

# Using Data to Assess Industrial Loading Fees

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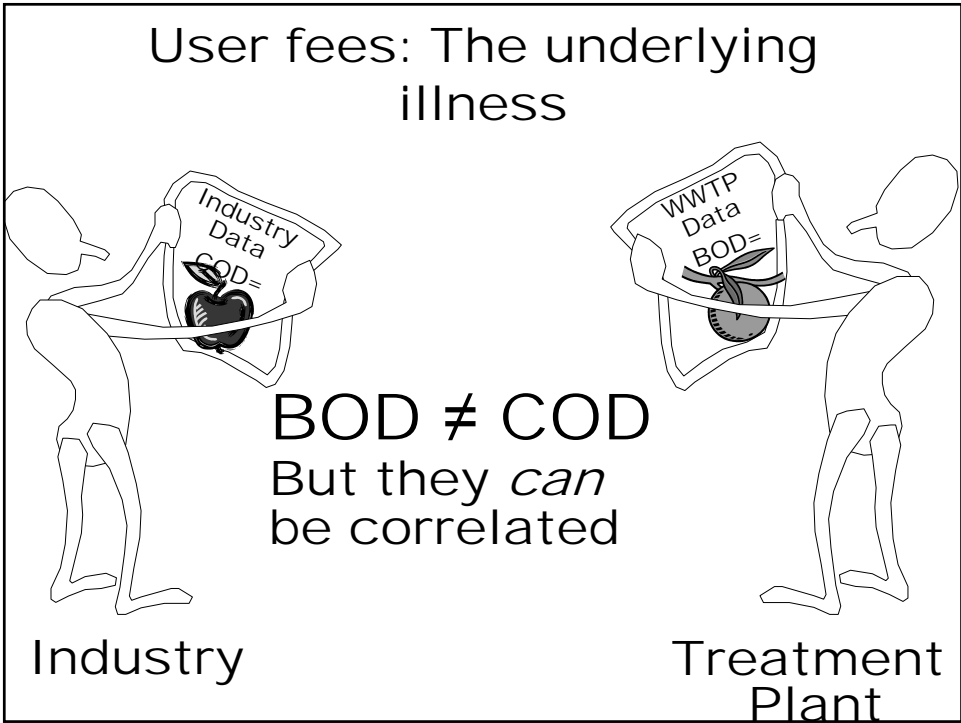
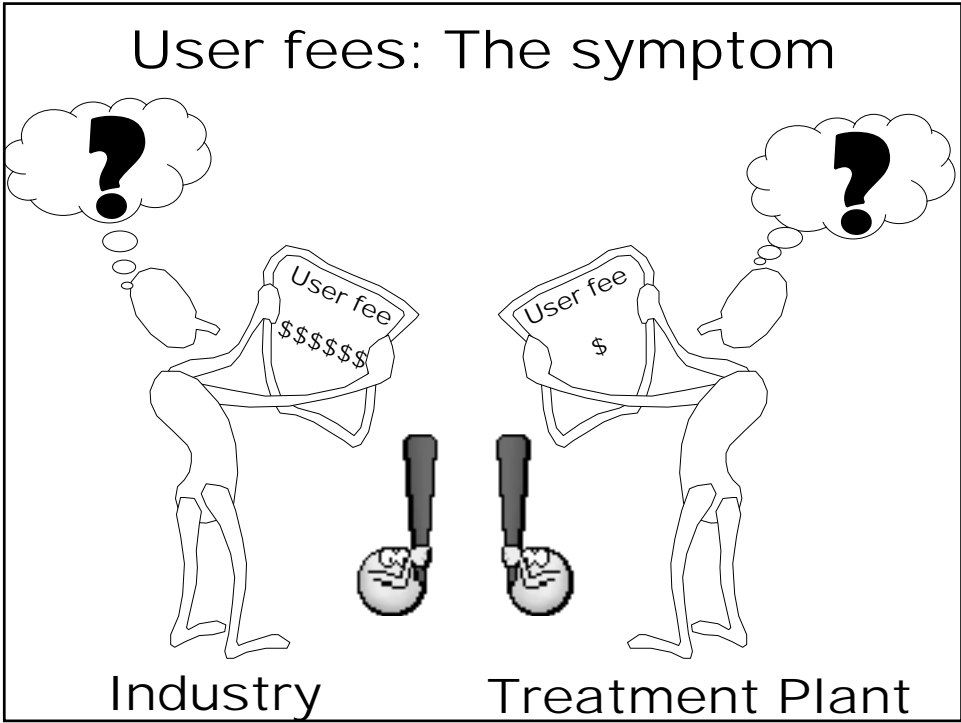


Wisconsin DNR



## Points to Ponder

- Review of what to do if you are doing "charge-backs" or user fees
- What if the discharger uses COD for their estimate and you only do BOD?
- What if it's a "toxic" waste--like industrial waste?
- How do you set your test up to ensure you have the right data ...and thus are charging the discharger appropriately?
- Remember: Errors could lead to under-charging (bad for YOUR budget) or over-charging (bad for THEIR budget and YOUR relationship)



## Dr. House's Diagnosis

Treating illnesses is why we became doctors. Treating patients is what makes most doctors miserable.



- You can correlate COD results to estimate BOD, **but** you must be certain that the BOD results used to determine a correlation to COD data are accurate.
- To ascertain accuracy of BOD results, you must test for underlying toxicity.
- If the waste proves toxic, you must develop an appropriate dilution scheme to obtain an accurate BOD result.

## BOD vs. COD

- BOD measures only the biochemical degradation of organic material, or "carbonaceous oxygen demand" of the sample, which results in the **underestimation of the energy** (in terms of oxygen demand) in the sample.
- Unless nitrification is suppressed, presence of nitrifying organisms in the treated sample may result in conversion of  $\text{NH}_3$  or  $\text{NH}_4^+$  to  $\text{NO}_3$ , giving an inflated value for the carbonaceous energy.
- COD gives a measure of the total energy in terms of oxygen by oxidizing all biodegradable **and unbiodegradable** organic materials
- Since ammonium is not oxidized, the test value reflects only the energy released due to oxidation of the carbonaceous compounds.
- High chlorides, reduced iron, and manganese contribute to COD, causing a bias
- COD can be correlated to BOD or CBOD
- the COD test takes only 2 hours so that the results can be used in the daily operation of a WWTP.
- COD test oxidizes both biologically degradable and unbiodegradable organic materials; the **energy** available for biological action **is usually overestimated**.

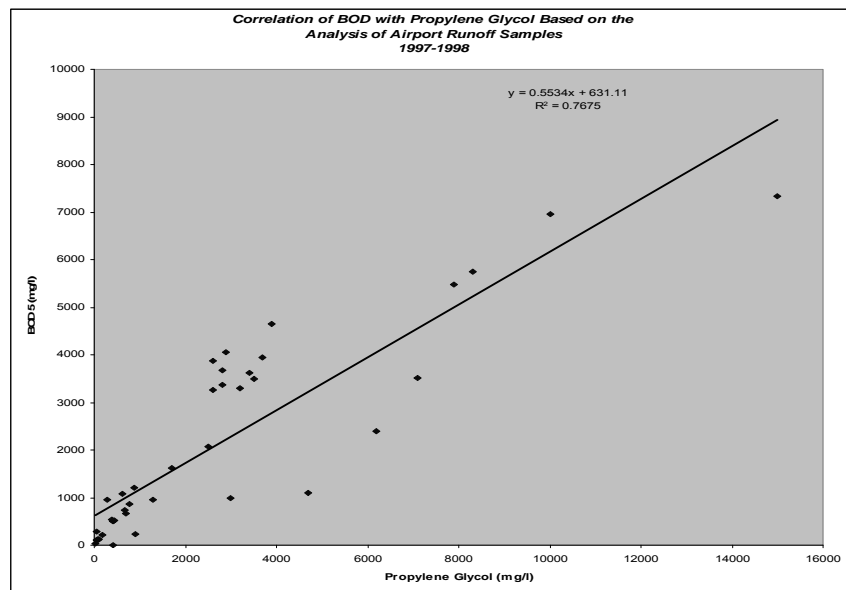
## BOD/COD ratios vary between wastes...

Characteristics of each grab wastewater sample tested.

	<b>Oakfield</b>	<b>Green Lake</b>	<b>Ashland</b>	<b>Campbellsport</b>	<b>Green Bay</b>
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

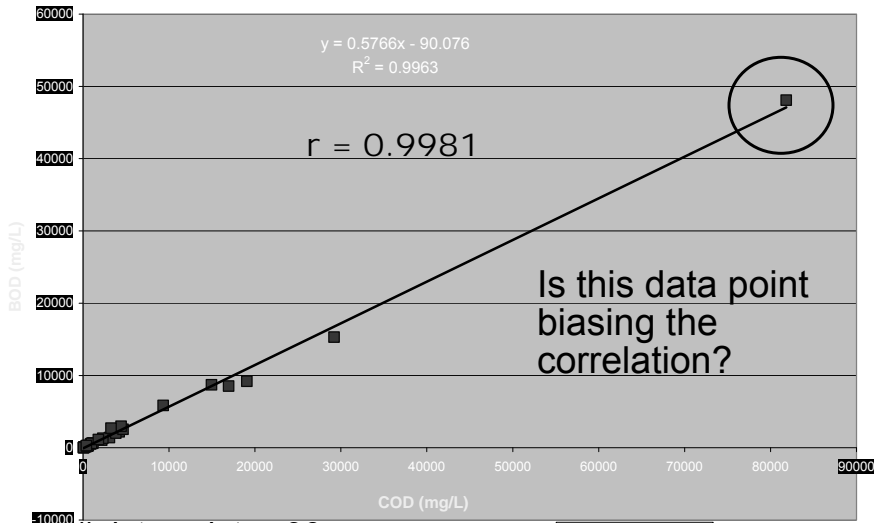
<http://www.dnr.state.wi.us/org/water/wm/ww/biophos/3bpr.htm>

## SLH experience: De-icing fluids



# SLH experience: BOD/COD ratios

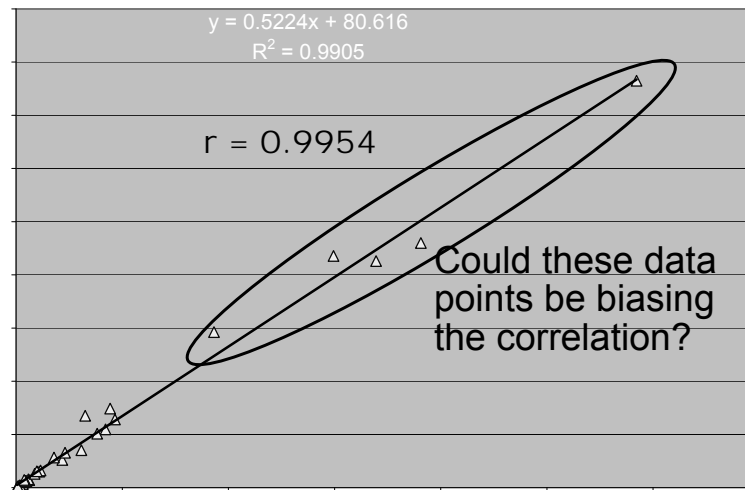
BOD vs COD (Airport runoff)



# data points= 36  
Mean = 0.531    Median = 0.528  
Range= 0.327 to 0.829

# SLH experience: BOD/COD ratios

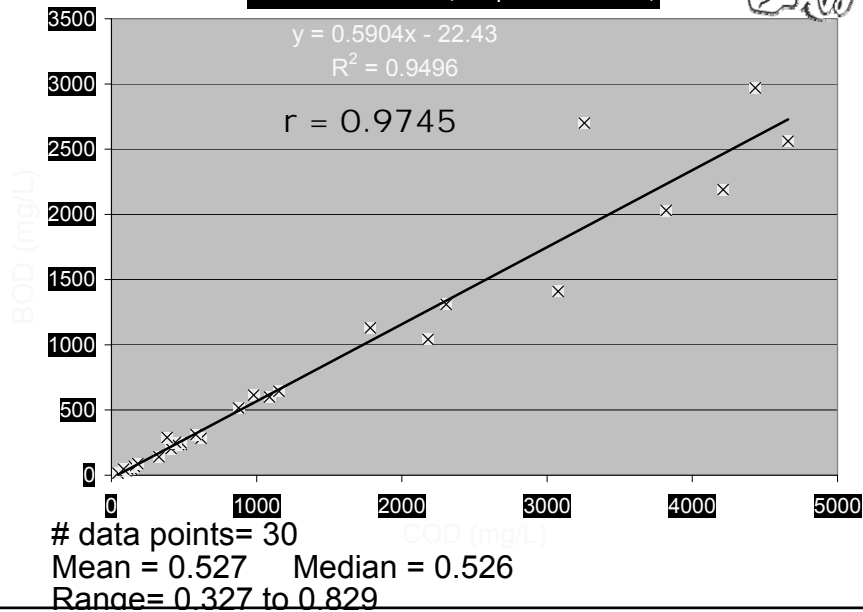
**BOD vs COD (Airport runoff)**



# data points= 35  
Mean = 0.529    Median = 0.524  
Range= 0.327 to 0.829

## SLH experience: BOD/COD ratios

BOD vs COD (Airport runoff)



## Dairy Industry BOD/COD ratios

BOD<sub>5</sub> and COD Values of Pure Dairy Products.

Product	BOD <sub>5</sub> (mg/l)	COD (mg/l)	BOD <sub>5</sub> /COD
Milk	104,600	173,000	0.60
Ice cream (10% fat)	292,000	540,000	0.54
Whey (acid)	32,000	70,000	0.54

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>

## Other Industry BOD/COD ratios

Typical Values of BOD<sub>5</sub> and COD for Different Food Plant Wastewater.

Type of Processor	BOD <sub>5</sub> (mg/l)	COD (mg/l)	BOD <sub>5</sub> /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>

## How to implement COD measurement for a process.

- In order to use the more readily measured COD in place of BOD<sub>5</sub>, both must be measured at specific points in the processing operation.
- These points may be floor drain outlets, wash water collection tanks, and other points where waste water is collected prior to being discharged to the sewer system.
- Data should be collected for a period of time to determine the degree of variability in BOD<sub>5</sub> and COD values at each point.
- Waste must be consistent for the correlation work.

## Bottom Line: BOD/COD ratios

- You can estimate BOD from COD.
- It is ONLY an estimate.
- Even with a large populations of data, the range is still quite broad.
- For user fees, focus on trends rather than absolute excursions from the norm.

## The Toxicity Problem

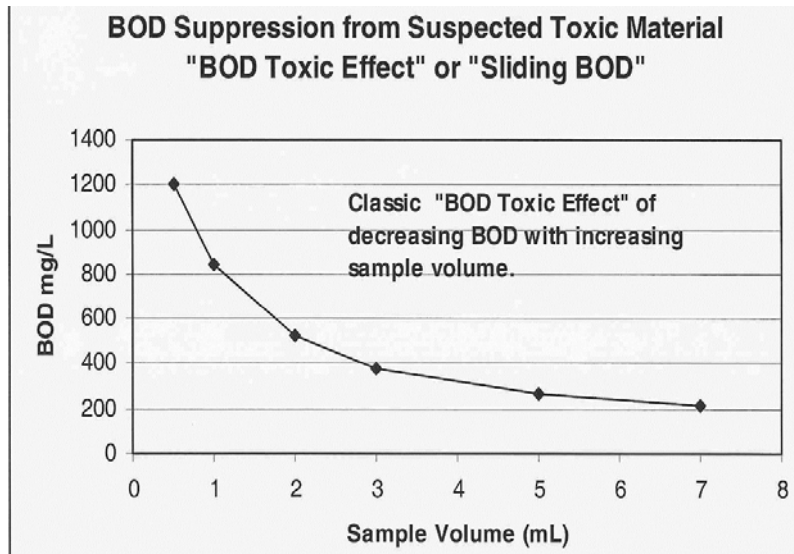


Toxicity can be insidious, and a real challenge... particularly if only a single dilution meets depletion acceptance criteria.

This is because operators often become programmed not to consider any dilution results for which the depletion exceed method-specified criteria.

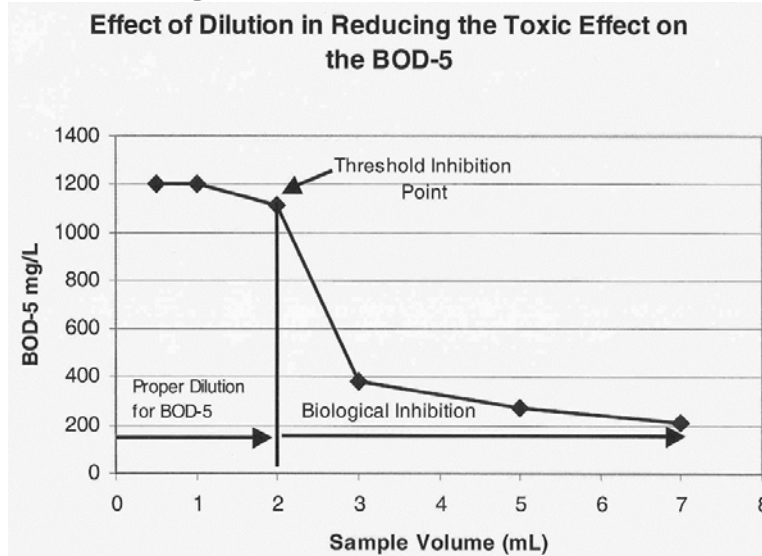


## What does toxicity look like?



As sample volume increases, BOD decreases

## Dealing with toxic samples



We need to dilute the sample until the toxic effect dissipates

# Toxicity example

1

Sample Volume	Initial Dilution	DO <sub>i</sub>	DO <sub>F</sub>	DO Depletion	BOD
100	1	8.31	3.14	5.17	16
50	1	8.40	4.12	4.28	26
25	1	8.49	0.10	> 8.39	Final DO <1.0 Too much depletion
Many operators might be inclined to stop here and report the average of the two dilutions (21).				<b>Average=</b>	<b>21</b>

The over-depleted sample, often overlooked, provides critical insight to this sample

Sample Volume	Initial Dilution	DO <sub>i</sub>	DO <sub>F</sub>	DO Depletion	BOD
100	1	8.31	3.14	5.17	16
50	1	8.40	4.12	4.28	26
25	1	8.49	0.10	> 8.39	>101

# Toxicity example

2

Sample Volume	Initial Dilution	DO <sub>i</sub>	DO <sub>F</sub>	DO Depletion	BOD
5	10	8.50	7.12	1.38	underdeplete
10	10	8.52	5.61	2.91	873
15	10	8.51	4.30	4.21	842
25	10	8.48	1.78	6.70	804
5	1	8.51	0.00	> 8.51	over deplete
10	1	8.48	0.00	> 8.48	over deplete
15	1	8.47	0.00	> 8.47	over deplete
25	1	8.49	0.10	> 8.39	over deplete
50	1	8.40	4.12	4.28	26
100	1	8.31	3.14	5.17	16

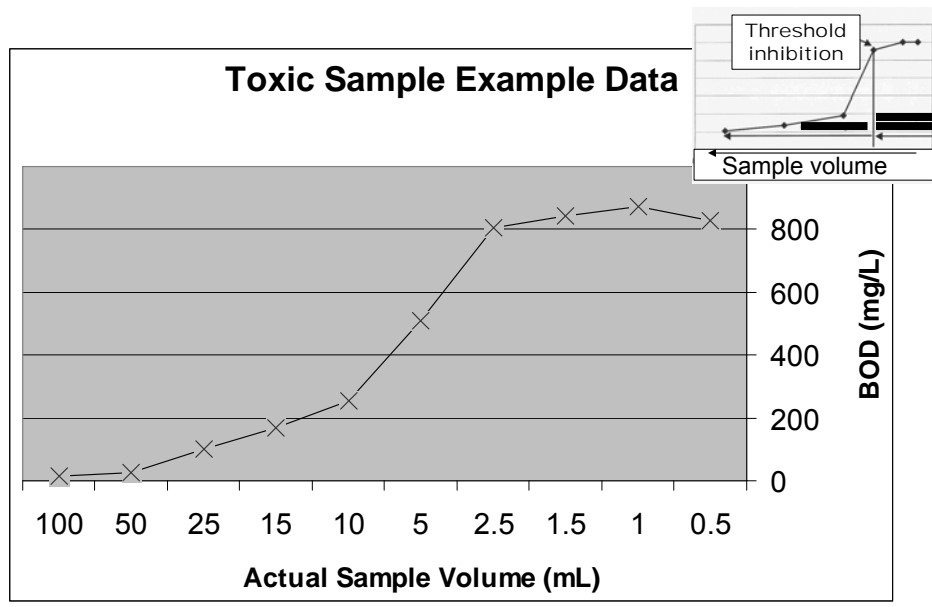
More dilutions clears the picture...are we done?

## Toxicity example

3

- So...is the actual BOD more like 840?
- Have we done enough work?
- As with the 1<sup>st</sup> stage of this process, we can look to the “un-useable” dilutions to help us “connect the dots”

## Toxicity Curve and Threshold Inhibition Point



## Toxicity example

4

Sample Volume	Initial Dilution	DO <sub>I</sub>	DO <sub>F</sub>	DO Depletion	BOD
5	10	8.50	7.12	1.38	828
10	10	8.52	5.61	2.91	873
15	10	8.51	4.30	4.21	842
25	10	8.48	1.78	6.70	804
5	1	8.51	0.00	> 8.51	511
10	1	8.48	0.00	> 8.48	254
15	1	8.47	0.00	> 8.47	169
25	1	8.49	0.10	> 8.39	101
50	1	8.40	4.12	4.28	26
100	1	8.31	3.14	5.17	16

## Determining Appropriate Dilutions

Sample Volume	Initial Dilution	DO <sub>I</sub>	DO <sub>F</sub>	DO Depletion	BOD
5	10	8.50	7.12	1.38	underdeplete
10	10	8.52	5.61	2.91	873
15	10	8.51	4.30	4.21	842
25	10	8.48	1.78	6.70	804

The ultimate goal of preparing the extensive toxicity dilution series is to identify a series of dilutions—for that particular waste— that will provide us with quality data without interference of toxic effects

It is at this point that data can be collected for development of a BOD/COD ratio specific to this waste.

## Reminders

- Dilutions of severely toxic samples COULD even have insufficient depletion---giving the appearance that the sample is “clean”.
- Sometimes sample odor could give a clue that low BOD results may not be accurate.
- 2 or even 3 dilutions is not enough
- Generally 5-10 dilutions may be needed
- You cannot “stop” until you reach the “plateau effect”.

## For more information:

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