO: 8.65 Final DO: 6.59
Depletion: 2.06
Seed Correction factor: 0.62
Depletion After seed correction: 1.44
Result: 1.57 mg/L
Do I record the result as 1.57 mg/L?
…or do I record as <2?
…or do I need more sample? Seed?

Defining Depletion

Reporting has to be dealt with separately.
We first have to decide whether we have a reportable value; and then –if we do– how do we deal with it?
The bottom line here is: "Was there adequate depletion?"

1. Is the depletion adequate?

Yes...but due to the supplement from the seed.
The larger issue is...how much of the depletion was due to the seed (*or, actually...how much of the depletion was due to sample*). Here, the analyst has it: It's 1.57 ppm... which is below the LOD of 2.2.

...as long as the combined deletion of sample + seed is at least 2 mg/L

2. What to report?

So...the analyst can report < 2.2.
The bigger issue is...the lab should use a full 300 mL bottle?

Throw all the seed at it you want… at the end of the day, it's still "<"

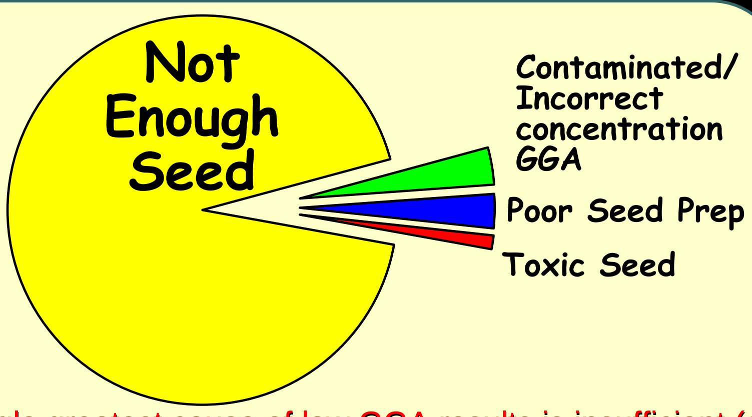
Sample	BotL#	A Sample mLs	Seed mLs	B DO_I	C DO_F	D Depletion B-C	E SCF	F DF 300/A	BOD F x (D-E)	REPORT
Dil'n Blank	X	300	0	8.5	8.4	0.1				
	U	300	0	8.5	8.4	0.1				
Seed Control	A		5	8.5	6.2	2.3	0.46			
	B		10	8.5	4.4	4.1	0.41			
	C		15	8.5	1.9	6.6	0.44			
GGA	L	6	2	8.5	3.5	5	0.87	50	206.3	
	T	6	2	8.5	3.5	5	0.87	50	206.3	204.7
	Z	6	2	8.5	3.6	4.9	0.87	50	201.3	
The Pristine Sample	VV	200	0	8.5	8.3	0.2	0	1.5	0.3	
	F	250	0	8.4	8.2	0.2	0	1.2	0.2	< 2 ??
	AN	300	0	8.4	8.2	0.2	0	1	0.2	
The Pristine Sample II	VV	250	2	8.4	7.5	0.9	0.87	1.2	0.0	UNDER
	VV	250	4	8.4	6.6	1.8	1.75	1.2	0.1	UNDER
	VV	250	6	8.4	5.7	2.7	2.62	1.2	0.1	
	VV	250	8	8.4	4.8	3.6	3.49	1.2	0.1	
	VV	250	10	8.4	3.9	4.5	4.37	1.2	0.2	< 2.4
	VV	250	12	8.4	3.1	5.3	5.24	1.2	0.1	
	VV	250	14	8.4	2.2	6.2	6.11	1.2	0.1	
	VV	250	16	8.4	1.3	7.1	6.99	1.2	0.1	
	VV	250	18	8.4	0.5	7.9	7.86	1.2	0.0	OVER
	VV	250	20	8.4	0	8.4	8.73	1.2	-0.4	OVER

GGA TROUBLES

GGA Troubleshooting

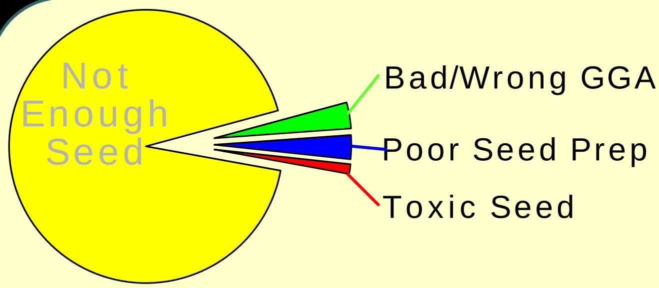
- Like Goldilocks and the 3 Bears, GGA can only be Too Low, Too High, or Just Right.
- Just Right is 198 ± 30.5 mg/L (167.5-228.5)

GGA TOO LOW (< 180)



The single greatest cause of low GGA results is insufficient (or inadequate) seed. Try running multiple bottles of GGA adding additional seed to each bottle. For example, if you typically use 2 mL of seed material, prepare 3 bottles of GGA: one with 2 mLs of seed, one with 4 mLs of seed, and one with 6 mLs of seed. If the seeding is the problem, you should see a rise in GGA with increasing seed volume until it passes.

GGA TOO LOW (Corrective Action)



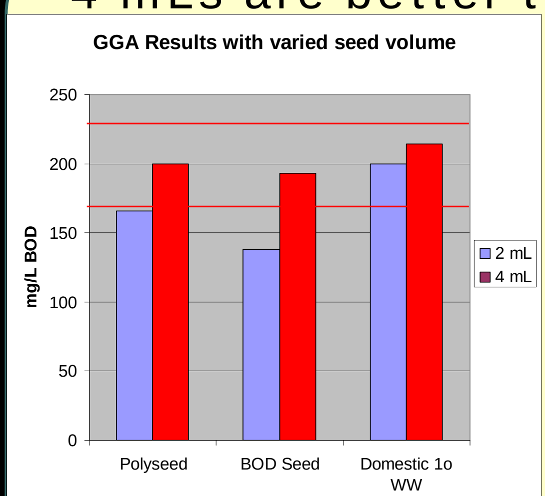
Bad/Wrong GGA: Re-prepare GGA or obtain fresh.

Poor Seed Prep: If using synthetic seed, check to be sure seed was prepared properly according to instructions. Allow to settle, carefully decant and pipet from that.

Toxic Seed: This should be a rare occurrence, and only associated with an externally obtained (non-synthetic) seed. Try a different seed material.

Increased Seeding DOES Affect GGA

4 mLs are better than 2 mLs



	GGA 2 mL	GGA 4 mL
Polyseed	166	200
BOD Seed	138	193
1º WW *(domestic)*	200	214

GGA & SEEDING – New Concept: DPMS

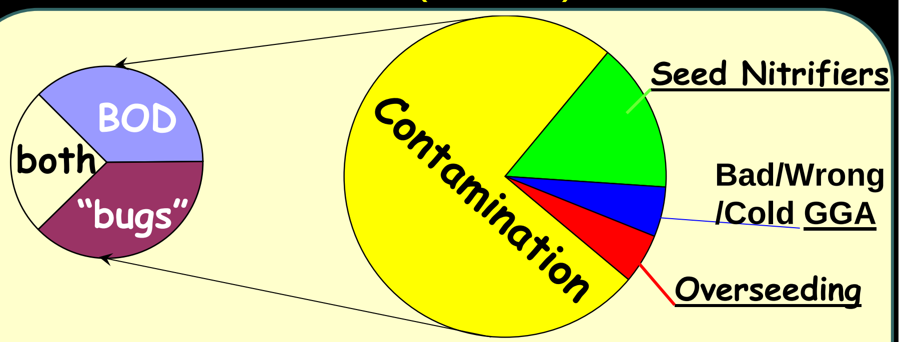
DPMS: mg/L DO Depletion Per mL of Seed

Many lab folks jump to the seed correction factor (SCF), which is the average DPMS. As with everything else, averages can be misleading. Look at the data that goes into the SCF!

Depletion per mL of seed: Monitor the depletion per mL of seed. Add enough seed to GGA which will result in a depletion of *about* 0.6 to 1.0 mg/L.

Consistency of seed controls: Most likely cause is drawing up settled seed. Consistency is critical. If you have 3 seed controls having depletions per mL of 0.2,0.4, and 0.6, two mL of seed will result in a depletion of between 0.4 and 1.2 mg/L. With a dilution factor of 50 for GGA, that's a range of 20-60 in your GGA. That could kill you.

GGA TOO HIGH (> 220)

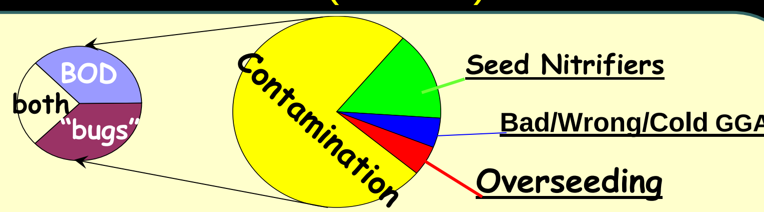


Contamination: This is the #1 source of high GGAs. GGA is more problematic than blanks because seed is added and a food source [the GGA] is already available. It becomes harder to rule possibilities out.

BOD Sources: Look for inadequately cleaned bottles, or poor quality tubing used to dispense dilution water. DI systems frequently can support biofilms. Alcohol used to clean benchtops and lab air fresheners also are BOD sources.

GGA Killers

GGA TOO HIGH (> 220)



Contamination ("Bugs"): Sources could be from the lab itself, or possibly from buildup in a lab reagent water system.

Nitrifiers in Seed: Recall that there is ammonia in dilution water (294 mLs!) and GGA contains significant nitrogen.

GGA prep: Contaminated GGA, incorrectly prepared GGA and use of GGA while cold can all cause high GGA bias..

OverSeeding: Literature sources cite this and it COULD happen, but as long as your SCF (**DPMS**!) is accurate, GGA should be fine.

SEEDING – A REVIEW

Seeding Review 1

		A	B	C	D	E	F		
		Seed			Depletion		DF	BOD	
Sample	BotL#	mLs	DO_I	DO_F	B-C	DPMS	300/A	F x (D-E)	SCF
Example 1: Good, Consistent Seed									
Seed Control	A	5	8.5	6.2	2.3	0.46	60	138	
	B	10	8.5	4.3	4.2	0.42	30	126	0.44
	C	15	8.5	1.9	6.6	0.44	20	132	

A good quality seed has a DPMS of about 0.35-0.5 (BOD of 130-180) and is consistent.

Seeding Review 2

		A	B	C	D	E	F		
		Seed			Depletion		DF	BOD	
Sample	BotL#	mLs	DO_I	DO_F	B-C	DPMS	300/A	F x (D-E)	SCF

Example 3: Weak Seed

Seed Control	A	5	8.5	7.9	0.6	**0.12**	60	36	
	B	10	8.5	7.1	1.4	**0.14**	30	42	0.14
	C	15	8.5	6.2	2.3	**0.15**	20	46	

A weak seed has a DPMS of <0.25 (BOD < 50). Too much seed volume is needed to pass GGA. Generally 2-4 mLs of seed should be enough.

Seeding Review 3

		A	B	C	D	E	F		
		Seed			Depletion		DF	BOD	
Sample	BotL#	mLs	DO_I	DO_F	B-C	DPMS	300/A	F x (D-E)	SCF

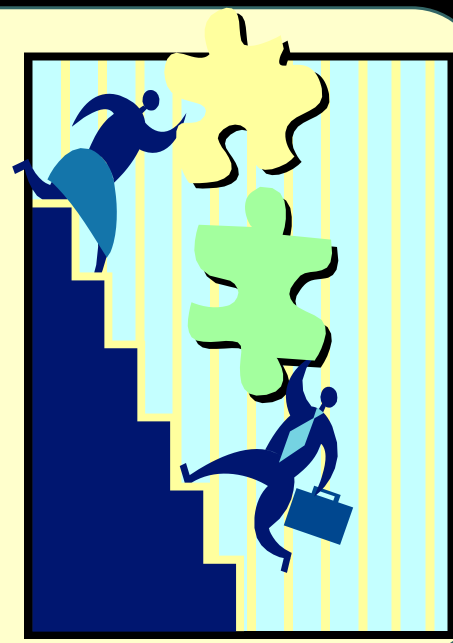
Example 5: Seed Toxicity

Seed Control	A	5	8.5	6.1	2.4	**0.48**	60	144	
	B	10	8.5	5.7	2.8	**0.28**	30	84	0.33
	C	15	8.5	5.2	3.3	**0.22**	20	66	

A toxic seed would look something like this. Leftover detergent or surfactant in a BOD bottle could cause this if not adequately rinsed and seeded added first.

Relationships

BOD
& TSS
& COD
& Others



BOD & TSS

In a perfect world, TSS roughly approximates BOD (**BOD:TSS ratio = 0.8 to 1.2**). In fact, some small labs analyze TSS and after a 1 hr dry time, they use the TSS value to determine what are the best dilutions to use for the BOD assay.

BOD:TSS Ratio	Possible Causes
0.25 to 0.67	Algae Loss of old sludge
0.8 to 1.2	Typical effluent
> 1.2	Soluble BOD Nitrification Poor treatment

Other ratios

Other ratios are often invaluable in performing detective work for a particular situation or facility.

BOD:COD ratios: Think of it as "available" carbon (BOD) vs. "total" carbon. COD is always greater than BOD. Without sufficient data and a fairly constant waste stream, COD provides a rapid estimate of BOD.

BOD:cBOD ratios: This is the most significant tool in detecting nitrification—but understand that cBOD will always be less than BOD. The extent to which it is less and other factors indicate nitrification.

BOD/COD ratios vary between wastes...

Characteristics of some grab wastewater samples

	Oakfield	Green Lake	Ashland	Campbellsport	Green Bay
BOD mg/L	93	121	190	205	157
COD mg/L	388	300	462	450	427
BOD/COD	0.24	0.40	0.41	0.46	0.37

Source: http://www.dnr.state.wi.us/org/water/wm/ww/biophos/3bpr.htm

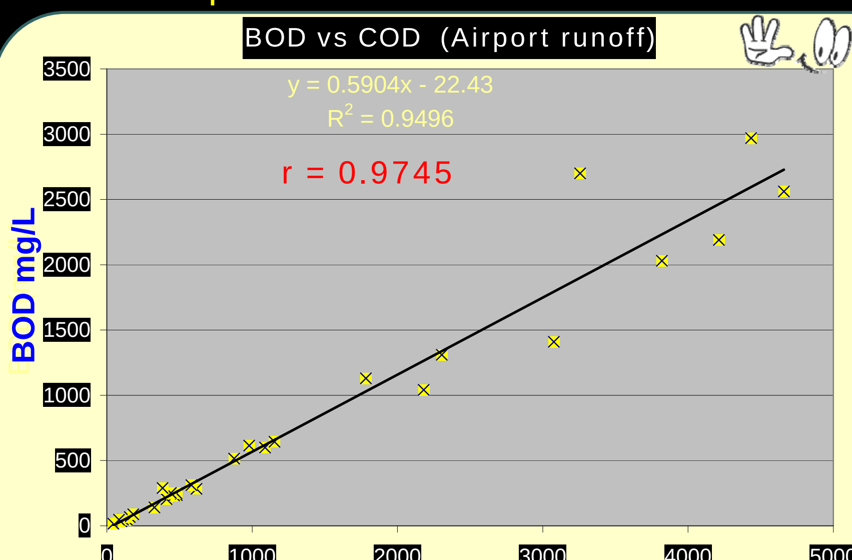
Other Industry BOD/COD ratios

Typical Values of BOD_5 and COD for Different Food Plant Wastewater.

Type of Processor	BOD_5 (mg/l)	COD (mg/l)	BOD_5/COD
Bakery products	3,200	7,000	0.46
Dairy processing	2,700	4,700	0.57
Jams and jellies	2,400	4,000	0.60
Meat packing	1,433	2,746	0.52
Meat specialties	530	900	0.59
Poultry processor	1,306	1,581	0.83

Source: ***Dairy Processing Methods to Reduce Water Use and Liquid Waste Load, K-State Research and Extension*** *March 1997. http://www.oznet.ksu.edu/library/AGENG2/mf2071.pdf*

SLH experience: BOD/COD ratios



data points= 30

Mean BOD/COD = 0.527 Median = 0.526 **COD mg/L**

Range= 0.327 to 0.829

BOD/COD/TOC ratios in PT samples

For a given "waste", analytical ratios can be incredibly consistent. Look at the consistency in PT samples.

	BOD	cBOD	COD	TOC	Ratio BOD/cBOD	Ratio BOD/COD	Ratio BOD/TOC	Ratio COD/TOC
Wibby WP0110	28	24.2	44.1	17	1.157	0.635	1.697	2.673
Wibby WP0210	124	107	197	74	1.159	0.629	1.682	2.673
NSI WP-158	107	91.9	173		1.164	0.618		
Absolute WP0041	139	120	231	92	1.158	0.602	1.519	2.525
Absolute QTA	146	126	243	96	1.159	0.601	1.522	2.534
ERA WP-180	75.3	64.8	122	48	1.162	0.617	1.562	2.531
ERA WP-181	29.6	25.6	47.7	19	1.156	0.621	1.574	2.537
ERA WP-182	58.1	50	93.8	37	1.162	0.619	1.566	2.528
ERA WP-183	98	84.4	158	63	1.161	0.620	1.568	2.528
ERA WP-185	41.9	36.1	67.5	27	1.161	0.621	1.569	2.528
				mean	1.160	0.618	1.585	2.562
				SD	0.003	0.0105	0.0631	0.0630
				%RSD	0.22%	1.70%	3.98%	2.46%

Why is the cBOD/BOD ratio so eerily consistent?

Sliding BODs → Sample Toxicity

Toxicity – a brief review

- Often referred to as "sliding" BODs
- BOD drops as sample volume increases (less dilute)
- Occurs frequently in systems receiving industrial waste
- Amounts to killing off (or severe shock to) "the bugs"
- Results in UNDER-reporting the BOD of a waste
- Failure to mix sample b/w dilutions can APPEAR as toxicity. (*the opposite can happen as well!)*
- Even pH adjustments can result in this effect
- Poor technique (pipetting, pouring samples)
- Sometimes we just can't determine (isolated cases)

If nitrification IS occurring

(*remember : dilution water contains* NH_3)

…as dilution ↑ , available NH_3 ↑ ==> final BOD ↑

What is NOT sliding BOD

300 mLs → 2 mg/L BOD

200 mLs → 3 mg/L BOD

100 mLs → 4 mg/L BOD

does NOT indicate sliding BOD

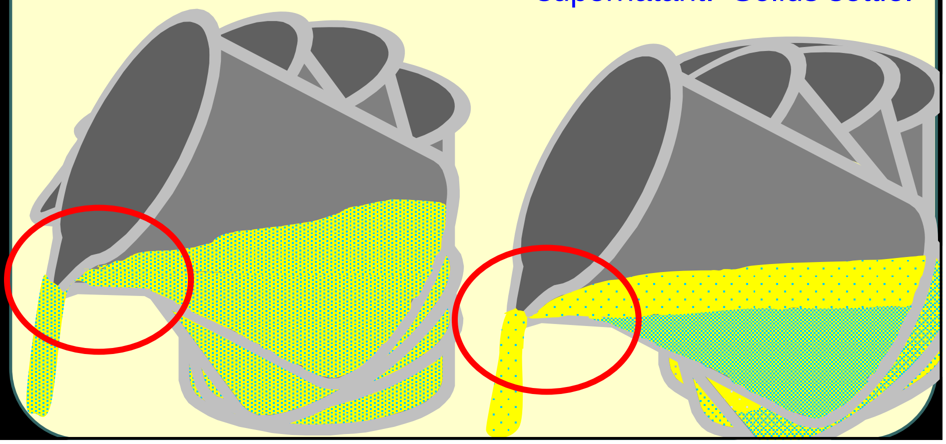
SM now says, "Identify samples in test reports when serial dilutions show more than 30% between high and low values."

Toxicity Look-A-Likes: Sub-sampling

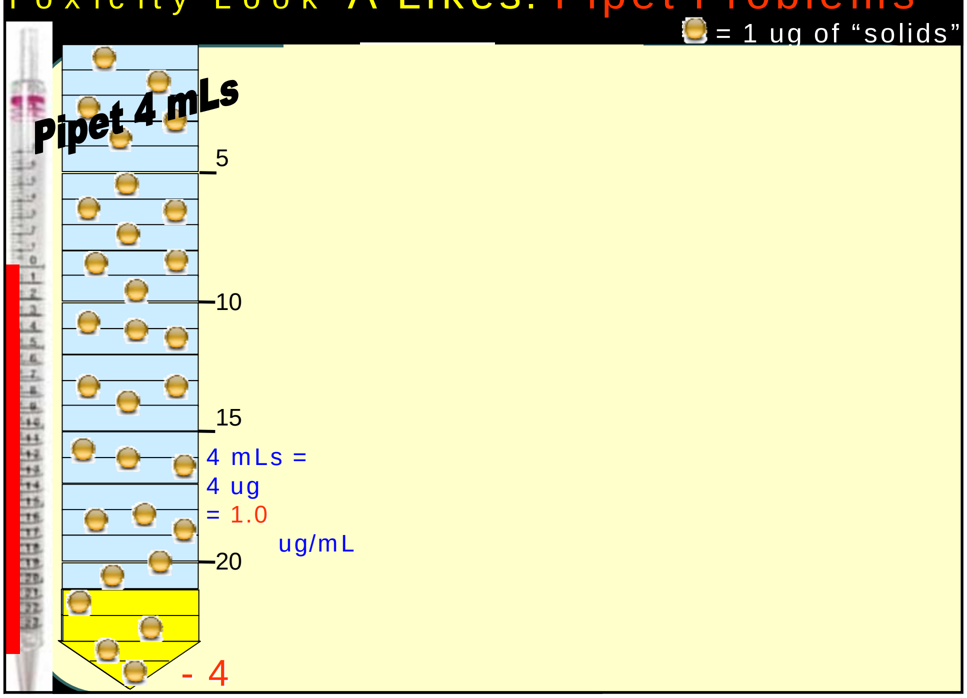
When pouring, solids are also actively settling during the entire transfer process

Pouring **quickly** favors an aliquot containing an even mix of sample.

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



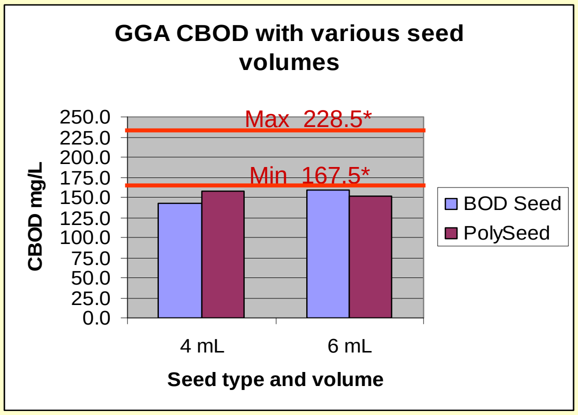
Toxicity Look-A-Likes: Pipet Problems



Nitrification Inhibition & Toxicity

Q: Is TCMP toxic to the carbonaceous BOD reaction?

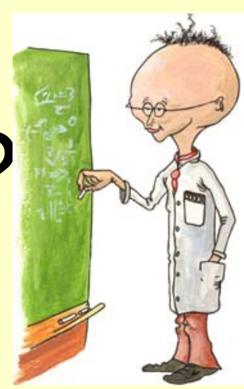
A: No scientific tests have shown any evidence of toxicity when TCMP is used properly, but the BOD Task Group recommends that all inhibited samples be seeded to reduce the possibility of interference.



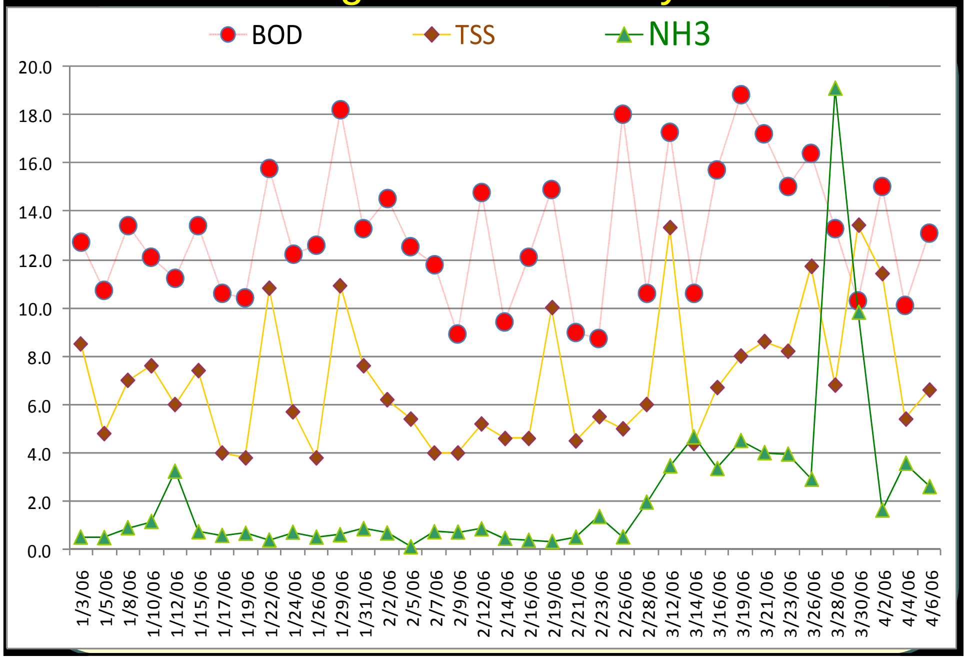
How else to explain lower results for inhibited GGA?

ce: Jim Young, Midwest Environmental Laboratory Stakeholders Summit, Dec. 2005

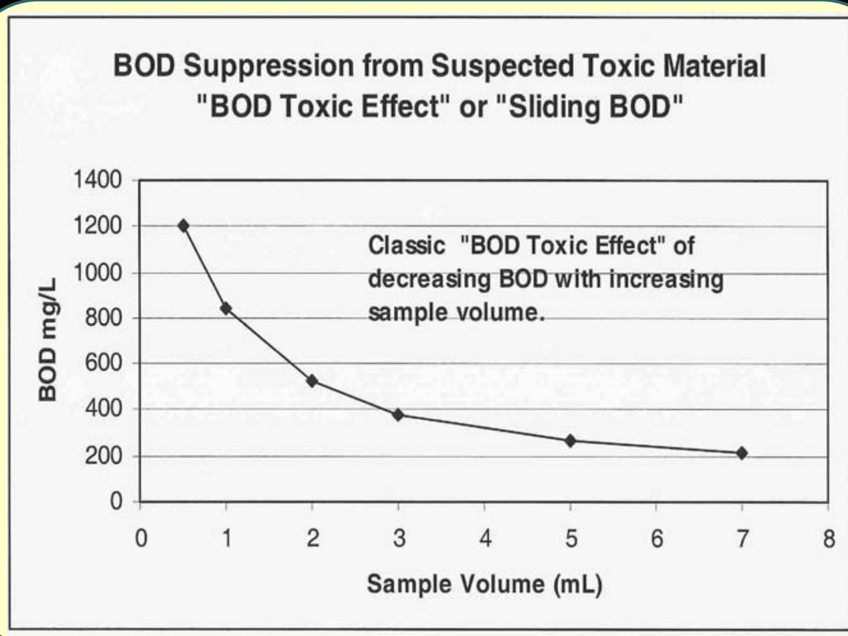
WHAT DOES TOXICITY LOOK LIKE?



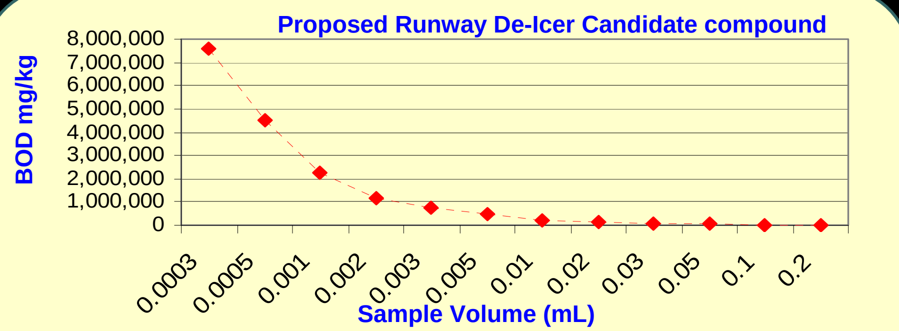
WWTP w/ significant dairy load



What Does Toxicity Look Like?

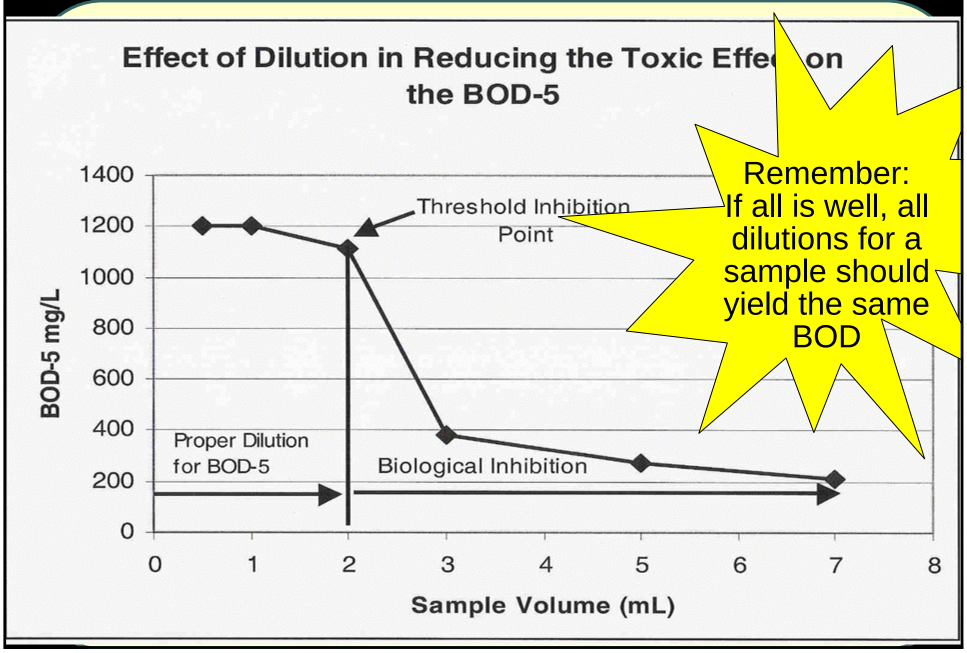


REAL toxicity data



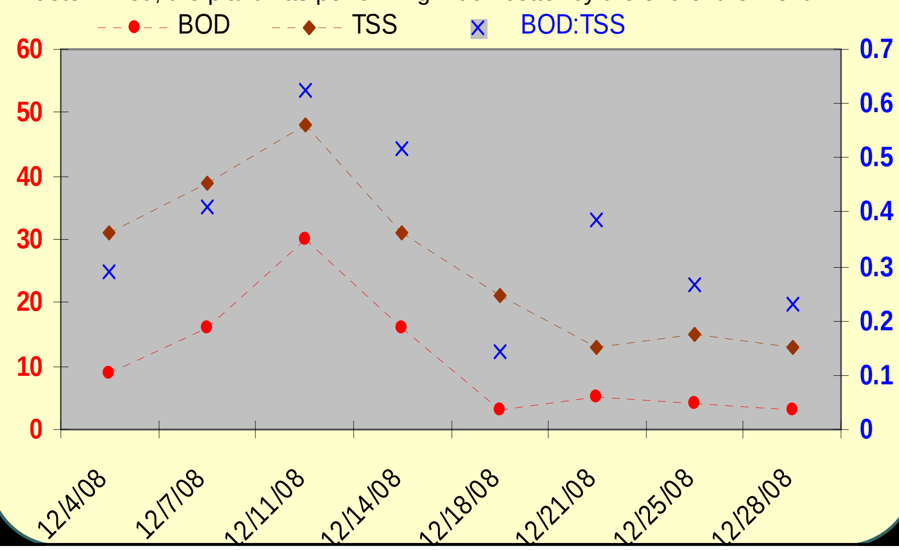
WSLH Sample #	CAS #	ACRP No	Field #	Proposed Runway De-Icer Candidate compound		
IS01777900	2163-42-0	71.12	1952952			
Dilution Volume	initial DO (mg/L)	End DO (mg/L)	Dilution factor	BOD remark	BOD mg/Kg	Comment
0.0003	8.6	8.37	1000000	<	7,600,000.00	too **little** depletion
0.0005	8.54	8.26	600000	<	4,524,000.00	too **little** depletion
0.001	8.58	7.27	300000	<	2,274,000.00	too **little** depletion
0.002	8.55	0.56	150000	>	1,132,500.00	too **much** depletion
0.003	8.61	0.04	100000	>	761,000.00	too **much** depletion
0.005	8.59	0.06	60000	>	455,400.00	too **much** depletion
0.01	8.51	0.06	30000	>	225,300.00	too **much** depletion
0.02	8.57	0.07	15000	>	113,550.00	too **much** depletion
0.03	8.56	0.1	10000	>	75,600.00	too **much** depletion
0.05	8.67	0.05	6000	>	46,020.00	too **much** depletion
0.1	8.76	0.05	3000	>	23,280.00	too **much** depletion
0.2	8.69	0.05	1500	>	11,535.00	too **much** depletion

Using Dilutions to Eliminate Toxicity



Example of a WWTP Toxic plant upset

Effluent TSS weekly limit failures for the first and second weeks of the month, as well as the monthly limit failure, were the result of a toxic discharge to the WWTP that upset the biological treatment system. Although no source was able to be determined, the plant was performing much better by the end of the month.



Dealing with Toxicity Part 1

Sample mLs	Initial Dilution	DO_I	DO_F	DO Depletion	BOD	Actual Sample mLs
50	1	8.49	0.10	> 8.39	Final DO <1.0 Too much depletion	50
100	1	8.40	2.40	6.00	18	100
200	1	8.31	5.19	3.12	5	200

Average= 11.3

Here we have is two dilutions--one with a BOD of 5 and the other with a BOD of 18. While this isn't the best precision in the world, many operators might be inclined to stop here and report the average of the two dilutions (11)

Dealing with Toxicity Part 2

Ultimately, however, now is the time to at least evaluate the other data we have and see what it tells us. If we look at the dilution that over-depleted (see below) we can see that --if calculated assuming a final DO of 0.1 mg/L was acceptable-- the result would be at least 50 mg/L. Now, the THREE results- 5, 18, and 50 mg/L-- look much more suspicious.

Sample Volume	Initial Dilution	DO_I	DO_F	DO Depletion	BOD	Actual Sample volume
50	1	8.49	**0.10**	> 8.39	> 50	50
100	1	8.40	2.40	6.00	18	100
200	1	8.31	5.19	3.12	5	200
				Average=	**11.3**	

Best answer: report ">" plus the highest BOD determined (> 50)

Furthermore, you MUST qualify these results as exhibiting "toxicity"

Dealing with Toxicity Part 3

Sample Volume	Initial Dilution	DO_I	DO_F	DO Depletion	BOD	Actual Sample volume
5	10	8.50	7.12	1.38		0.5
10	10	8.52	5.61	2.91	873	1
15	10	8.51	4.30	4.21	842	1.5
25	10	8.48	1.78	6.70	804	2.5
5	1	8.51	0.00	> 8.51		5
10	1	8.48	0.00	> 8.48		10
30	1	8.47	0.00	> 8.47		30
50	1	8.49	0.10	> 8.39		50
100	1	8.40	2.40	6.00	18	100
200	1	8.31	5.19	3.12	5	200

Once again, however, we need to look at ALL the data to discern the big picture. In this table, BOD has been calculated for all dilutions, whether or not they met depletion criteria, in an effort to determine whether the plateau or Threshold Inhibition Point has been achieved.

Dealing with Toxicity Part 4

Again, if we at least LOOK at dilutions that did not meet depletion criteria, it becomes clearer that we are "over the hump" and onto the coveted plateau zone of steady BOD..

Sample Volume	Initial Dilution	DO_I	DO_F	DO Depletion	BOD	Actual Sample volume
5	10	8.50	7.12	1.38	828	0.5
10	10	8.52	5.61	2.91	873	1
15	10	8.51	4.30	4.21	842	1.5
25	10	8.48	1.78	6.70	804	2.5
5	1	8.51	0.00	> 8.51	511	5
10	1	8.48	0.00	> 8.48	254	10
30	1	8.47	0.00	> 8.47	85	30
50	1	8.49	0.10	> 8.39	50	50
100	1	8.40	2.40	6.00	18	100
200	1	8.31	5.19	3.12	5	200

Got the Sliding BODs?

Dear Gonzo & Rock…
My BODs look like the neighborhood kids on their Slip N' Slide and final clarifier effluent BOD is higher than my final effluent.

WTH???!!!

Day 1 Sample Volume (mLs)	Day 1 BOD mg/L	Day 4 Sample Volume (mLs)	Day 4 BOD mg/L	Day 6 Sample Volume (mLs)	Day 6 BOD mg/L	Day 7 Sample Volume (mLs)	Day 7 BOD mg/L
50	7.4	50	8.2	150	3.6	25	10.9
200	2.7	200	3.3	200	2.7	50	8.7
250	4.4	250	4.6	250	3.6	200	3.7
						250	4.9

Help! I think I have toxicity!

Let's take a closer look at one of the data sets that seem to best suggest toxicity.

Sample	Volume	Initial D.O. mg/l	Final D.O. mg/l	Difference mg/l	Multiplier	BOD_5 mg/l	Avg
Blank	0	8.45	8.42	0.1	*****	*****	*****
Seed	20	8.47	5.21	3.46	*****	*****	*****
Seed	25	8.47	4.83	4.51	*****	*****	*****
STD	6				50		******
Effluent	25	8.45	6.62	1.93 - .92 = .91	12	10.9	5.8
Effluent	50	8.45	6.08	2.37 - .92 = 1.4	6.0	8.7	
Effluent	200	8.46	5.05	3.41 - .92 = 2.4	1.5	3.7	
Effluent	250	8.47	3.48	4.99 - .92 = 4.0	1.2	4.9	
Influent	6	8.4	5.74	2.66	50	133.0	138
Influent	10	8.34	3.58	4.76	30	143.0	
Influent	15	8.29	1.46	6.93	20	137.0	
Final Clar Eff	50	8.49	5.9	2.59 - .92 = 1.6	6.0	10.0	7.1
Final Clar Eff	150	8.52	5.48	3.04 - .92 = 2.1	2.0	4.2	

You need help…but you don't have toxicity

Sample	Volume (mLs)	DO_I mg/L	DO_F mg/L	Depletion	seed correction (6 mL)	Adjusted depletion	DF	BOD5 mg/L	BOD Avg
Blank	0	8.45	8.42	0.1			*****	*****	*****
Seed	20	8.47	5.21	3.46	0.1630	DPMS	*****	*****	53
Seed	25	8.47	4.83	4.51	0.1456	DPMS	*****	*****	
Effluent	25	8.45	6.62	1.83	0.93	0.90	12	*10.9*	4.3
Effluent	50	8.45	6.08	2.37	0.93	1.44	6.0	*8.7*	
Effluent	200	8.46	5.05	3.41	0.93	2.48	1.5	3.7	
Effluent	250	8.47	3.48	4.99	0.93	4.06	1.2	4.9	
Influent	6	8.4	5.74	2.66	0.00	2.66	50	133	137
Influent	10	8.34	3.58	4.76	0.00	4.76	30	143	
Influent	15	8.29	1.46	6.83	0.00	6.83	20	137	
Final Clar Eff	50	8.49	5.9	2.59	0.93	1.66	6.0	*10*	4.2
Final Clar Eff	150	8.52	5.48	3.04	0.93	2.11	2.0	4.2	

Average DPMS = 0.1543 mg/L per mL of seed
6 mLs of seeded added to samples

Depletion due to seed=
6 X 0.1543 mg/L = 0.93 mg/L

How did we do that!

1. We fixed some errors in the spreadsheet/benchsheet calculations.
   - *Slight error in seed correction*
   - *An ‘oops’ in calculated depletion*
   - *Errors in how dilutions are assessed*
   - *Errors are additive and all leads to a bad result.*
2. We re-evaluated the seed in terms of “DPMS”
3. We looked at BOD of individual dilutions relative to the effective LOD for a particular dilution.
4. When all that is done, toxicity concerns disappear.

The Case of the Sliding BODs...Maybe

- Be wary of how you interpret data that hovers around the LOD.
- Remember: for a 25 mL dilution, the effective LOD for THAT ONE dilution is 2 mg/L X 12 = 24 mg/L (consider EACH dilution).
- Because you have a dilution of 250 mL, you can report down to 2.4 mg/L
- In the Jan 13 th data look at it this way:
  - 25 mL 12x BOD =10.9...but LOD is 24
  - 50 mL 6.0x BOD= 8.7...but LOD is 12
  - 150 mL 1.5x BOD=3.7...and LOD is 3.0...so this is a detect
  - 250 mL 1.2x BOD=4.9...and LOD is 2.4...so this is a detect
  - So report the average of (3.7,4.9) or 4.3...with LOD of 2.4
- Now...neither of those values is above the LOQ...right?
- “LOQ” would be about 6-10
- So the results of the dilutions fall in that "gray" area where quantitation is much less accurate/reliable.
- Therefore...you cant make any real/valid statement about toxicity because 2 of the 4 results are below the LOD The other 2 results are below the LOQ.
- For toxicity, we're usually dealing with samples well over the LOQ

Looking back at our toxicity example and “dilution LODs”

Sample Volume	LOD	BOD	Actual Sample volume	DF
5	1200	828	0.5	600
10	600	873	1	300
15	400	842	1.5	200
25	240	804	2.5	120
5	120	511	5	60
10	60	254	10	30
30	20	85	30	10
50	12	50	50	6
100	6	18	100	3
200	3	5	200	1.5

Nitrification

Nitrogenous Oxygen Demand (NOD)

Reduced Nitrogen + Oxygen → Nitrite (NO_2) → Nitrate (NO_3)

NH_3 + 1.5 O_2 → HNO_2 + H_2O + cells
HNO_2 + 0.5 O_2 → HNO_3 + cells

NH_3 + 2 O_2 → HNO_3 + cells

Theoretically 1 mg/L of NH_3-N requires 4.57 mg/L O_2 to oxidize NH3 to NO3-N

- NH_3-N in dilution water alone can contribute up to 2.04 mg/L NOD without accounting for any dilution factor or NH3 from the sample itself.
- The addition of a "one bottle" nutrients package adds the equivalent of 0.49 mg/L as N.
- A 200 mL sample dilution, to which additional nutrients are added contains as much as 4.4 mg/L of BOD in the form of NOD.

Dilution Water NOD

BOD Phosphate buffer 445.3 mg/L as N

1.7 **g** NH4Cl **/L** N= 14 NH4Cl= 53
NH4Cl= 26.19% as N

1.7 g NH4Cl **/L** X 26.19% = 0.4453 g /L
= 445.3 mg /L

"One shot" HACH Nutrients= 445.3 mg/L as N

(same as BOD Phosphate buffer)

BOD Dilution water 0.445 mg/L as N

Equivalent O2 demand (x 4.57) = 2.04 mg/L

prep includes 1 mL of phosphate buffer diluted to 1 L)

$$445.3\ \text{mg/L} \times \frac{1\ \text{mL}}{1000\ \text{mL}} = 0.445\ \text{mg/L}$$

Nitrogenous Demand of BOD Nutrients

1 "pillow" of extra nutrients in a 300mL bottle is equivalent to 0.49 ppm on NH3-N. Even more comes from dilution water.

Sample Volume (mLs)	Dilution Water (mL)	**NH3 from Dil. H20 (mg/L)**	**NH3 from extra Nutrients**	Total NH3 mgL added	Nitrogenous demand (NOD)	BOD Dilution factor	**BOD equivalent**
300	0	0	0.490	0.48983	2.239	1	**2.2** mg/L
250	50	0.07422	0.490	0.56405	2.578	1.2	**3.1** mg/L
200	100	0.14843	0.490	0.63826	2.917	1.5	**4.4** mg/L
150	150	0.22265	0.000	0.22265	1.018	2	**2.0** mg/L
100	200	0.29687	0.000	0.29687	1.357	3	**4.1** mg/L
75	225	0.33398	0.000	0.33398	1.526	4	**6.1** mg/L
60	240	0.35624	0.000	0.35624	1.628	5	**8.1** mg/L
50	250	0.37108	0.000	0.37108	1.696	6	**10.2** mg/L
25	275	0.40819	0.000	0.40819	1.865	12	**22.4** mg/L
10	290	0.43046	0.000	0.43046	1.967	30	**59.0** mg/L
3	297	0.44085	0.000	0.44085	2.015	100	**201.5** mg/L

NH3 from extra nutrients (0.33 mL of Phophate buffer= 1 HACH "nutrient pillow"

$$\frac{445.3\ mg}{1000\ mL} \times 0.33\ mL = 0.146949\ mg \times \frac{1}{0.3\ L} = 0.49\ \frac{mg}{L}$$

GGA NOD

GGA **Nitrogenous Demand**

Glucose	150 mg/L	C6H12O6	MW = 180.16 g/mol
Glutamic acid	150 mg/L	C5H9**N**O4	MW = 147.13 g/mol
		N *MW*	*=14*

N%= 9.5% of Glutamic acid

N mg= 14.3 mg/L *(9.5% x 150 mg/L)*

$$14.3\ \frac{mg}{L} \times \frac{6}{300} = 0.29 \times 4.57 = 1.3\ mg/L$$

x 50= **65.1 mg/L just from GGA**

GGA + Dilution water

294/300 x 0.4453	0.43639 mg/L		
+ 6/300*14.25	0.285		
	0.72139	x 4.57=	3.2967706
		x 50=	164.839

GGA+ dilution water NOD= 164.839

What Exactly IS Soluble BOD?

Soluble BOD is the BOD of water that has been filtered in the TSS test. Soluble BOD is a measure of food for microorganisms that is dissolved in the water being treated and readily available to bugs.

Typical domestic wastewater BOD5 is usually 40-50% soluble with the remainder being particulate (filterable).

A high soluble BOD5 in the effluent (more than 30% of the total) may indicate poor treatment.

The soluble BOD5 test is similar to the regular BOD5 test, with the sample being first filtered through a 0.45 um membrane filter before the BOD test.

Nitrification Benchmarks

- If TSS is 50% or less of the BOD result (BOD: TSS ratio > 2:1) then consider…don't assume…the possibility of nitrification.
- Look at NH3 levels. If there's no measurable NH3, it can't be Nitrogenous Demand!
- NH3 x 4.57 = potential "BOD" due to nitrogenous oxygen demand (NOD).
- Nitrification occurs most often in warmer months. Nitrification doesn't occur below 10ºC.
- Look at soluble BOD: run side-by-side an effluent BOD and the effluent BOD after passing effluent thru a TSS filter. Soluble BOD can cause high BOD:TSS ratios.
- Finally, run side-by-side cBOD/BOD determinations. cBOD should be considerably less than BOD (*depends on available NH3, of course!*). cBOD is about 80-90% of BOD if no nitrification is occurring.

Nitrification: 4 Legged Stool

Sure, a 3-legged stool is sturdy enough, but a 4-legged stool is better!

BOD, TSS and NH3 data will generally be enough to identify nitrification, but the clincher is having paired BOD:cBOD data in addition.

Nitrification & Other Parameters

- Ammonia N (NH3-N) – [Inf and eff] - If substantial nitrification is taking place you would see a significant decrease.
- Nitrite(NO2) – [Eff] -generally <0.5 mg/L, anything greater would be considered high.
- Nitrate (NO3) – [Eff] - Expect around zero if there is no nitrification taking place. If nitrification is occurring, expect nitrates anywhere from 3-15 mg/L or greater ***depending on NH3 levels***.
- Alkalinity (measured as CaCO3) [Inf and Eff] - Expect a significant decrease if nitrification is taking place. Effluent concentrations <50 mg/L indicates potential for pH problems.

Lower Isn't Enough

Just having a cBOD that is less than BOD is not enough to make a claim that nitrification is occurring

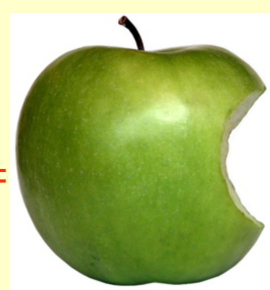
- Addition of cBOD nitrification inhibitor reagent will ALWAYS lower BOD.
- Hello!…**McFly!** It's a toxin!
- It's the EXTENT of the reduction (BOD:cBOD ratio) that tells the tale.

The Inhibitor DOES have an effect

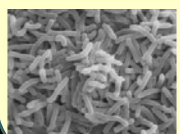
Adding inhibitor to a BOD bottle is like taking antibiotics….which is… you know…like the…

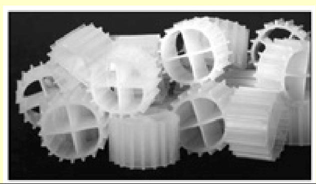
=

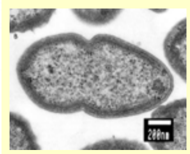
=

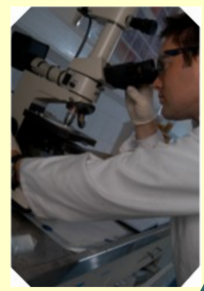


WHAT DOES NITRIFICATION LOOK LIKE?

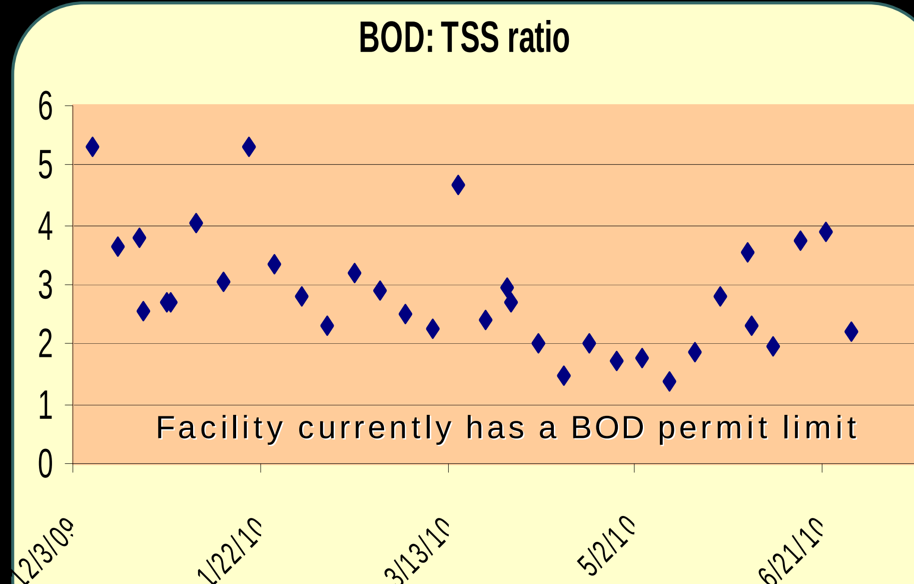








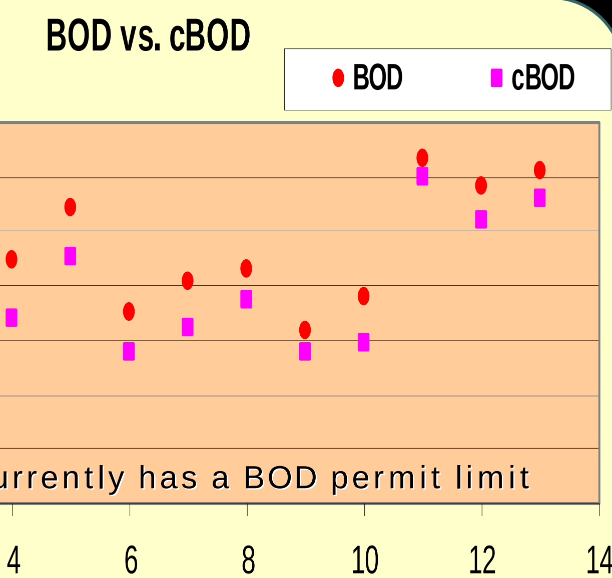
Pelican WWTP: Is this Nitrification?



What can we tell from the TSS ratio?

Pelican WWTP: Is this Nitrification?

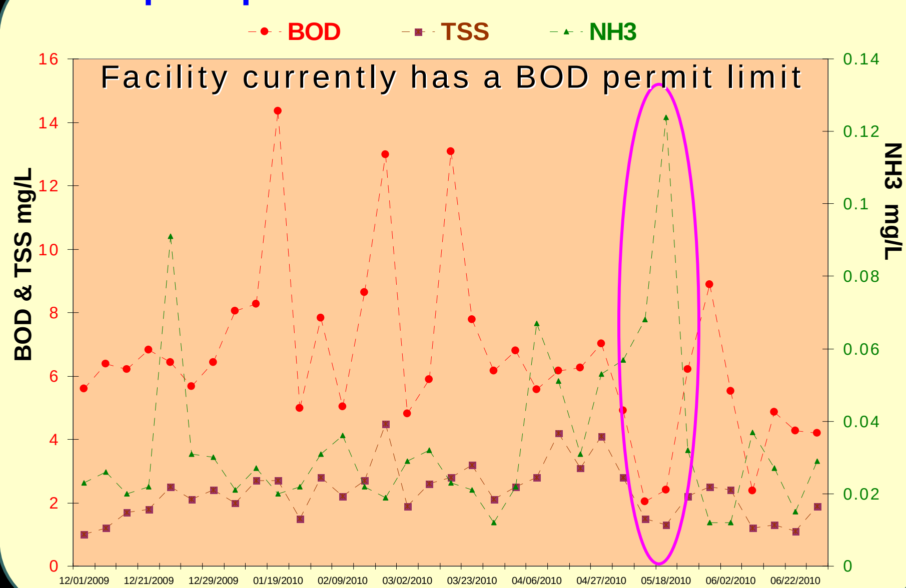
We have some limited paired BOd-cBOD data



Does the BOD: cBOD ratio shed any light?

Pelican WWTP: Is this Nitrification?

Complete picture. Candidate for cBOD limit?



Be Careful What You Wish For…

- Remember that if you switch from BOD to cBOD, your permit limits do NOT stay the same.
- cBOD permit limits are lower than BOD limits.
- Some facilities get year-round reductions, others just get reduced limits during warmer months (May – October).
- Examples of real limits:
- BOD monthly avg.10 mg/L Nov-Apr; 6.8 mg/L May-Oct
- BOD monthly avg.10 mg/L Nov-Apr; 5 mg/L May-Oct

  TSS 10 mg/L year-round
- cBOD rear-round 25 mg/L monthly; 40 mg/L avg weekly (BOD would be 30/45)
  - TSS 30/45

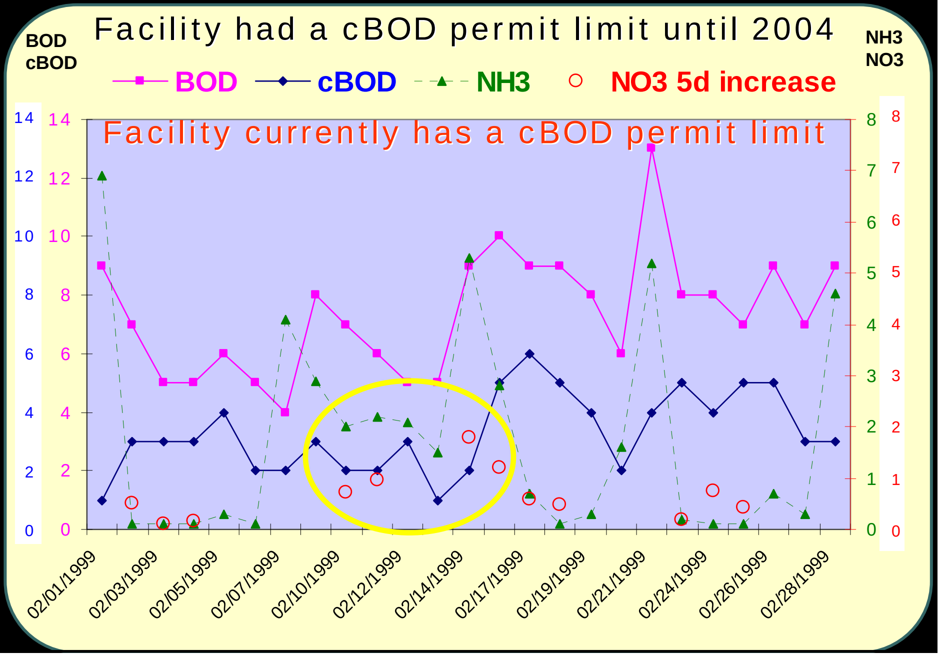
Pelican WWTP: Is this Nitriification?

Sample contains some NH3 0.03 mg/L

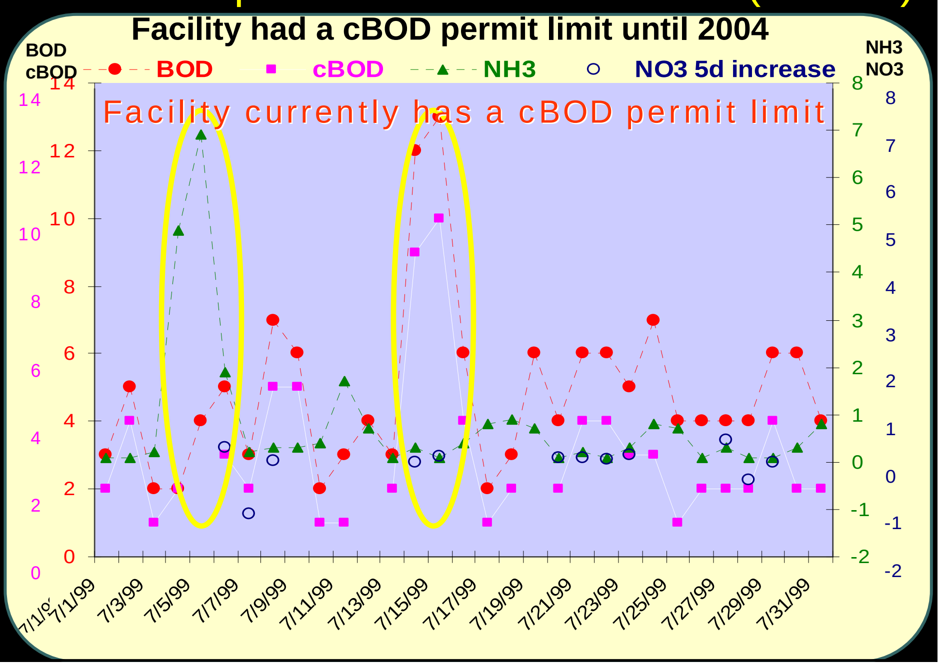
Sample Volume (mLs)	Dilution Water (mL)	**NH3 from DilH20 (mg/L)**	**NH3 from extra Nutrients**	**NH3 from sample**	Total NH3 mgL added	Nitrogenous demand (NOD)	DF	**BOD equivalent**
300	0	0	0.490	0.030	0.51983	2.375623	1	**2.4** mg/L
150	150	0.22265	0.000	0.015	0.23765	1.086061	2	**2.2** mg/L
100	200	0.296867	0.000	0.010	0.3068667	1.402381	3	**4.2** mg/L

- If the average NH3 level is about 0.03 ppm, that only explains about 2.4 ppm of “BOD”.
- The difference between BOD and cBOD is less than the Nitrogenous demand of dilution water and sample NH3
- NH3 levels increase on several occasions and BOD actually drops.

Pine Stump WWTP Nitrification (Cold)



Pine Stump WWTP Nitrification (Warm)



Pine Stump WWTP: Nitrification?

Cold weather

- The increase in nitrate formation is a clear indicator of nitrification
- BOD and cBOD track very well, but would have expected higher BOD:cBOD ratios.
- BOD tracks better with ammonia

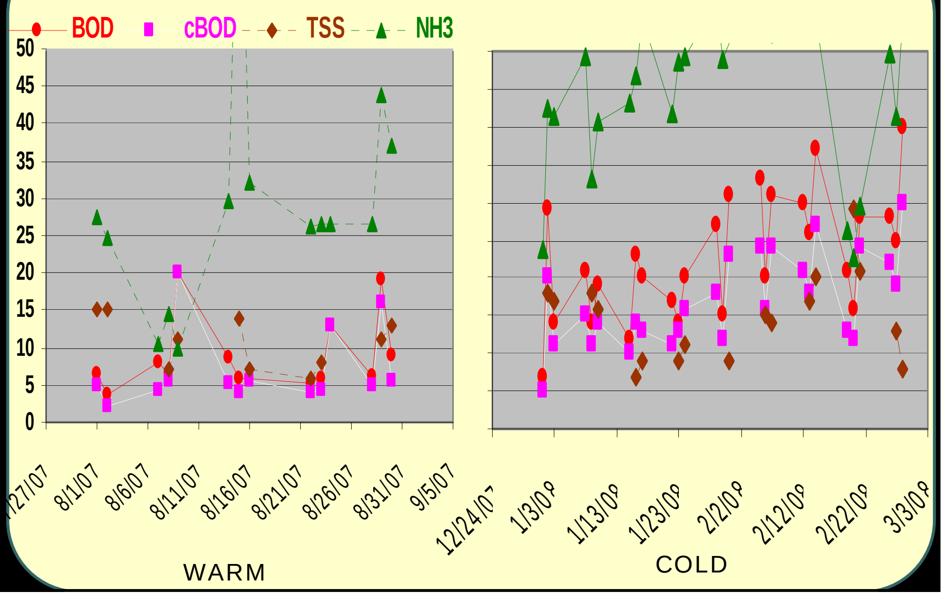
Sample contains some NH3: **2.00 mg/L**

Volume (mLs)	Dilution Water (mL)	**from DilH20 (mg/L)**	**from extra Nutrients**	**NH3 from sample**	Total NH3 mgL added	Nitrogenous demand (NOD)	DF	**BOD equivalent**
200	100	0	0.490	1.333	1.8231633	8.331856	1.5	**12.5** mg/L
150	150	0.22265	0.000	1.000	1.22265	5.587511	2	**11.2** mg/L
100	200	0.296867	0.000	0.667	0.9635333	4.403347	3	**13.2** mg/L
50	250	0.371083	0.000	0.333	0.7044167	3.219184	6	**19.3** mg/L

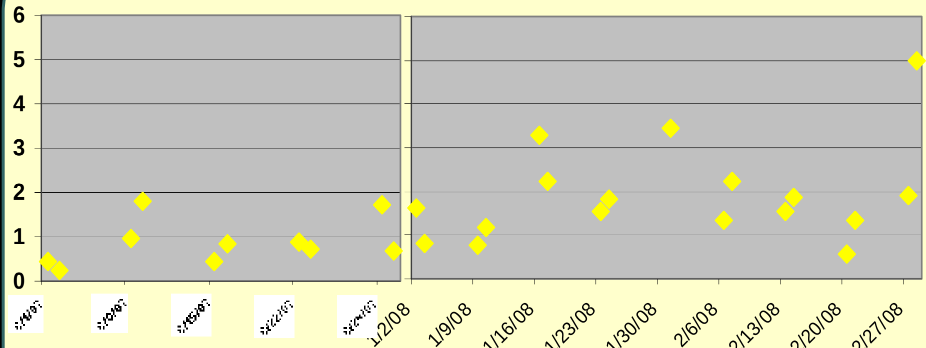
Warm weather

- Does not fit the expected nitrification pattern
- A steep jump in NH3 but BOD/cBOD dropped
- A big increase in BOD/cBOD where NH3 actually dropped

Moose WWTP Nitrification?

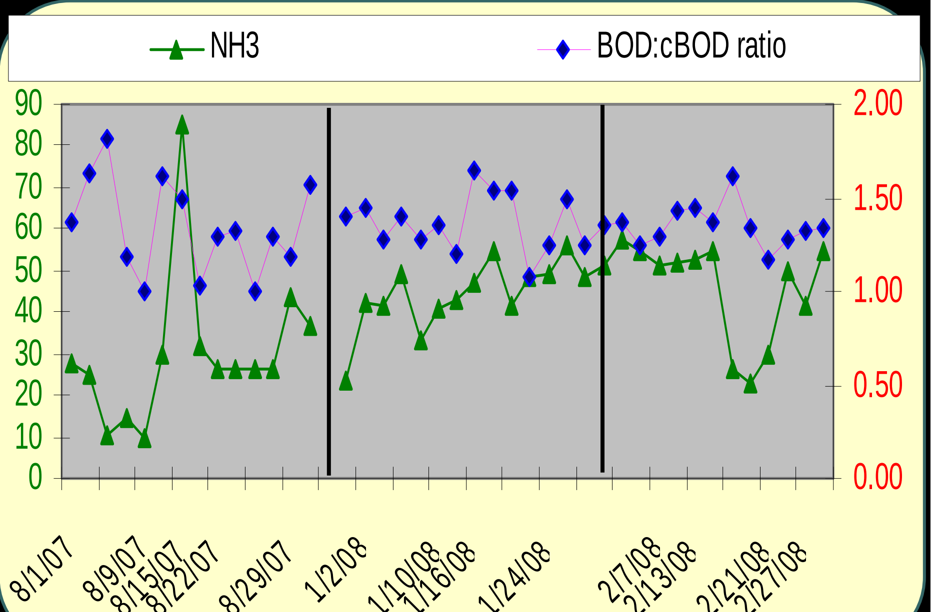


Moose WWTP - BOD: TSS ratios

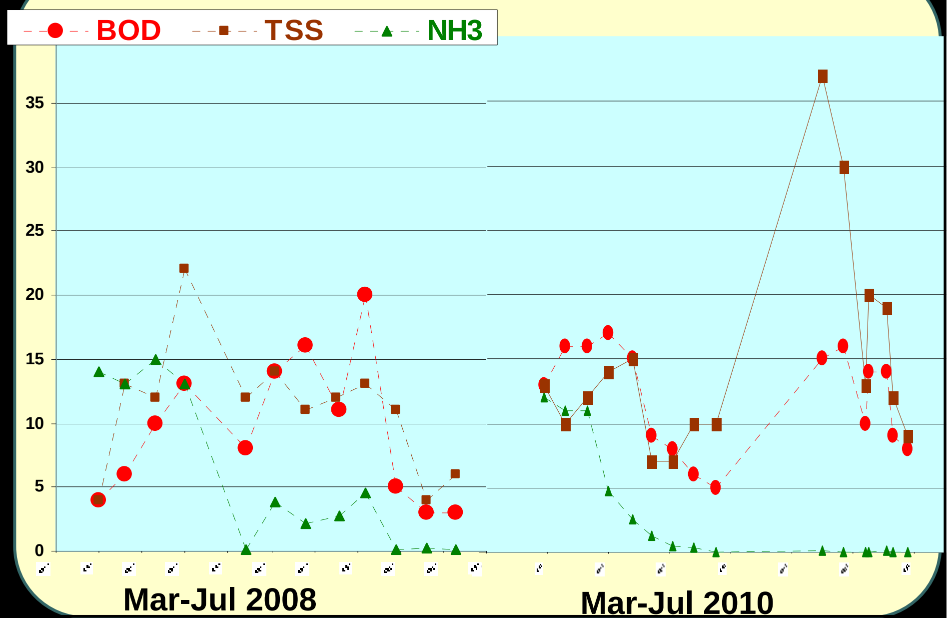


Despite very high NH3 levels, BOD: TSS ratios only rarely exceed 2:1

Moose WWTP - BOD:cBOD ratios vs. NH3



Very small plant had cBOD; now does not



Very small plant; had cBOD; now does not

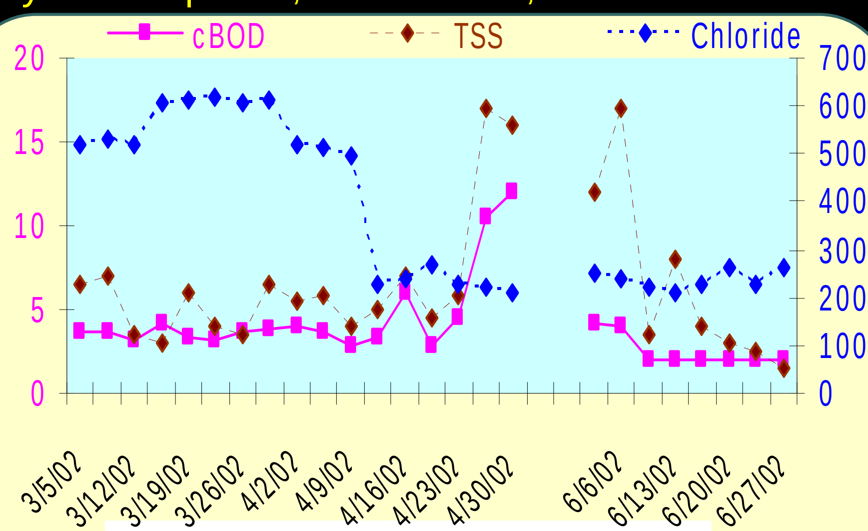
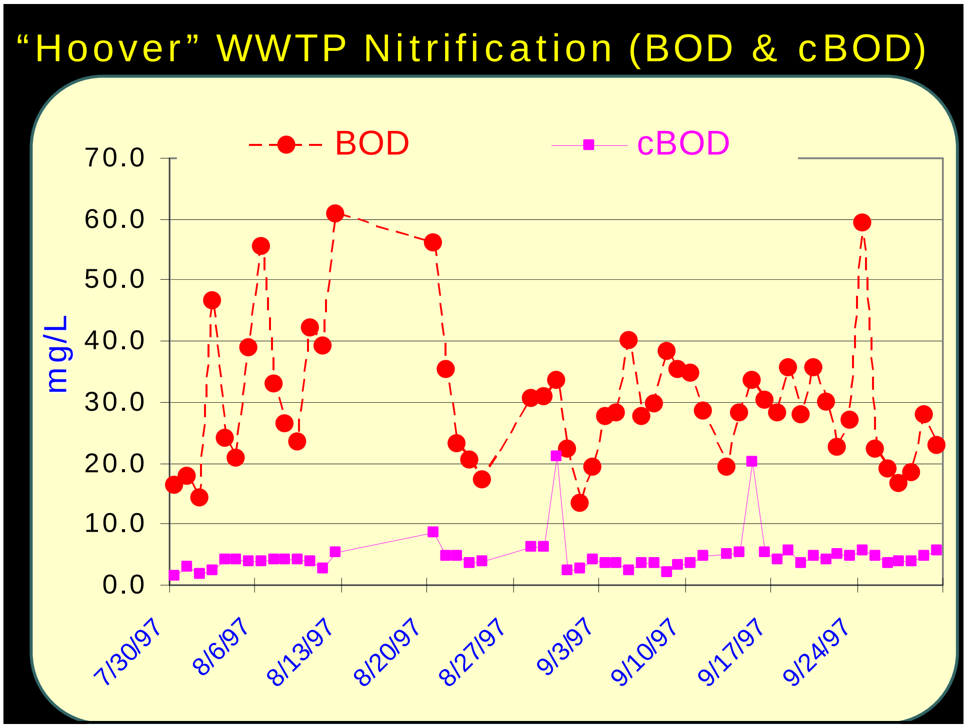
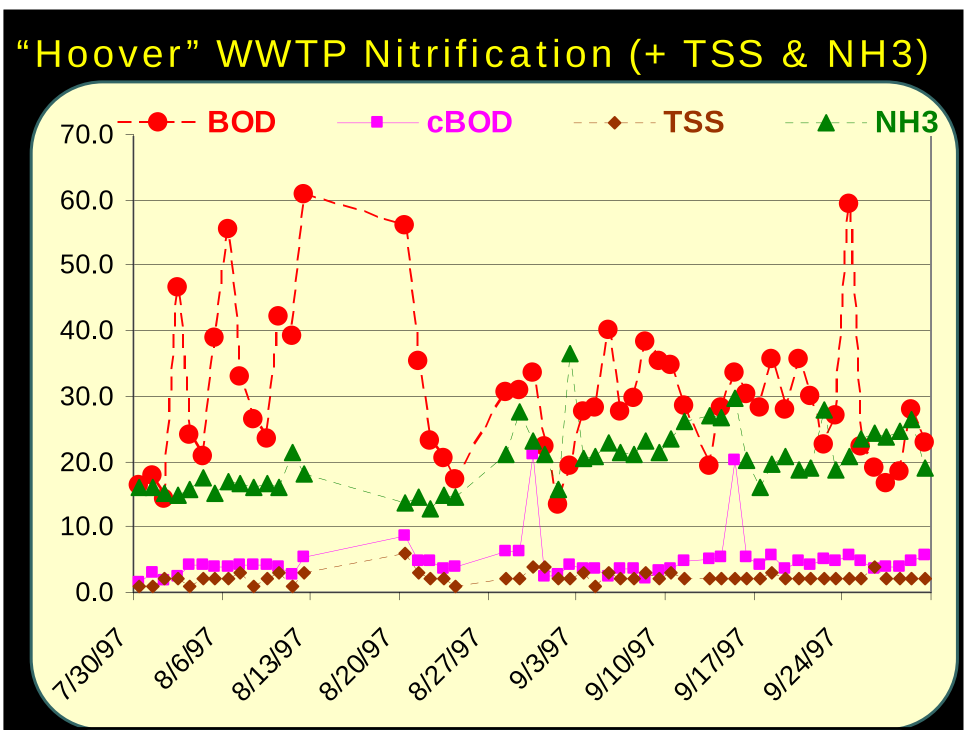


Table 1. National Aquatic Life Criteria for Chloride

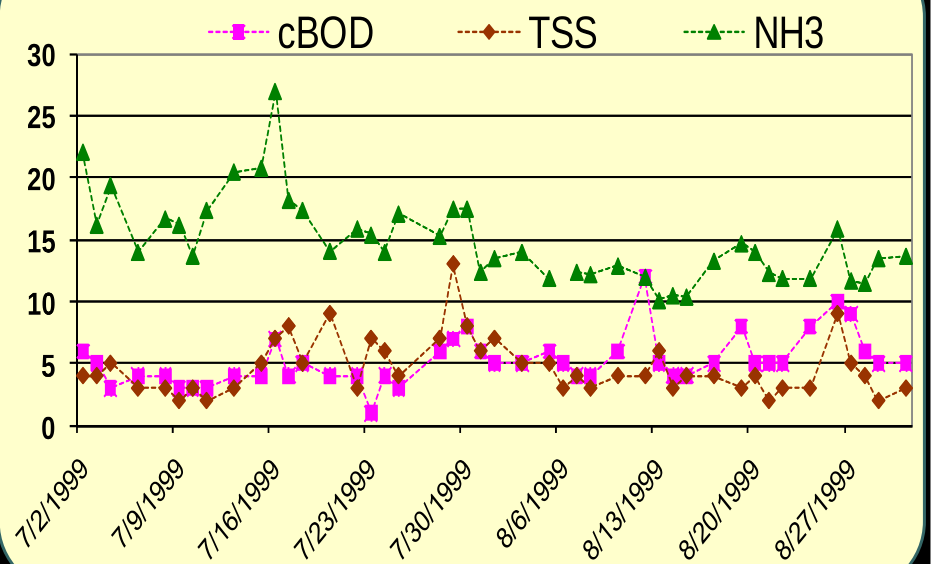
Parameter	National Criteria (mg/l)	
	Acute	Chronic
Chloride	860	230


"Hoover" WWTP Nitrification (BOD & cBOD)
BOD
cBOD
mg/L
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
7/30/97
8/6/97
8/13/97
8/20/97
8/27/97
9/3/97
9/10/97
9/17/97
9/24/97

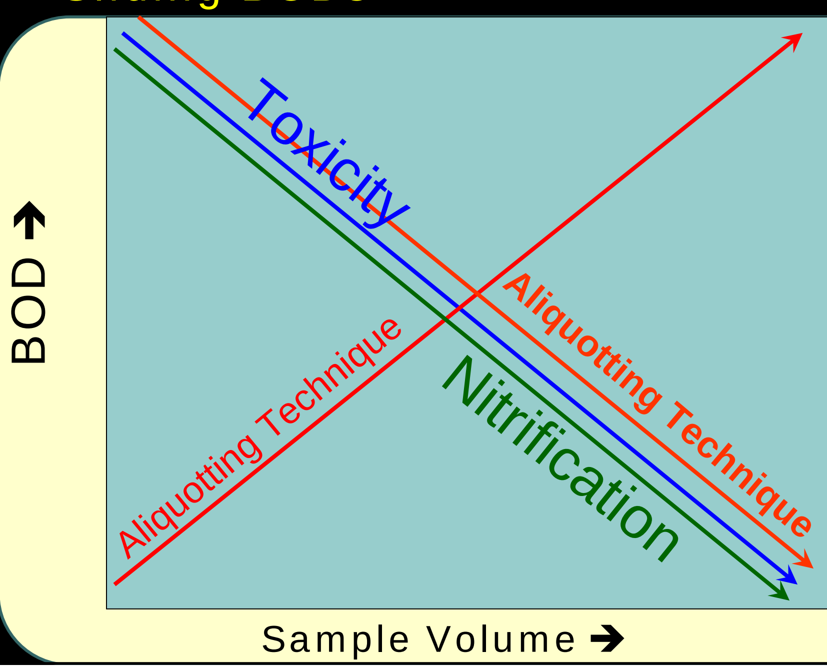

"Hoover" WWTP Nitrification (+ TSS & NH3)
BOD
cBOD
TSS
NH3
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
7/30/97
8/6/97
8/13/97
8/20/97
8/27/97
9/3/97
9/10/97
9/17/97
9/24/97

“Hoover” WWTP Nitrification (after switch)

- AFTER permit switch to cBOD



Sliding BODs



Q & A