INDUSTRIAL USER SELF-MONITORING

NC Pretreatment Consortium
Industry Day – "Pretreatment 101"
November 2025

WHY DOES POTW SAMPLE YOU? WHY DO YOU SAMPLE YOU?

POTW Monitoring of SIUs:

- EPA [40 CFR Part 403.8] and NCDWR [15 NCAC 2H .0908] require POTW to sample SIUs at least annually

SIU Self Monitoring:

- EPA requires SIUs to conduct semi-annual sampling

Options:

- POTW Can Do All the Required SIU Sampling OR
- POTW Can Require SIU to Conduct Some Self-Monitoring [POTW must still sample as well]

GOALS OF PRETREATMENT PROGRAM SAMPLING

- Evaluate SIU Compliance
- Determine Impact of Industrial Wastes on POTW
- Support SIU Permit development/ reissuance
- Support enforcement actions
- User charge [surcharge] data

OTHER SAMPLING/MONITORING REQUIREMENTS…

- All Pretreatment Program Samples [and NPDES samples] MUST Be Analyzed By a Wastewater Laboratory Certified By the State of North Carolina to Conduct Each Specific Analyses [per NC-DWR]
- All Pretreatment Program Sampling/ Monitoring MUST Comply with 40 CFR Part 136 [per EPA]

IU SELF-MONITORING
Topics For Today

1. Items/Documents You Will Need
2. Wastewater Sampling
3. 40 CFR Part 136
4. Laboratory Issues and Requirements
5. Laboratory Analyses
6. Data Analysis and Interpretation
7. Reporting and Recordkeeping

1. ITEMS/DOCUMENTS YOU WILL NEED

Significant Industrial User Permit

Sewer User Ordinance

40 CFR Part 136

Sampling Equipment

Monitoring Equipment

ITEMS YOU WILL NEED: Significant Industrial User Permit

- Limits/Monitoring Requirements Page
- Sampling Point Description
- General Conditions
- Special Conditions
  - Special Monitoring Reports (Baseline Monitoring Report, 90 Day Compliance Report, etc.)
- Definitions
  - Total Toxic Organics [TTO] List (if applicable)
  - Report "Submittal" [Due dates]

ITEMS YOU WILL NEED: Sewer Use Ordinance (SUO)

- Definitions Section
  - Daily, Monthly, Quarterly
  - "Composite" Sample
- Report Submittal Instructions
  - How to Submit [US Mail, email, fax, etc.]
  - Due Date(s)
    - Postmarked or Received
- Local Limits
  - Some discharge limits are local limits default values from SUO

ITEMS YOU WILL NEED: 40 CFR Part 136

- Title 40 of Code of Federal Regulations, Part 136
  - Federal Register Available on-line
- Approved Methodology for specific *wastewater* analyses
- Required Sample Containers
- Sample Holding Times
- Required Sample Preservation

ITEMS YOU WILL/MAY NEED: Sampling/Monitoring Equipment

- pH Meter
- Flow Meter
  - Effluent Meter
  - Incoming Water Meter
- Automatic Composite Sampler
  - Rent or Purchase Sampler
  - Composite Capabilities Only
  - Discrete and Composite Capabilities

2. WASTEWATER SAMPLING

Sample Location
Types of Samples
Sampling/Monitoring Equipment
Sampling Techniques
Sampling Frequency
Sample Labeling
Chain of Custody

SAMPLING LOCATION: SIU Effluent Sampling Point

- SIU Permit Sampling Point Should:
  - Be representative of the discharge
    - Include all regulated wastestreams
  - Be appropriate for the wastestream conditions
  - Have no bypass capabilities
  - Allow for unrestricted access at all times
  - Be where flow is turbulent and well-mixed
  - Include all outfalls that appear in the Permit
    - Most POTWs use “Pipe 01” and “Pipe 02” to differentiate more than one outfall

YOUR SIU PERMIT LISTS THE "PERFECT" SAMPLING SITE….

- NOW…..
  - Mark with Paint or Other Means and ALWAYS Sample at Exact Same Location
  - If Commercial Laboratory does your sampling, ensure that the Laboratory knows EXACTLY where to take sample
    - Provide copy of your permit to laboratory
  - Keep Sampling Devices at Sampling Sites
    - Use of same sampling device at multiple sites risks cross-contamination
  - Determine what Sampling "Day" is representative

TYPES OF SAMPLES: GRAB SAMPLE

- Individual sample, usually taken manually
  - Collected over period of time <15 minutes
- Used for parameters that cannot be held, are unstable or difficult to preserve
- Sample volume depends on number of analyses to be performed [Don't forget QA/QC samples…duplicates, "Murphy"]
- Represents conditions that exist at time of sampling [and not necessarily conditions at any other time]

WHEN DO WE COLLECT GRAB SAMPLES?

- If Your Permit Tells You To!
  - Batch Discharges
  - Screening to see if a pollutant is present
  - Where statistical relationship can be established between grab/composite data
  - When SIU Permit has instantaneous limit, based on grabs
  - When checking for extreme conditions
  - For certain parameters……

WHEN MUST WE COLLECT GRAB SAMPLES?

Always for certain parameters:

- pH
- Temperature
- Dissolved Oxygen
- Residual Chlorine
- Volatile Organic Analyses [VOAs]**
- Sulfides**
- Cyanide**
- Phenol**
- Low Level Mercury [Method 1631]
- Oil and Grease**

***Can use "Grab Composites" for these parameters*

TYPES OF SAMPLES: COMPOSITE SAMPLE

- Formed by a number of discrete samples
  - Collected over period of time >15 minutes
  - Collected over a workday
- Can be taken with automatic sampler or manually (with POTW permission)
- Used to determine average concentration during compositing period
- Used for most compliance samples
  - SIU Permit limited parameters (categorical standards and local limits)

TYPES OF COMPOSITE SAMPLES

- Time Composite
  - equal volumes taken at equal time intervals
- Flow Proportional Composite Method 1
  - equal time intervals with sample volume varying according to flow
- Flow Proportional Composite Method 2
  - equal volumes taken at varying time intervals in proportion to the flow
- "Grab Composite"

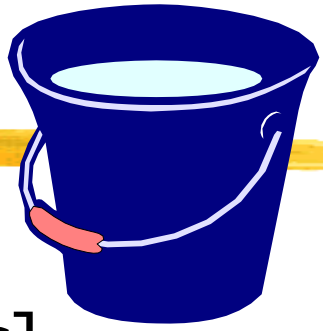
"GRAB COMPOSITE" SAMPLES

- Mutiple grab samples taken over a 24 hour period may be composited under certain circumstances
  - Allowed/explained in the 2006 EPA Pretreatment Streamlining Regs (40 CFR Part 403.12)
  - Cyanide, total phenols and sulfides may be composited in the laboratory OR in the field
  - Volatile organics and Oil and Grease may be composited in the laboratory only

TYPES OF SAMPLES: Typical SIU Analyses

- Grab Sample
  - pH
  - Cyanide
  - Oil and Grease
  - Phenol
  - Volatile Organic Compounds [VOCs] [EPA Method 624.1]
- Composite Sample
  - Biochemical O_2 Demand
  - Chemical O_2 Demand
  - Suspended Solids
  - Phosphorus
  - Nitrogen [Total and Ammonia]
  - Metals
  - Acid Extractable and Base Neutral Organics [EPA Method 625.1]

SAMPLING EQUIPMENT



- Can be complex or simple
  - Automatic samplers [ISCO, Sigma, etc]
  - Weighted bucket with a rope
  - Valved taps in flowing pipe lines
- Avoid materials that contaminate sample
  - No mayonnaise jars or Pepsi bottles!!!
  - No galvanized buckets for metals samples!
  - Plastic devices less likely to contaminate

SAMPLING EQUIPMENT

- Automatic Samplers
  - Timesavers BUT require maintenance
    - Clean sample jug and sampler tubing after each use
    - Change tubing if it cannot be cleaned adequately
    - Dirty sampler may introduce contaminants that may cause permit violations or increased high strength waste surcharges
  - Permanent Installation vs. “Portable”
  - Portable unrefrigerated [must put ice in sampler]
  - Maintain thermometer in sampler storage chamber
  - Flow Proportional Sampling requires flow meter be interfaced with sampler

MONITORING EQUIPMENT

- Flow Meter [for Flow Monitoring]
  - Take flow readings to correlate with composite sampling start and end times
  - Flow Meter Calibration Requirement
    - Some POTWs require outside "qualified" contractor
    - Other POTWs allow SIU personnel to calibrate flow meter
    - Calibration frequency determined by POTW
    - Usually included in SIU Permit
  - Effluent Meter
    - Measures discharge leaving the SIU
  - City "Water Meter"
    - Measures incoming water to facility and/or process

SAMPLING TECHNIQUES

- If Sample is a Composite…MIX WELL before pouring into sample bottles
  - SOP should say how many times to shake!
- After collection, samples must be handled to ensure they remain unchanged
  - Proper Preservation [chemical or refrigeration]
  - Proper Transport [usually on ice]
- Important: Keep all sampling containers and measuring devices clean
  - Contaminants can be introduced that could affect results.

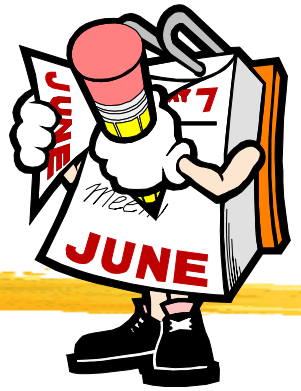
SAMPLING TECHNIQUES

- Note physical characteristics of sample and site
  - Any observations may explain problems you encounter with erroneous sample results
  - Could help you avoid SIU permit violations
  - Things to look for/document:
    - Unusual odors, high solids, color, turbidity [cloudiness], weather conditions

SAMPLING FREQUENCY: General Information

- SIU Permit Specifies Requirements
  - Required Frequency
    - Daily, weekly, monthly, quarterly, semi-annually, annually
  - Required Sampling Point(s)
  - Required Parameters for Analysis
    - Parameters with Discharge Limits
    - Monitoring Only Parameters with no Limits
    - Some cities now include EPA Contaminants of Emerging Concern (CEC) such as PFAS (Per-and Poly-Fluoroalkyl Substances) and 1,4-dioxane

SAMPLING FREQUENCY: Definitions [Permit/SUO]



- Daily
  - At least one sample taken Monday, Tuesday, Wednesday, Thursday and Friday except holidays
- Weekly
  - At least one sample taken each Sunday thru Saturday
- Monthly
  - At least one sample taken each calendar month
- Quarterly
  - At least one sample taken in each of the following periods: January-March, April-June, July-September and October-December

SAMPLING FREQUENCY: Determining Factors

- Factors Affecting Frequency of IU Sampling
  - Past compliance history of SIU
  - Flow volume and constituents
  - Extent and number of problems in collection system/POTW resulting from SIU discharge
  - Quality of SIU self-monitoring data
  - New or additional PT standards/requirements
  - Changes to facility operations
  - Seasonal production

SAMPLING FREQUENCY: Event Duration

- SIU Permit Limits May Dictate Event Duration
  - Electroplating Categorical Standards specify daily maximum and 4-Day Average limits
- Most Federal Categorical Standards specify a daily maximum and a monthly average limit
  - Permissible to take just one sample during the month and compare to daily maximum and monthly average
  - One sample = 2 compliance judgment points
- Some POTW's take more than one sample per "event" [i.e. three 24-hour composites]

SAMPLE LABELING

- All Samples MUST be Labeled
- Waterproof Labels and Ink Should Be Used [No Felt Tipped Pens!!!]
- Label Should Include:
  - Sample ID/Location
  - Date and Time of Sample Collected
  - Initials of Person Collecting Sample
  - Preservation Method/Sample Pretreatment
  - Requested Analyses

CHAIN OF CUSTODY CONTENTS

- Name of SIU
- SIU Permit #
- Sampling Location
- Sample ID
- Initials of Collector
- Composite Start Time
- Composite End Time
- Grab Sample Time
- Container(s) Description
- Preservative(s) Used
- Sample Pretreatment
- What tests to be run
- Relinquished and Received Spaces
- Comments Section

SAMPLE PACKING AND TRANSPORT

- Samples in glass containers should be protected [bubble-wrap, vermiculite]
- VOC vials should be put in same cooler to reduce number of trip blanks
- Use wet ice [NO Blue ice/cooling packs]
- Shipping Containers
  - Should be insulated and sealed [tape/locks etc.]
  - Delivered by Sampling Team or common carrier
  - Paperwork in plastic bag taped to cooler lid

3. 40 CFR PART 136 [from Federal Register]

Contains Rules For……

Sample Containers

Sample Preservation

Other Requirements

Sample Holding Times

EPA-Approved Wastewater Analytical Methods

SAMPLE CONTAINERS General Information

- Usually provided to SIU by Commercial Laboratory
  - MUST comply with 40 CFR Part 136
  - Glass or Plastic
    - If you can choose, choose plastic!!!
  - Must be made of chemically resistant material that does not effect pollutant to be measured
  - May require special cleaning procedures
  - Label containers clearly/completely
  - Can use disposable single-use containers

SAMPLE CONTAINERS: Specific Parameters

- Plastic Only
  - Fluoride
- Glass Only
  - Oil and Grease
  - Phenols
  - All Organics
    - VOCs
    - Acid-Extractables
    - Base-Neutrals
- Plastic or Glass
  - BOD/CBOD
  - COD
  - Cyanide
  - Nutrients
  - Metals
  - WET [Bioassay]
  - Bacteriological

SAMPLE CONTAINERS: Sample Collection

- Actual Sampling Container MUST be used for collecting the following samples:
  - Oil and Grease
  - Volatile Organic Compounds [VOCs]
  - Bacteriological [Fecal Coliform]
- Sample containers with pre-measured amounts of preservatives should not be used to collect these samples

SAMPLE PRESERVATION: General Information

- Proper preservation ensures that sample does not change significantly from the time it is collected until final analysis is completed
- Composite samples must be kept at ≤6°C during compositing
- Samples must be iced [no blue-ice!!] during transport [or document downward temperature trend]
- Samples for multiple analyses [with different preservatives] may need to be placed in separate containers

SAMPLE PRESERVATION: Specific Parameters [Take 1]

- NONE REQUIRED- Analyze immediately
  - pH
  - Temperature
  - Dissolved Oxygen [with D.O. Probe]
- NONE REQUIRED
  - Fluoride
  - Bromide
  - Chloride

SAMPLE PRESERVATION: Specific Parameters [Take 2]

- Cool to ≤6° C
  - BOD/CBOD
  - Acidity
  - Alkalinity
  - Color
  - Conductivity
  - Nitrate
  - Nitrite
- Cool to ≤6° C
  - Solids
    - Total Suspended Solids
    - Total Dissolved Solids
    - Total Volatile Solids
  - Whole Effluent Toxicity
  - Surfactants
  - Turbidity

SAMPLE PRESERVATION: Specific Parameters [Take 3]

- Cool to ≤6° C , pH < 2 with Sulfuric Acid [H_2SO_4]
  - Ammonia-Nitrogen
  - Total Kjeldahl Nitrogen
  - Nitrate/Nitrite Combined
  - Phenols
  - Total Phosphorus
  - Chemical Oxygen Demand [COD]

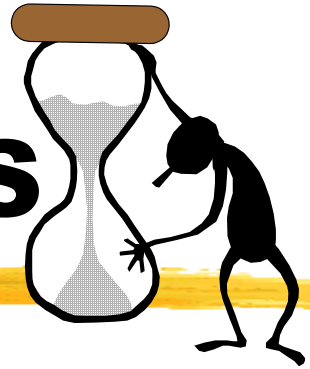
SAMPLE PRESERVATION: Specific Parameters [Take 4]

- Cool to ≤6° C , pH < 2 with Hydrochloric Acid [HCl] or Sulfuric Acid [H_2SO_4]
  - Oil and Grease
- pH < 2 with Nitric Acid [HNO_3]
  - Metals [except Chromium VI]
  - Do NOT Ice Metals!]
- Cool to ≤6° C , pH > 12 with Sodium Hydroxide [NaOH]
  - Cyanide

OTHER SAMPLE REQUIREMENTS

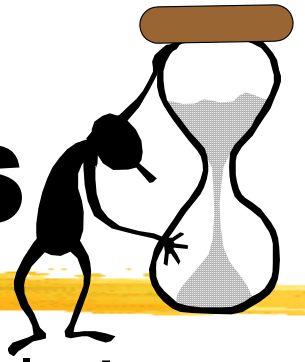
- Screening/Pretreatment of Samples to Remove Interferences
  - Cyanide samples-Remove residual chlorine with one of 4 chemicals listed in 40 CFR Part 136
  - Ammonia Nitrogen-Remove residual chlorine with sodium thiosulfate
- Filtering Sample
  - For ortho-phosphate and soluble metals
- Zero Head Space [Full with no air bubbles]
  - For volatile organics [VOA] samples

SAMPLE HOLDING TIMES



- 48 Hours
  - BOD/CBOD
  - Nitrate
  - Nitrite
  - Color
- 7 Days
  - Solids [TSS, TDS, TVS]
- 14 Days
  - Acidity
  - Cyanide [A and T]
  - VOCs
- 28 Days
  - Ammonia-Nitrogen
  - Nitrate/Nitrite
  - Oil and Grease
  - Mercury
  - COD
  - TKN
  - Total Phosphorus
- 6 Months
  - Metals [except mercury and chromium VI]

SAMPLE HOLDING TIMES



- Holding Time starts at exact moment sample is collected *not* when it arrives at the laboratory
- For composite, holding time begins when last portion of sample is added to composite
- Holding Time is considered to be *exact*
  - Seven days is considered to be exactly 7 * 24 hours and 0 minutes
  - BOD run at 47 hours 59 minutes and 59 seconds is wonderful…BOD run one minute later is "invalid" [Oh, what a difference a minute can make when you're in court!]

Holding Time for Composites

- From 40 CFR Part 136 (Footnotes):

  "For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), the holding time begins at the time of the end of collection of the composite sample. For a set of grab samples composited in the field or laboratory, the holding time begins at the time of collection of the last grab sample in the set."

EPA APPROVED METHODOLOGY

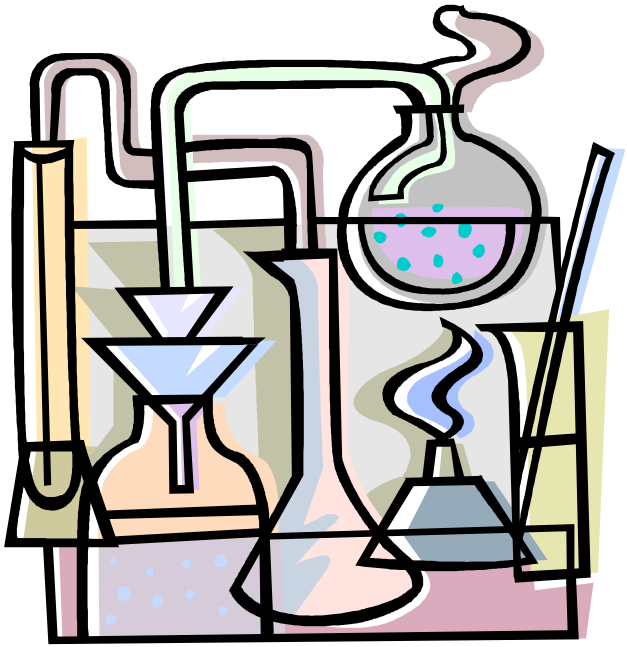
- Only Those Listed in 40 CFR Part 136
- Not all EPA Methods are approved by EPA for Pretreatment or NPDES compliance monitoring
- Not all *Standard Methods* procedures are approved by EPA for Pretreatment or NPDES compliance monitoring
- SIU must be familiar with approved methods for each analysis
- Note: Currently no EPA approved wastewater method for PFAS (but maybe in early 2023)

REQUIRED METHODOLOGY

- SIU, not the laboratory, is responsible for proper methodology on SIU analyses
- Any method not specifically listed in 40 CFR Part 136 is prohibited for SIU compliance analyses
- Be very careful with organic analyses…. [Methods 6010, 8260 and 8270, etc. are NOT approved for wastewater]

4. LABORATORY ISSUES AND REQUIREMENTS

- Laboratory Certification
- What Your SIU Permit Says About Sampling
- Detection Limits
- Sample Volumes
- Sample Scheduling



NC WW LAB CERTIFICATION: General State Requirements

- 15 NC Administrative Code 2H .0800s
- Mandatory WW Lab Certification Program
  - Commercial, Municipal and Industrial Laboratories that conduct:
    - NPDES Program analyses for reporting
    - Pretreatment Program Analyses for reporting
    - Groundwater Analyses for reporting
- Parameter/method specific certification

WHAT YOUR SIU PERMIT SAYS ABOUT SAMPLING

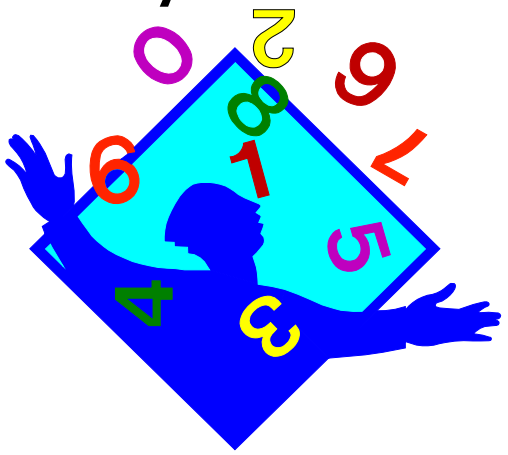
- How often? [Daily, Weekly, Monthly, etc.]
- At specific times? [i.e., specific months]
- What points? [Pipe 01, Pipe 02]
- Sample Type? [Grab or Composite]
- Must Use 40 CFR Part 136 [per EPA]
- Must Use Laboratory Certified by NC-DWR To Conduct That Analysis [per NC-DWR]
- All samples/analyses must be reported
  - No, you CANNOT pick the "best" number!
- Detection Limits [in some cities]

THE PERMIT SAYS….
What Tests Will We Run?

- Remember: Parameter Selection Determines:
  - Sample Type
    - Grab or Composite
  - Sample Container
    - per 40 CFR Part 136
  - Sample Volume
    - Determined somewhat by analytical method, also
  - Sample Preservation
    - per 40 CFR Part 136
  - Sample Holding Time
    - per 40 CFR Part 136

LABORATORY ISSUES: Detection Limits [DLs]

- SIU MUST be familiar with laboratory methods and resulting DLs
- Some DLs are standard
  - BOD = 2 mg/l
- Other DLs are <u>method</u> specific
  - Metals-Flame AA vs. Graphite Furnace AA
- What detection limits do you <u>really</u> need?
  - Effluent Compliance Sampling



SIU COMPLIANCE SAMPLING DETECTION LIMITS

- Purpose to Determine Compliance with:

  Metal Finishing Standards [40 CFR Part 433]

  - cadmium DM = 0.11 mg/l MA = 0.07 mg/l
  - chromium DM = 2.77 mg/l MA = 1.71 mg/l
  - copper DM = 3.38 mg/l MA = 2.07 mg/l
  - lead DM = 0.69 mg/l MA = 0.43 mg/l
  - nickel DM = 3.98 mg/l MA = 2.38 mg/l
  - zinc DM = 2.61 mg/l MA = 1.48 mg/l
  - silver DM = 0.43 mg/l MA = 0.24 mg/l

- Do you <u>really</u> care if the DL is 0.010 mg/l or 0.050 mg/l????? [Probably not….]

PARAMETER SELECTION
Sample Volume*

- 50 milliliters/analysis
  - pH
  - COD
- 100 milliliters/analysis
  - Conductivity
  - Turbidity
  - Total Phosphorus
- 250 milliliters/analysis
  - Metals
  - TSS/TDS

*Guidance Only

- 500 milliliters/analysis
  - BOD/CBOD
  - Ammonia-Nitrogen
  - TKN
- 1000 milliliters/analysis
  - Oil and Grease
  - WET [Mini-chronic]
- 3000 milliliters/analysis
  - Semi-volatile Organics
  - 5-Dilution WET

LABORATORY ISSUES: Sample Scheduling

- Contact Laboratory [Commercial/SIU] Prior to Finalizing Special Sampling Dates
  - Ensure sample containers/coolers will be ready
  - Ensure lab can accommodate samples with short holding times [BOD sample to lab at 4:30 Friday afternoon=Dead SIU Contact!]
  - Notification of holidays/scheduled shut downs
- Notify Lab Immediately if Changes are Made to Sampling Schedule

5. WASTEWATER ANALYSES

pH
Suspended Solids
Biochemical Oxygen Demand
Chemical Oxygen Demand
Nitrogen
Phosphorus
Oil and Grease
Metals
Organics

WASTEWATER ANALYSES: pH

pH is a measure of the hydrogen ion concentration

- pH scale ranges from 0 to 14 [7.0 is "neutral"]
  - Readings below 7.0 are acidic and readings above 7.0 are basic [alkaline]
- "Logarithmic" scale
  - pH of 5.0 is 10 X more acidic than pH of 6.0
- Domestic wastewaters have a pH near 7
  - Industrial wastewaters can be at either end of the pH scale

WASTEWATER ANALYSES: pH

- Federal EPA Lower pH limit prohibits any discharge <5.0 pH units
  - But, pH $\leq$ 2.0 pH units is "hazardous waste"
- No Federal EPA Upper pH limit
  - But, pH $\geq$ 12.5 pH units is "hazardous waste"
- pH sample must be analyzed "immediately" (within 15 minutes of collection)
- NPDES permits issued to cities in North Carolina have 6.0-9.0 pH limits

pH ANALYSES

- When calibrating a pH meter:
  - Always use fresh buffer
  - Use buffers that "bracket" the sample value(s)
  - Rinse/dry pH probe each time it is taken out of one buffer and placed into another
  - Use 2 buffers to calibrate and a third as a "QC Check"
    - Calibrate meter with 4.0 buffer and 10.0 buffer
    - Run 7.0 buffer as "QC Check"
      - 7.0 buffer should read within 0.1 pH units [6.90-7.10]

WASTEWATER ANALYSES: Total Suspended Solids

- "Non-Filterable Residue"
- Domestic Concentration ~200-250 mg/l
- Industrial TSS range: 300-10,000^{+} mg/l
  - Many cities have TSS surcharge program
- Holding Time: 7 Days
- Most NPDES permits issued to WWTPs in North Carolina have 30 mg/l limit

WASTEWATER ANALYSES: Biochemical Oxygen Demand

- "Biological test" that measures amount of oxygen required to "break down" organic matter in sample
  - BOD is a "measurement" not a specific "pollutant"
- Domestic Concentration: ~200-250 mg/l
- Industrial BOD range: 300-10,000^{+} mg/l
  - Many cities have BOD surcharge program
- Takes 5 Days to Complete BOD test
- Holding Time: 48 hours
- Some NC NPDES permits have BOD limits of 4 mg/l
- Some PT Programs have specific BOD limits for SIUs

WASTEWATER ANALYSES: Chemical Oxygen Demand [COD]

- "Chemical test" that measures the oxygen-consuming capacity of organic/inorganic matter
  - Can rapidly [3-4 hours] "estimate" BOD
  - Based on *chemical oxidation* of the sample
  - COD results should be higher than BOD
    - BOD-to-COD ratios can be developed for specific samples by running parallel tests
  - COD can measure "strength" of wastes that are "toxic" in BOD test (biological test)
    - Some cities surcharge COD if COD is >3X BOD
  - 28 Day Holding Time

WASTEWATER ANALYSES: Nitrogen

- In wastewater, nitrogen occurs in four forms:
  - Organic Nitrogen, Ammonia [NH_3-N], Nitrate [NO_3], Nitrite [NO_2]
- All forms can be converted to other forms biologically
  - Different analytical test for each "form"
- "Total nitrogen" [TN] is sum of organic nitrogen, ammonia, nitrate and nitrite
  - TN of domestic wastewater is 20 to 85 mg/L
  - Some North Carolina WWTPs have TN limits of 5.5 mg/l
    - If they discharge to "Nutrient Sensitive Waters"

WASTEWATER ANALYSES: Ammonia-Nitrogen [NH_3-N]

- Ammonia is present naturally in surface and wastewaters
- Typical Ammonia Concentrations in wastewater
  - Domestic wastewater = ~20-40 mg/l
  - Industrial Wastewater = 30-1000 mg/l
- Holding Time 28 days
- Most WWTPs in North Carolina have ammonia limits, some as low as 1.0 mg/l
  - Very sensitive biological treatment process required to remove ammonia [nitrification]

WASTEWATER ANALYSES: Phosphorus

- Total phosphorus [TP] is the amount of all the phosphorus present, regardless of the form
  - Phosphorus can be present as orthophosphate, polyphosphate and organic phosphate.
- Too much phosphorus in surface waters can lead to overgrowth of algae
  - Some North Carolina WWTPs have TP limits if they discharge to "Nutrient Sensitive Waters" with some NPDES Limits as low as 0.5 mg/l
- Domestic TP concentration:~5-9 mg/l
  - From automatic dishwashing detergents, people waste
- Industrial TP concentration: 10-500 mg/l
  - Some cities surcharge for phosphorus

WASTEWATER ANALYSES: Fats, Oil and Grease [FOG]

- FOG can enter the WWTP as discrete floatable particles, as emulsified material or a solution
  - Composed of gasoline, heavy fuel, lubricating oil, asphalt, soaps, fats or waxes
  - FOG can cause treatment problems at WWTPs
- Can cause Sanitary Sewer Overflows by coating/clogging sewer lines
- Some cities have IU discharge limits on petroleum O&G and/or animal/food derived O&G
  - Limits range from 100 mg/l to 300 mg/l

WASTEWATER ANALYSES: Metals

- Metals can be toxic to biological processes at WWTP and/or in the receiving streams
- Methods of Analysis:
  - Flame Atomic Absorption, Graphite Furnace Atomic Absorption, ICP [Inductively Coupled Plasma]
  - Choose method based on detection limit & cost
- Holding Time: 6 months! [except mercury]
- North Carolina has established water quality standards/action levels for many metals…limits in some WWTP NPDES permits
  - *Some limits more stringent than drinking water limits!!!*

REGULATED METALS OF CONCERN

Pollutant	SLUDGE REGS**		
Arsenic	LA	IN	SD
Beryllium		IN	
Cadmium	LA	IN	
Chromium		IN	SD
Copper	LA		
Lead	LA	IN	
Mercury	LA	IN	
Molybdenum	LA		
Nickel	LA	IN	SD
Selenium	LA		
Zinc	LA		

**LA = Land Application IN = Incineration SD= Surface Disposal

ORGANICS

- Part of EPA "Priority Pollutant" List
- EPA Method 624.1 ["Volatiles]
  - Benzene, chloroform, methylene chloride, carbon tetrachloride, trichloroethane, dichlorobenzenes, etc.
  - Must be Grab sample [40 ml Vial] with no air bubbles
- EPA Method 625.1 [Semi-Volatiles]
  - Phthalates, phenols, naphthalene, pyrene, fluorene, chrysene, anthracene, acenapthylene, etc.
  - Can be grab or composite sample
- "Detection"
  - Detection limits vary for different parameters

6. DATA ANALYSIS AND INTERPRETATION

Signs and Sources of Trouble in Laboratory Land…….

Units of Measure

How to Avoid Trouble

Data Review/Analysis

Did You Calculate Correctly?

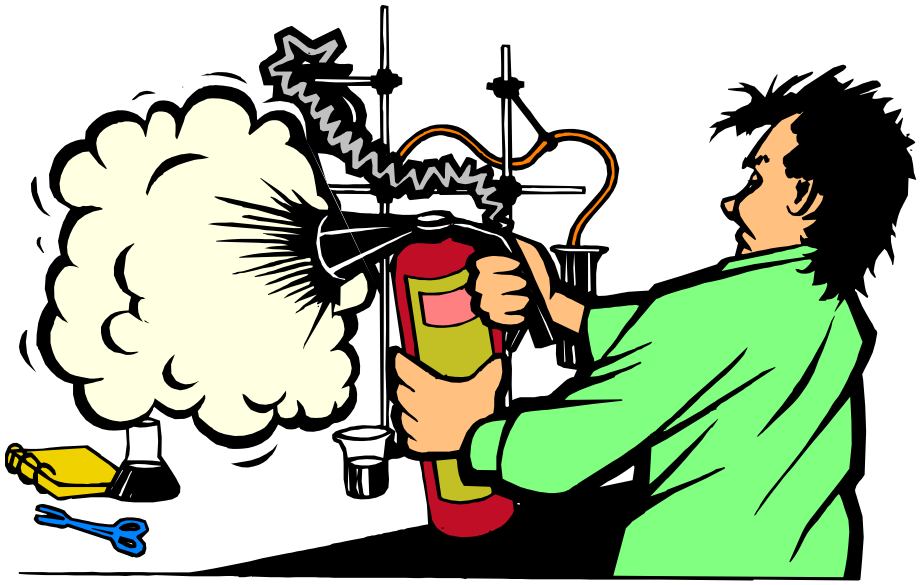
"Sampling Troubles"

Results of a $35 Lab Analysis Have the Potential to:

- Result in a civil penalty of $25,000 for an Industry in Significant Noncompliance with SIU Permit; OR….
- Cost an Industry $10,000+ per month in surcharges for high strength waste; OR…..
- Be used as the basis for the design and construction of a multi-million $$$ pretreatment system for an industry

SIGNS OF TROUBLE IN LABORATORY LAND……

- "Double" Numbers
- COD vs. BOD
- Lots of > Values
- Metals, Metals Everywhere???
- Clerical/Decimal Errors



SOURCES OF TROUBLE: Units of Measure

- Environmental analytical laboratory results are usually expressed in the units of parts per million [ppm], parts per billion [ppb] or parts per trillion [ppt]
- Different meanings depending on matrix
  - With Liquids, the units are mass/volume
  - With Solids, the units are mass/mass

SOURCES OF TROUBLE: Units of Measure

Units are often interchanged based on assumption that density of water is 1.000 g/ml (1.000 kg/l)

Unit	Liquids	Solids
ppm (parts per million)	mg/l (milligrams per liter)	mg/kg (milligrams per kilogram)
ppb (parts per billion)	µg/l (micrograms per liter)	µg/kg (micrograms per kilogram)
ppt (parts per trillion)	ng/l (nanograms per liter)	ng/kg (nanograms per kilogram)

SOURCES OF TROUBLE: Units of Measure

mg/l = ppm [milligrams per liter=parts per million]

µg/l = ppb [micrograms per liter=parts per billion]

ng/l = ppt [nanograms per liter=parts per trillion]

mg/l [ppm] =	µg/l [ppb] =	ng/l [ppt]
1.0 mg/l =	1000 µg/l =	1,000,000 ng/l
0.010 mg/l =	10 µg/l =	10,000 ng/l
0.000012 mg/l* =	0.012 µg/l * =	12 ng/l*

*North Carolina Mercury Stream Standard

PPM and PPB IN EVERYDAY UNITS OF MEASURE

- 1% = 10,000 parts per million
- 1 part per million [mg/l] =
  1 inch in 16 miles
- 1 part per billion [ug/l] =
  1 inch in 16,000 miles
- 1 part per trillion [ng/l] =
  1 inch in 16,000,000 miles

HOW TO AVOID TROUBLE…

- Do your Laboratory Homework
  - Provide copy of SIU Limits page to Lab
- Develop/Maintain Good Relationship with Lab
- Ask other SIUs about Lab Before You Use It
- Have Lab Report Data to you in Required Units (i.e. metals and cyanide in ug/l)
- Sample Early in Reporting Period!
  - Determine lab turn-around time…in time for report to POTW…in time for re-run if problems??
- SIU Can Control What Outside Lab You Use… Get Your Needs Met!

DATA REVIEW/ANALYSIS

- Review Your Data Carefully
- Review Your Data Early
  - If there are problems you may be able to have the sample reanalyzed
- Remember: Your sample is just a sample "number" to the bench chemist
- You do NOT have to be a chemist or know how to run the test to know that the result is wrong!
  - Don't be afraid to ask you lab about a questionable #
- What Are the Odds????

"Who Am I to Question the Lab Data? They are Chemists….I'm not."

You DO NOT have to be a chemist or know how to do the analysis to know there is something wrong with the data…

You just have to KNOW your data…

"The Troubles You'll See…"

Biosolids [Sludge] Analyses

Month	Molybdenum	Month	Molybdenum
2-02	9.6 mg/kg	9-02	17.6 mg/kg
3-02	13.4 mg/kg	10-02	19.1 mg/kg
4-02	15.6 mg/kg	11-02	15.3 mg/kg
5-02	16.9 mg/kg	12-02	11.9 mg/kg
6-02	15.2 mg/kg	1-03	1110 mg/kg*
7-02	24.4 mg/kg	2-03	12.4 mg/kg
8-02	27.9 mg/kg	*What are the odds????*	

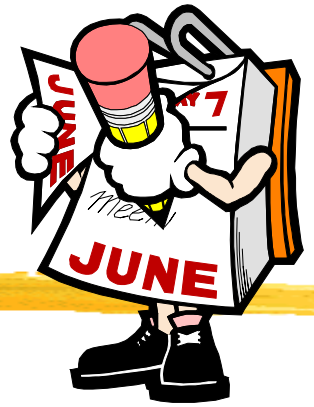
*Calculation Error-Actual Value was 11.1 mg/kg

Note: 40 CFR Part 503 Ceiling Limit is 75 mg/kg

BIOSOLIDS ANALYSES FOR 503 SLUDGE REPORT

Metal [mg/kg dry weight]	**Feb 2006**	**March 2006**	**April 2006**	**May 2006**	**503 ↑ Quality Limit**	**May 2006 Recalc**
Arsenic	5.18	4.19	4.20	33.6	**41**	5.90
Beryllium	<1.80	<0.95	<0.93	<5.14	**No limit**	<0.90
Cadmium	3.63	4.36	2.7	13.7	**39**	2.4
Chromium	106	112	80.8	450	**No limit**	79.2
Copper	305	364	319	1400	**1500**	246
Lead	37.0	25.5	23.4	135	**300**	23.6
Mercury	0.755	1.70	1.56	7.39	**17**	1.30
Molybdenum	11.7	14.5	16.7	84.5	**75**	14.9
Nickel	40.3	38.5	39.3	129	**420**	22.6
Selenium	4.6	6.8	8.01	31.9	**100**	5.61
Zinc	642	657	494	2700	**2800**	481

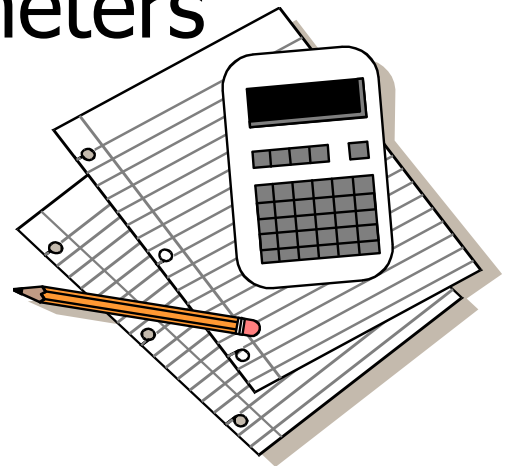
PERMIT LIMIT CALCULATIONS



- Daily Average
  - Arithmetic average of all samples taken during that calendar day [however defined by your facility]
- Weekly Average
  - Arithmetic average of all samples taken from Sunday through Saturday [one sample can be an "average"]
- Monthly Average
  - Arithmetic average of all samples taken during a calendar month [one sample can be an "average"]
- Quarterly Average
  - Arithmetic average of all samples taken in a calendar quarter [one sample can be an "average"]

DID YOU CALCULATE THE REPORT VALUE CORRECTLY?

- Arithmetic Mean for Most Parameters
  - Less Than (<) Values
    - Some cities use "Zero"
    - Some cities use ½ detection limit
  - Greater Than (>) Values
    - Most cities use the value and/or require resample
  - What Happens If Your Laboratory Detection Limit is Greater than Your Permit Limits?
    - XXXXXXXXX



SAMPLING TROUBLES: Chain of Custody [COC]

- Make sure Chain of Custody is completely and accurately filled out
- Problems We've Seen
  - No address of Facility
  - No *exact* sampling location, e.g. "Effluent"
  - Name of Person collecting sample not recorded
  - Type of Sample Taken not recorded
  - Composite Times not recorded
- Permittee is Responsible for proper COC even if you have hired commercial lab to do sampling

SAMPLING TROUBLES: "Split Samples"

- Most cities do not allow "Split Sample" to count as one of <u>your</u> compliance samples
- Some cities do not allow SIU Sample to be Taken on Same Calendar Day that POTW is Sampling
- If you split sample with City and have it analyzed you MUST submit data to City
  - Data from the split samples will be averaged per EPA policy (if both samples meet all QA/QC criteria)

SAMPLING TROUBLES: Noncompliance Resampling

- Noncompliance with Permit Limits
  - You MUST Resample and submit a results within 30 Days of becoming aware of violation [per EPA]
    - Only have to resample for noncompliant parameter(s)
  - City is not responsible for notifying you about your own self-monitoring data
    - If you receive data from your commercial laboratory and it is noncompliant, then you need to resample *immediately.*
  - City will contact you about "City Data"
  - Failure to complete resampling within 30 days will result in another Notice of Violation

SAMPLING TROUBLES: Additional Monitoring

- City may require additional monitoring with written notification
  - Noncompliance with limits
  - New pollutant(s) of concern
- If SIU monitors more frequently than permit requires at permitted sampling location and uses an approved analytical methods, *ALL data must be submitted*
  - SIU cannot pick and choose data!

SAMPLING TROUBLES: "The Dog Ate My Homework…"

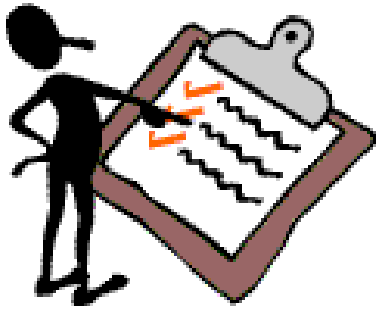
- "The guy who knew about the permit died.."
- "Nobody told me I had a permit…"
- "Nobody told me I had to collect samples.."
- "Production never tells me before they dump a tank…so I couldn't get a sample"
- "Production never tells me about production changes…so I didn't know they were running again…."
- "I hired that lab to do all that and they didn't…"

7. REPORTING AND RECORD KEEPING

Self-Monitoring Reporting

- Certification Statement
- Report Submittal

Record Keeping



Signatory Requirements

- All reports and information submitted for an SIU permit must be signed and certified by "Signatory Official"

- All data including resampling data must be signed and certified by the signatory official

Required EPA Certification/ Signatory Statement

"I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, *true, accurate and complete.* I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations."

REPORTING:

- What to Submit?
  - Different in each City…look at your permit:
    - Copy of Chain of Custody, Flow Records/Charts, Copy of All Laboratory Reports, Compliance Statement [i.e. # violations recorded], Calculations for mass or production based limits
- Submit letter if "No Discharge" during whole reporting period and thus, no samples taken
- When and How to Submit?
  - Postmarked By or Received By? Due on Holiday?
  - Hand Delivered, Faxed, Emailed, Snail Mailed?

RECORD KEEPING

- Important that SIUs keep well-maintained, organized, and accurate records to demonstrate to regulatory agencies that their facility is meeting all of the permit conditions, requirements and limitations.
- Maintain all records for at least 3 years
  - Longer if enforcement action is on-going

QUESTIONS?