

Hazen

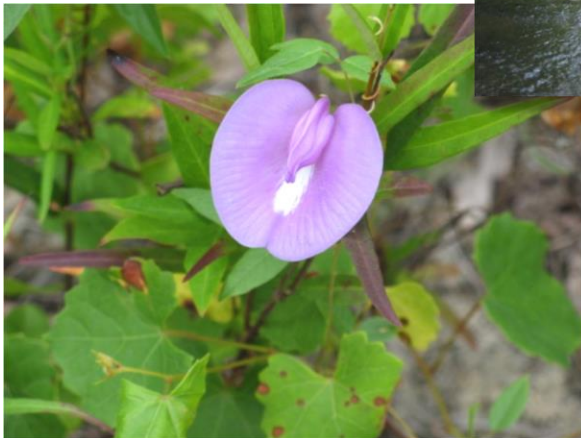
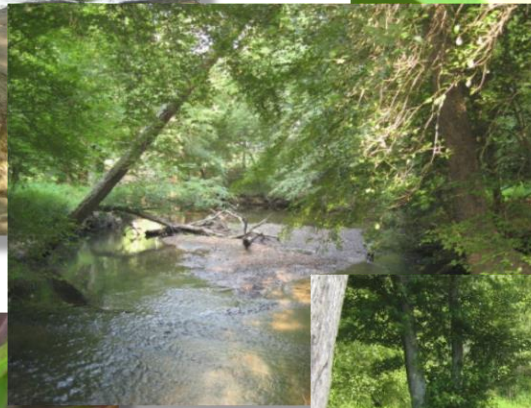


Performing a Water Effects Ratio for Silver

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Ryan Faw



Asheville, NC | October 14 – 16 | 2019





**NPDES
Permitting
Process**

**National
Aquatic Criteria
Development**

**Site-Specific
Criteria Methods**

**Raleigh
Silver WER**

**Pretreatment
Impacts**





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- North Carolina has replaced total recoverable metal standards with dissolved metal standards
 - Federal rule requires that NPDES permit limits for toxic metals be total recoverable
 - Hardness dependent (receiving stream and effluent)
 - Adjustment to published criterion necessary to calculate water quality-based effluent limit (WQBEL) in NPDES permits
- Action levels were NOT retained for copper, zinc, and silver
- Raleigh anticipated impact at Neuse River RRF permit and Pretreatment Program due to new silver criteria



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Metal	Former Total Freshwater Aquatic Life Standard (ug/L)	Current Freshwater Dissolved Aquatic Life Standard (ug/L)	
	Chronic at 50 mg/L Hardness	Chronic 25 mg/L	Acute 25 mg/L
Arsenic	50	150	340
Beryllium	6.5	6.5	65
Cadmium	2 / 0.4 trout	0.15	0.82 / 0.51 trout
Chromium (total)	50	Removed	
Chromium III	none	24	180
Chromium VI	none	11	16
Copper	7 (AL)	2.7	3.6
Iron	1 (AL)	Removed	
Lead	25	0.54	14
Nickel	88	16	140
Silver	0.06 (AL)	0.06	0.30
Zinc	50 (AL)	36	36



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- National criteria based on toxicity data for species with populations in North America
 - Short term acute toxicity – short term exposure, 48 to 96 hours
 - Chronic toxicity – long term exposure, 96 hours through life span
- Developed under Section 304(a) of Clean Water Act
- Water quality aquatic life criterion:
 - Highest concentration of a pollutant in water that is not expected to pose a significant risk to majority of species in a given environment
- Organisms exposed to single pollutant in laboratory water
 - Site-specific parameters (e.g., form and metal speciation) will affect toxicity of a pollutant that may over or under-estimate an aquatic criterion



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- Test results obtained in “laboratory” conditions as total recoverable in 1980s
- In early to mid 1990s, EPA changed course and recommended that criteria be applied as a “dissolved” criteria
 - Dissolved metals represent bioavailable fraction
- EPA provided acute conversion factors (ACFs) & chronic conversion factors (CCFs) to convert the laboratory-derived total recoverable criteria to “dissolved”
- Most states’ criteria are hardness-dependent equations
- Hardness, dissolved organics, and suspended solids reduce toxicity
 - The softer the water, the more toxic the water



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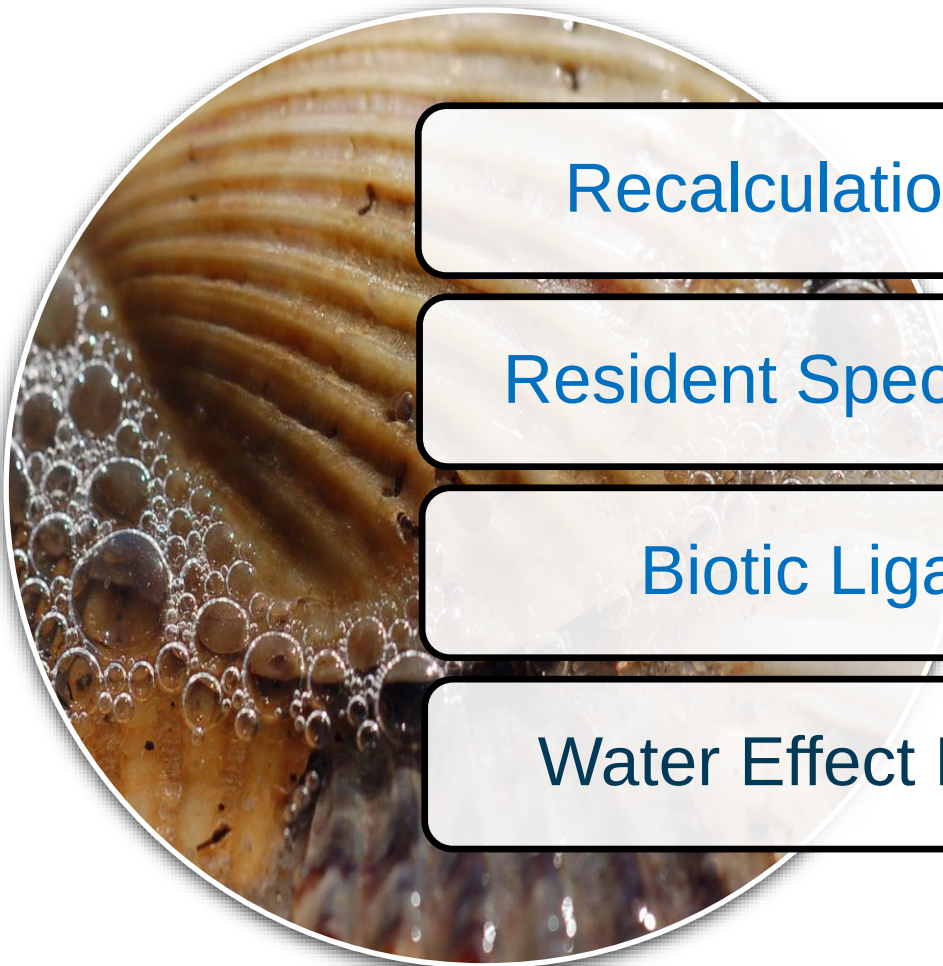
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- Compliance with dissolved metal criterion is based on EPA-derived conversion factors
 - Represents the fraction of total recoverable metal that is dissolved
- A **Translator** is needed to convert the dissolved metal criterion to a total metal concentration for NPDES permit compliance

Total Criterion → Dissolved Criterion → Total Criterion



- Three approaches:
 - Assume all metal is in dissolved form (1:1 relationship)
 - Linear partitioning method
 - Site-specific chemical translator



Recalculation Procedure

Resident Species Procedure

Biotic Ligand Model

Water Effect Ratio Method



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	Advantages	Disadvantages
Recalculation Procedure	• Inexpensive • Performed quickly if field data is available	• Expensive if fieldwork required • Difficult to prove a species is not present if habitat is present • Not a favorable outcome
Resident Species	• Bioavailability of pollutant based on characteristics of receiving water	• Expensive • Difficult to obtain large database for statistical comparison. • Least used method
Biotic Ligand Model	• Results input directly in calculated criterion as hardness replacement • Data collection less expensive • Successful outcome	• Time involved in data collection • Model only for copper • Not widely used



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Water Effect Ratio (WER) Method

- Ratio of the toxicity of a metal in site water to toxicity of the same metal in standard laboratory water
 - Used to derive site-specific limits for certain metals from national and state aquatic life criteria originally developed using laboratory toxicity data
 - Compensates for site-specific factors such as hardness, alkalinity, organic carbon, etc.
 - Influence the bioavailability and toxicity of metals
- More common and popular method with generally good results



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Water Effect Ratio

Advantages	Disadvantages
Procedure can be applied to any metal	Moderately expensive
Procedure can be applied to freshwater and salt water systems	Six month timeframe to complete testing
Rules allow for a NPDES permit approach (e.g., no rulemaking or EPA involvement)	Screening test should be conducted to assess feasibility
Popular method	
Generally produces a successful outcome	



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Water Effect Ratio (WER) Method

Interim Method, 1994

- Published in 1994
- Use with any metal
- 3 testing events with a primary species
- 1 testing event with a secondary species
- Uses actual flows to create SIMSTREAM
- Sampling events with 3- week intervals
- Complicated derivation of final WER
- 6 months

Copper Streamlined, 2001

- Published in 2001 for copper only
- 2 testing events with one species
- Sampling events with a 4-week interval, need low dry weather stream flow
- Uses design flows to create SIMSTREAM
- Final WER is the geometric mean of the two WERs
- 4 months



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Water Effect Ratio (WER) Screening Analysis

- Literature review
 - Typically produces wide range in WER values
- Quick toxicity “screening” study to validate pursuit of a full study
 - Estimate of flow conditions
- Results are an estimated value and only meant to convey feasibility
 - Full test results could be very different
- WER study plan must be submitted to DWR for review and approval prior to proceeding with WER study

Step 1: Sample collection

Upstream receiving stream and final effluent samples are collected and transported to the laboratory

Step 2: SIMSTREAM constructed at laboratory

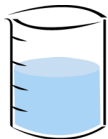
Final effluent and receiving stream are combined to create a simulated downstream water sample



Step 3: Prepare Lab Water Treatments

- Spike lab water with increasing amounts of metal
- Submit each treatment for total and dissolved metal
- Acute toxicity tests (48 hr) are used to conduct WER for chronic criteria (CCC)
 - Hybrid approach used whereby CMC is used to establish chronic criteria (CCC)
 - Valid if test species (e.g., *Ceriodaphnia dubia*) has 48-hour mortality endpoint between CCC and CMC values
 - Apply cmcWER result to cccWER
 - Use of acute test much less expensive than chronic tests

Control



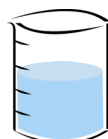
2.8 ppb



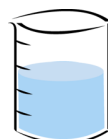
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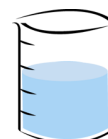
6.6 ppb



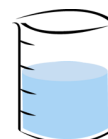
10.1 ppb



15.6 ppb



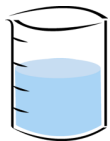
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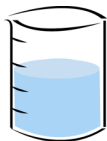
Step 4: Prepare SIMSTREAM Treatments

- Spike SIMSTREAM with increasing amounts of metal
- Submit each treatment for total and dissolved metal
- Use each treatment in a 48-hour toxicity test
 - Hybrid approach to apply cmcWER to cccWER

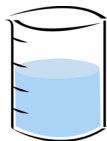
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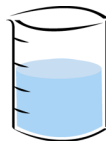
14 ppb



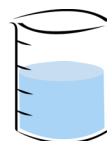
16 ppb



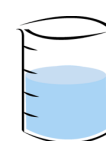
37 ppb



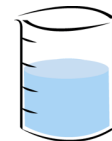
52 ppb



76 ppb



120 ppb



Step 5: Conduct Toxicity Test

- Lab water and site water toxicity tests result in LC50 values.
- The LC50 represents the metal concentration that causes 50% of the test organisms to die during the test.



Step 6: Calculate the Water-Effect Ratio

- Normalize LC50 results to same hardness
- Water Effect Ratio =

LC50 in Site Water / LC50 in Lab Water



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Sample #1 LC50 Calculations (*C. dubia*) - May 1, 2019

Test	Test Results			Normalized Test Results		
	Total	Dissolved	Hardness, mg/L	Total	Dissolved	Normalized Hardness, mg/L
Labwater	2.209	1.81	44	0.7238	0.5931	23
Simstream	13.4	4.902	23	13.40	4.90	23

$$\text{Dissolved WER} = \frac{LC_{50 \text{ sitewater}}}{LC_{50 \text{ labwater}}} = \frac{0.5931}{4.9} = 8.265$$

$$\text{Total WER} = \frac{LC_{50 \text{ sitewater}}}{LC_{50 \text{ labwater}}} = \frac{0.7238}{13.4} = 18.51$$

Type II test: Q_{upstream} between 2x and 10x Q_{NRRRF}



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Sample #1 LC50 Calculations (*P. promelas*) - May 1, 2019

Test	Test Results			Normalized Test Results		
	Total	Dissolved	Hardness, mg/L	Total	Dissolved	Normalized Hardness, mg/L
Labwater	5.29	4.658	44	1.7334	1.5263	23
Simstream	33	15.31	23	33.0	15.31	23

$$\text{Dissolved WER} = \frac{LC_{50 \text{ sitewater}}}{LC_{50 \text{ labwater}}} = \frac{1.5263}{15.3} = 10.03$$

$$\text{Total WER} = \frac{LC_{50 \text{ sitewater}}}{LC_{50 \text{ labwater}}} = \frac{1.7334}{33} = 19.04$$

Type II test: Q_{upstream} between 2x and 10x Q_{NRRRF}



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Sample #2 LC50 Calculations (*P. promelas*) - May 23, 2019

Test	Test Results			Normalized Test Results		
	Total	Dissolved	Hardness, mg/L	Total	Dissolved	Normalized Hardness, mg/L
Labwater	3.345	2.671	56	1.957	1.5624	41
Simstream	41.2	24	41	41.20	24.00	41

$$\text{Dissolved WER} = \frac{LC_{50 \text{ sitewater}}}{LC_{50 \text{ labwater}}} = \frac{1.5264}{24} = 15.36$$

$$\text{Total WER} = \frac{LC_{50 \text{ sitewater}}}{LC_{50 \text{ labwater}}} = \frac{1.957}{41.2} = 21.06$$

Type I test: Q_{upstream} between 1x and 2x Q_{NRRRF}



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Sample #3 LC50 Calculations (*P. promelas*) - June 19, 2019

Test	Test Results			Normalized Test Results		
	Total	Dissolved	Hardness, mg/L	Total	Dissolved	Normalized Hardness, mg/L
Labwater	7.256	6.096	40	3.929	3.301	28
Simstream	42.11	31.01	28	42.11	31.01	28

$$\text{Dissolved WER} = \frac{LC_{50 \text{ sitewater}}}{LC_{50 \text{ labwater}}} = \frac{3.301}{31.01} = 9.39$$

$$\text{Total WER} = \frac{LC_{50 \text{ sitewater}}}{LC_{50 \text{ labwater}}} = \frac{3.929}{42.11} = 10.72$$

Type II test: Q_{upstream} between 2x and 10x Q_{NRRRF}



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Summary of WER Results

Study Date	Species	Total WER	Dissolved WER	hWER	WER Type
May 1, 2019	<i>P. promelas</i>	19.04	10.03	436.3	Type 2
May 2, 2019	<i>C. dubia</i>	18.51	8.265	---	---
May 23, 2019	<i>P. promelas</i>	21.06	15.36	55.65	Type 1
June 19, 2019	<i>P. promelas</i>	10.72	9.39	57.89	Type 2

hWER = Highest theoretical WER of the receiving stream



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- 1994 Method contains a complicated derivation of Final WER depending on the test type (Type I or II)
 - Procedures for two or more Type I WERs
 - Procedures for one Type I WER
 - Procedures for no Type I WERs
- Raleigh fell under procedure for one Type I WER:

Lowest Type 1 Total WER =	21.06	
Lowest hWER =	55.65	
Geometric Mean of all Total WERs =	16.26	(geometric mean of <i>P. promelas</i> tests)
Final Silver Total WER =	16.26	(Minimum of the above tests)



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Total Recoverable WER
Method

Published Criterion,
acute, total
Recoverable

x [WER_{total recoverable}]
** geomean of measured WERs

Site-specific
criterion, total
recoverable

Total Recoverable WER
Method (Acute)

$\exp \{1.72 \times [\ln (42)] + (-6.59)\} = 0.85 \text{ ug/L}$

x [16.26]

13.83 ug/L

Acute standard for silver is hardness dependent and has an EPA published translator of 1 (e.g., no linear translator). The translator is not needed in the total WER calculation.



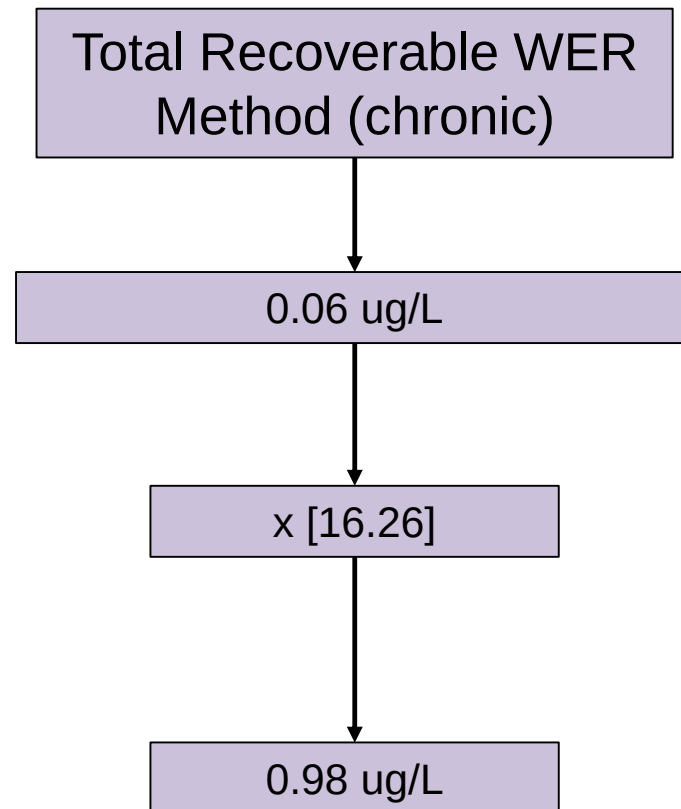
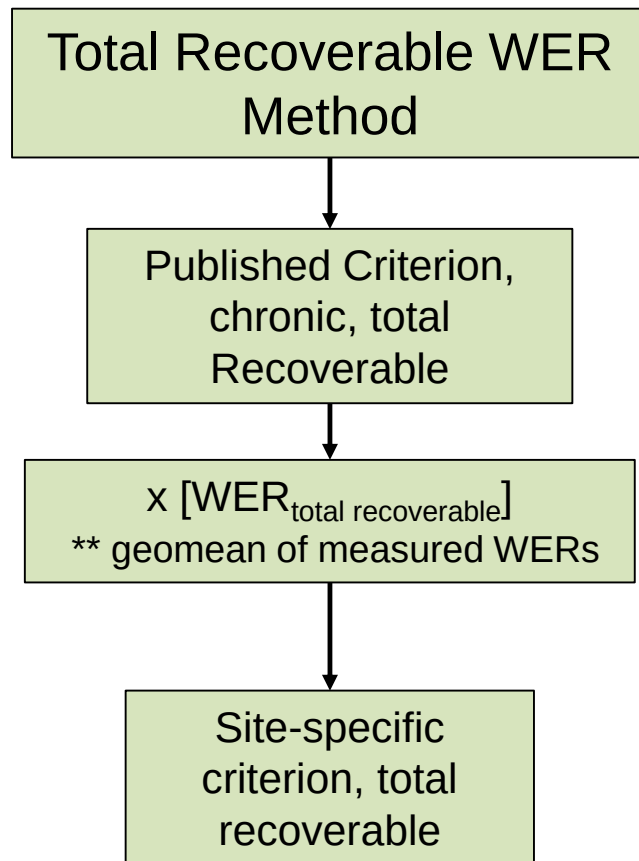
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Chronic standard for silver is not hardness dependent and has a translator of 1 (e.g., no linear translator). The translator is not needed in the total WER calculation.



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Wasteload Allocation

- Allowable discharge concentration, daily maximum:

$$C_{WLA,acute} = [(1Q10 + Q_{WWTP}) \times C_{s,acute} - 1Q10 \times C_b] / Q_{WWTP}$$

$$C_{WLA,acute} = [(1Q10 + Q_{WWTP}) \times 13.83 - 1Q10 \times C_b] / Q_{WWTP} = 23.2 \text{ ug/L}$$

- Allowable discharge concentration, monthly average

- Basis for permit limit assessment

$$C_{WLA,chronic} = [(7Q10 + Q_{WWTP}) \times C_{s,chronic} - 7Q10 \times C_b] / Q_{WWTP}$$

$$C_{WLA,chronic} = [(7Q10 + Q_{WWTP}) \times 0.98 - 7Q10 \times C_b] / Q_{WWTP} = 1.8 \text{ ug/L}$$



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- Silver is a particular issue:
 - EPA has not adopted chronic criteria for silver
 - DWR adopted a chronic silver criteria without input or vetting of impacts
- Raleigh study demonstrates that silver is not as toxic as DWR chronic standard
 - A total WER of 16.26 is an excellent result!
- Raleigh has moved to a silver detection level of 1 ug/L
 - Current data indicates reasonable potential even though all of the data is non-detect
 - New data set with lower detection should remove reasonable potential



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- Maximum Allowable Headworks Load (MAHL)
 - Total load at headworks that a WWTP can accept without violating water quality standards, biosolids criteria, inhibition thresholds, and safety standards
- MAHL without WER = 0.219 lb/d
 - Neuse River RRF was over-allocated for silver based on domestic sources with chronic silver standard
- MAHL with WER = 3.58 lb/d
 - Silver WER allows capacity for economic development and future domestic growth



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Basis	Action Level	Chronic Stream Standard of 0.06 ug/L	Chronic Stream Standard of 0.98 ug/L (WER)
MAHL from HWA (lb/d)	95.221	0.219	3.578
Uncontrollable loading (lb/d)	0.981	0.981	0.364
Total Allowable for Industry (MAIL) (lb/d)	94.240	- 0.762	3.214
Permitted to industry (lb/d)	0.672	0.672	0.672
MAIL left (lb/d)	93.567	- 1.435	2.542
Percent MAIL available (%)	99.3 %	188.2 %	79.1 %
Percent MAHL available (%)	98.3 %	- 655.1 %	71.0 %
5 Percent MAHL (lb/d)	4.761	0.011	0.179
NPDES limit, ug/L	N/A (Action Level)	0.11	1.8

What To Do prior to NPDES Renewal Application

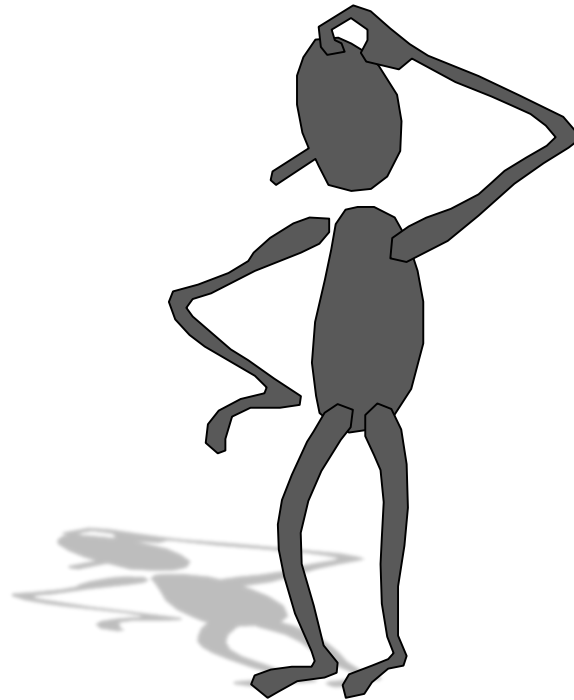
- Monitor LTMP and Priority Pollutant Analysis data carefully
- Consider use of lower MDLs
 - Silver
- Trial run using the translator method to calculate condition-specific criteria
- Determine if a site-specific study is necessary
 - Screening analysis

[illegible]



Hazen

Questions?



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