Pretreatment Conference – Colorado River Basin

Sampling & Monitoring

Proper sample technique is critical for good analysis results. Trash in = Trash out.

January 2009

Purpose of sampling

- Determine impact of industrial waste on POTW
- Verify compliance with limits
- Verify the quality of self-monitoring data
- Support enforcement
- Support local limit development
- Verify sampling location specified in permit is adequate
- Support permit development
- Determine user fees

Sampling Plan – Standard Operating Procedures (SOP)

- Type of sample (grab vs. composite)
- Sample location
- Order of sampling
- Type of flow measurement
- Parameter for analysis
- Sample volume
- Sample containers
- Preservation techniques
- Sample identification procedures
- Packaging and shipping
- Safety concerns
- Hazardous waste
- Chain-of-custody
- QA/QC procedures

Sample Collection Method

- Specify collection method.
  - Grab sample
  - Composite sample
    - Time proportional
    - Flow proportional
- Specify sampling period (e.g. 24-hour, 8-hour)
- Specify minimum number of aliquots
- Specify minimum number of grab samples
- Need to match sewer use ordinance requirements

Grab Samples

- **Taken from a wastestream on a one-time basis without consideration of the flow rate of the wastestream and without consideration of time**
  - **Permit Limits that have instantaneous maximum concentration limits. *Checking for extreme conditions.***
  - **Must be used to monitor certain pollutants (e.g., pH, volatile organics, cyanide) –Why?**
    - **Allow compositing of grab samples? (Pros/Cons).**
  - **On a case-by-case basis – may be used for monitoring batch discharges**

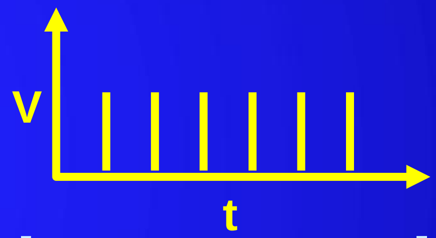
Grabs: do NOT skim surface or drag bottom of wastewater stream

Composite Samples

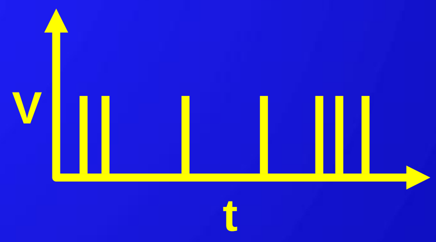
- **<u>Composite</u>: Sample composed of two or more discrete aliquots. The aggregate sample will reflect the average water quality over the sample period.**
  - **More representative measure of the discharge of pollutants over a given period of time**
  - **Accounts for variability in pollutant concentration and discharge flow rate**
  - **May be sequential discrete samples or a single combined sample**
    - **24 hr Time Discrete sample example: 24 bottles with 4 samples collected every 15 minutes in each bottle.**

Types of Composite Samples

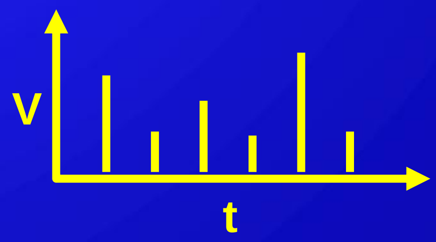
- **Composite Sample is defined by the time interval between aliquots, and the volume of each aliquot (t, V).**
  - **<u>Time Proportional</u> (t_c, V_c): Interval time and sample volume are constant**



  - **<u>Flow Proportional</u>: Interval time <u>or</u> sample volume may vary**
    - **Constant volume (t_v, V_c)**



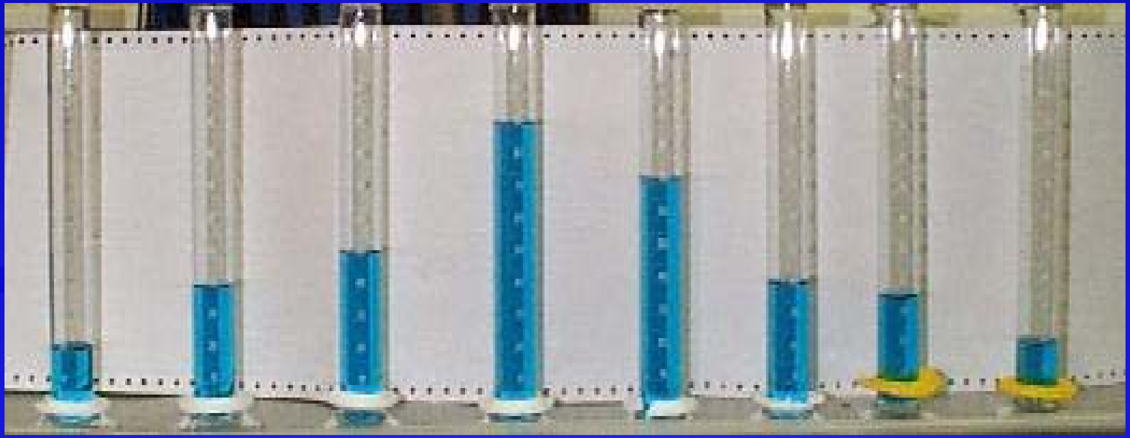
    - **Constant time (t_c, V_v)**

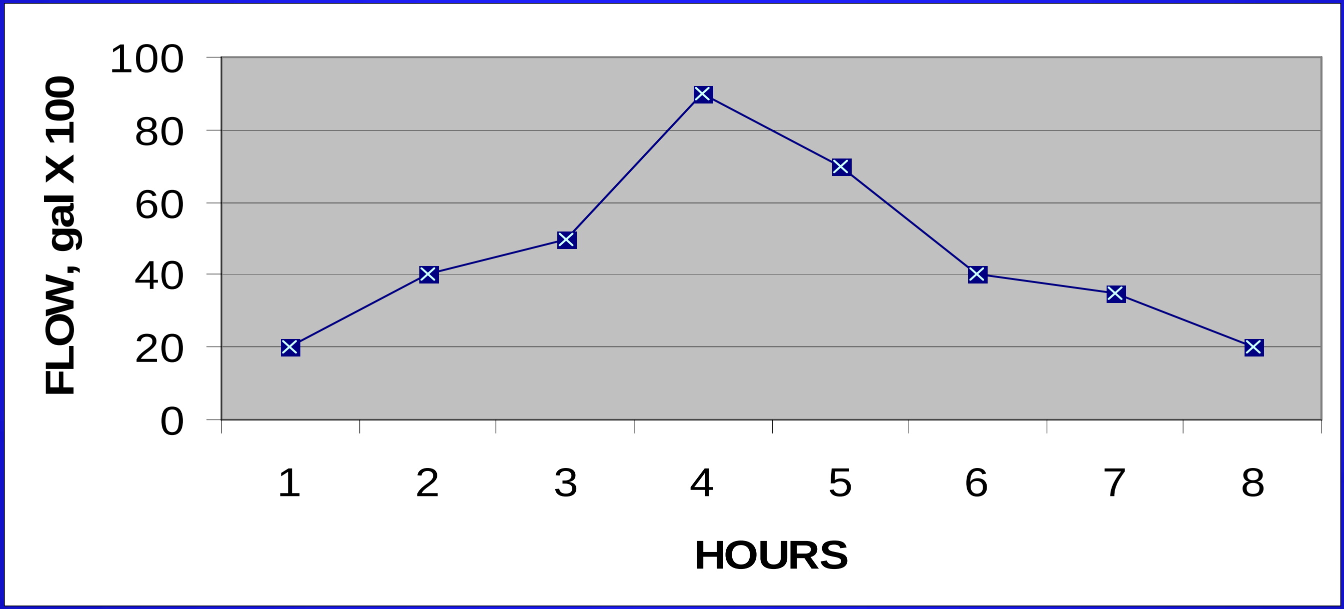


Flow Proportional Composite Set-up

- Joe’s Chicken Factory discharges 24,000 gallons per day over a 24 hour period
- Frequency of sample: every 300 gallons.
- Number of samples: 80
- Volume per sample: 120 mls. {this would provide 9,600 mls (9.6 liters) for the composite sample.}

Determine sample frequency and sample volume that will provide representative sample.

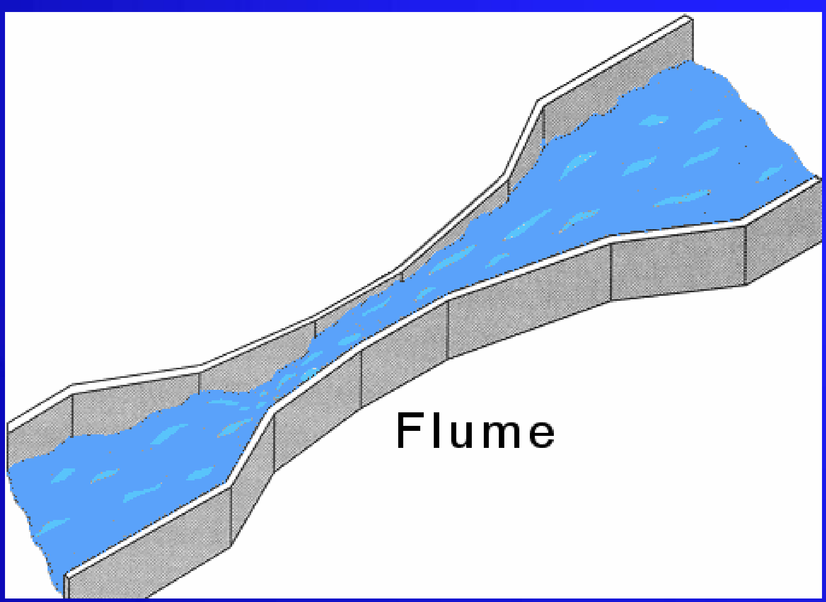


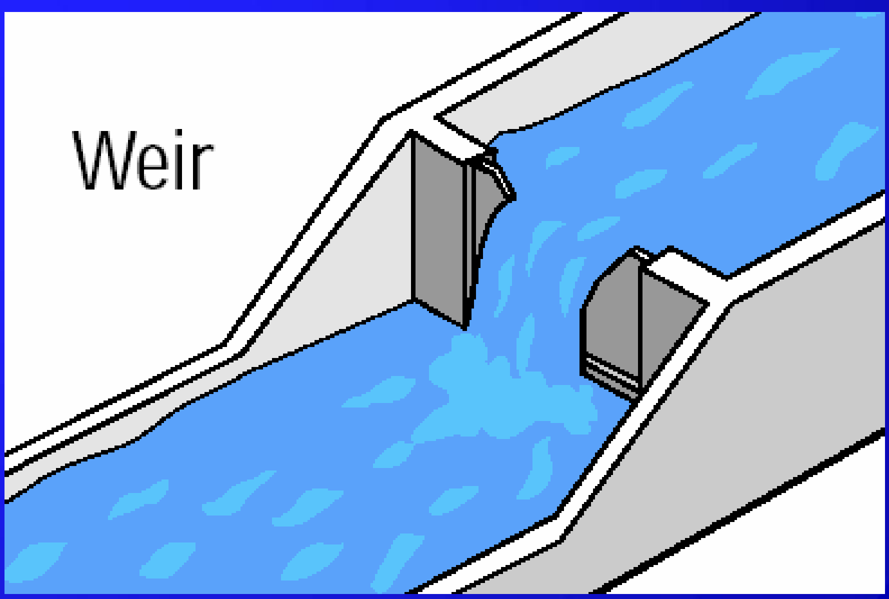


If an eight bottle discrete based sample was collected (one bottle per hour), a flow proportional sample could be prepared by using hourly flow data

Flow Measurement - Primary Devices

- Weirs and flumes are the most common primary flow measurement devices.
- These devices are hydraulic structures, installed in the flow stream, which create a geometric relationship between flowrate and depth of flow.





Flow Measurement - Secondary Devices

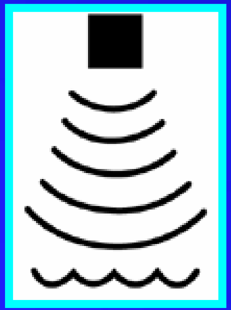
Typical secondary devices:

- measure level
- convert level to flow rate
- display data

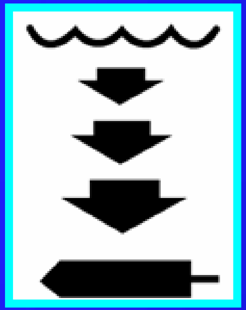
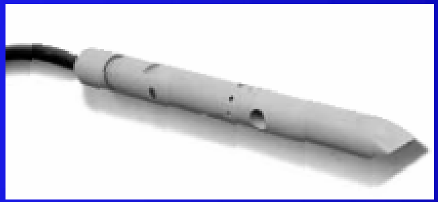
Level/Depth Measurement

Three most common technologies utilized are:

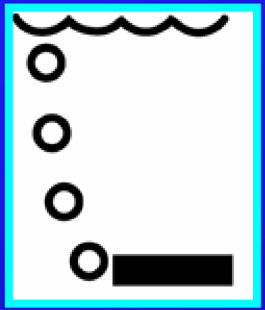
1. Ultrasonic - the sensor transmits high frequency pulses which hit the surface of the liquid and return to the sensor. The electronics measure the time it takes the sound to return




2. Pressure Transducer - water pressure is sensed by mechanical elements in the sensor which converts the pressure to a voltage

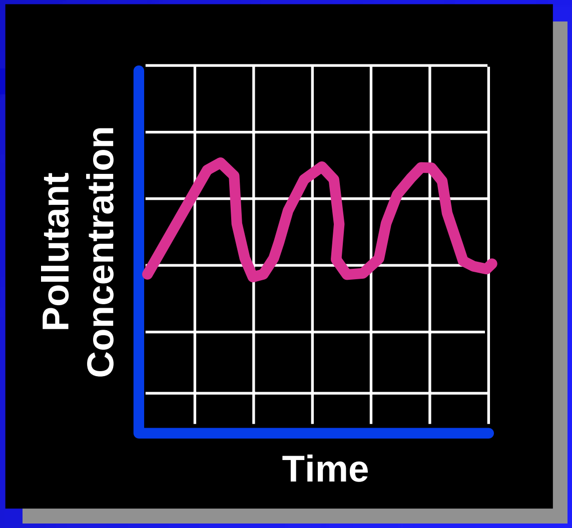
3. Bubbler - A constant flow of bubbles are continuously pushed through a small tube in the flow stream and the backpressure changes in proportion to the liquid level in the flow stream

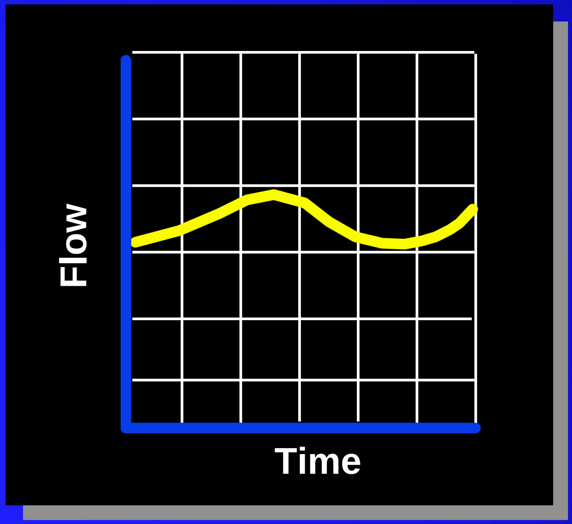



Continuous Sample

- **Continuous Sample: Automated collection and analysis of a parameter in a discharge**
  - **Typically used for pH and flow**
  - **Permit should define the conditions for a violation, significant noncompliance, etc...**

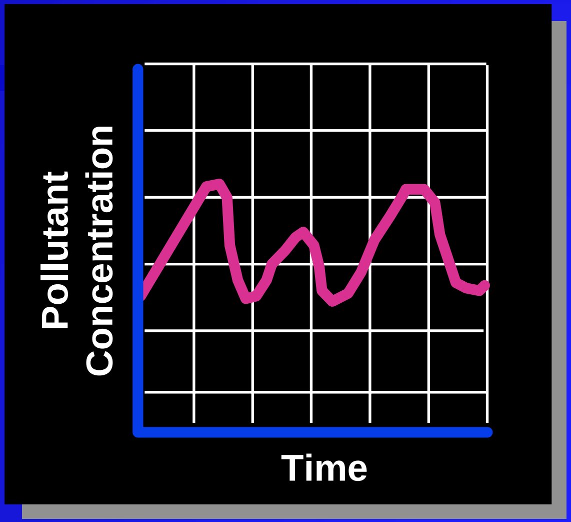
Example Situation – Case #1

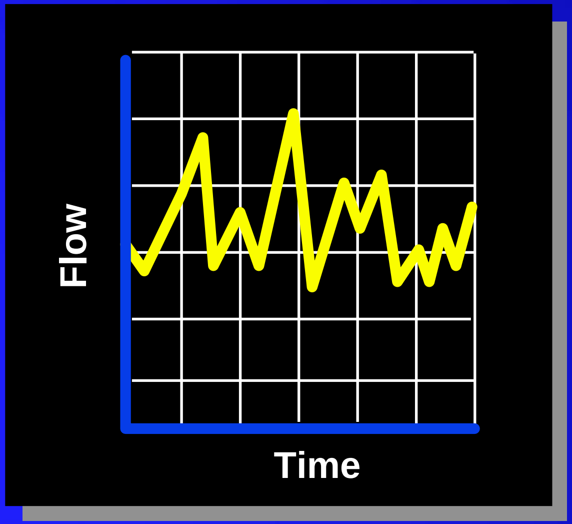




- Regular fluctuations in pollutant loading over the course of the day
- Very slight fluctuations in flow
- Recommendation: Time Proportional Composite

Example Situation – Case #2

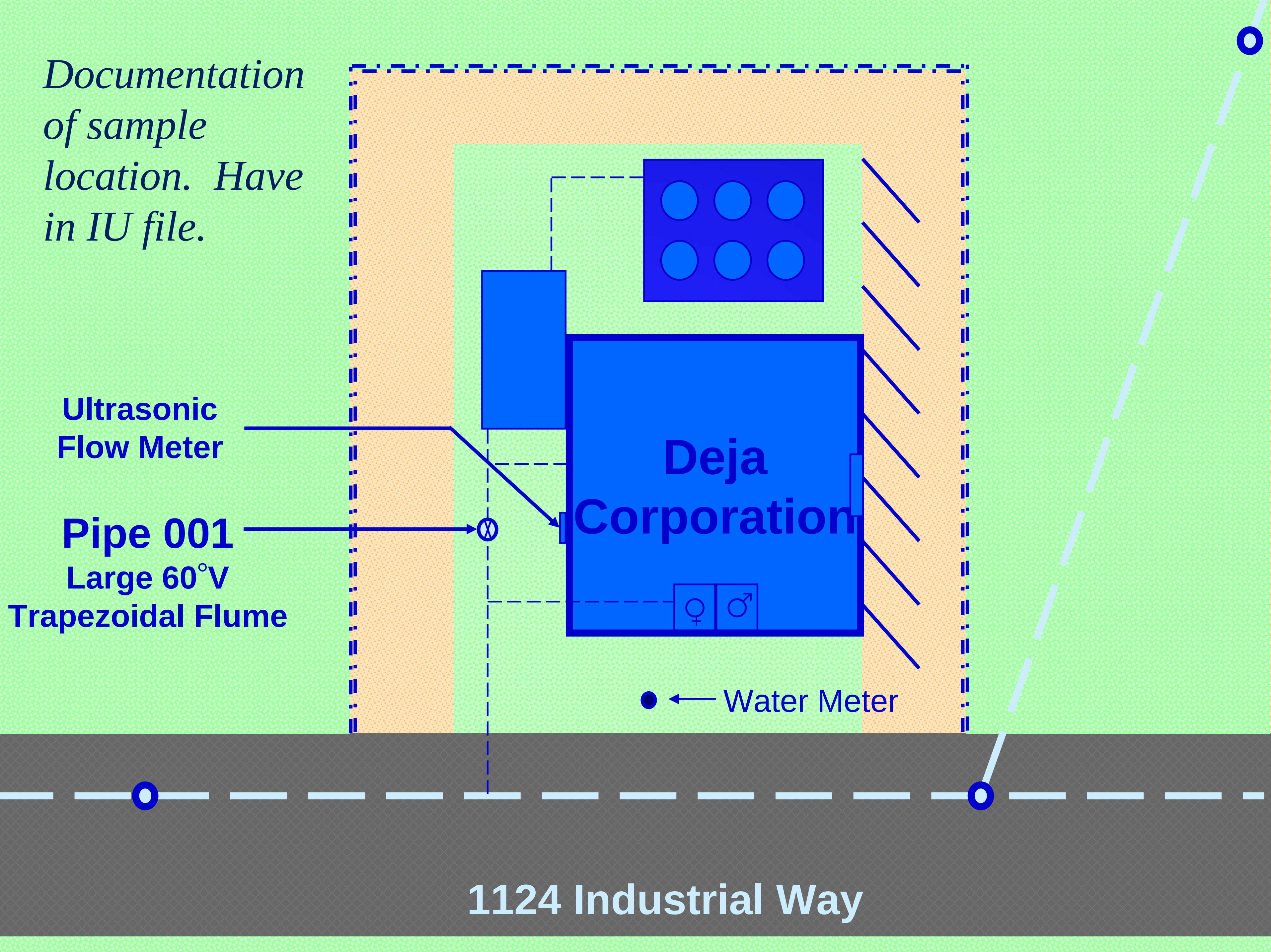




- **Irregular fluctuations in pollutant loading over the course of the day**
- **Erratic fluctuations in flow**
- **Recommendation: Flow Proportional Composite**

Sampling Location

- Must coincide with the point(s) at which the effluent limits apply
- Must produce a sample "representative" of the nature and volume of the industrial user's effluent
- Must be safe, convenient, and accessible to industrial user and Control Authority personnel.
- Make sure industry and POTW are sampling at proper sample location.
- Recommend photograph, provide diagram in file



Documentation of sample location. Have in IU file.
Ultrasonic Flow Meter
Pipe 001
Large 60°V Trapezoidal Flume
Deja Corporation
Water Meter
1124 Industrial Way

Field Considerations

- Field Log Book – Bound w/ hardback cover. Got to have it, record all field readings, times, dates.
- pH meter calibration- fresh buffers of 4, 7, and 10 std. units, calibrate daily, DI water to rinse probe thoroughly, prevent carryover to sample.
- Other equipment for indicator: Conductivity meter - related to TDS and salinity, can correlate with metals.

Pollutant Types

- Conventional – compatible w/ POTW or POTW designed to treat
  - BOD5, TSS, O&G, Fecal or Total Coliform, Ammonia
- Non-conventional – POTW not designed to remove, but incidental removal can occur
  - Metals, organics, cyanide, phenols

Know what you are sampling, info on pollutant and basis for analysis so you can properly collect sample and interpret data.

BOD (type?), Solids (type?)

BOD5, CBOD5, NOD

Total Solids,
Total Suspended Solids,
Total Dissolved Solids

TSS sample and Temp example*

Analysis Variation

- Ammonia
  - Seasonal variation in domestic sewage
    - Domestic sewage: Higher in summer, lower in winter
  - POTW designed to treat ammonia?
  - > anaerobic conditions then > ammonia (Denitrification)
- TKN
  - Ammonia plus Organic N
  - Interferences in analysis? Nitrates >10 mg/L

Wet Chemistry

- Total Phenols
  - Can be high at landfills. (see pollutant sources handout)
  - Interferences primarily sulfide and color, as with most wet chemistry analysis
- Cyanide
  - Check if chlorine present; then add ascorbic acid and then NaOH
  - Low level detection (< 0.10 mg/L) can have interferences

Metals

Inductively Coupled Plasma (ICP)

Total vs Dissolved
Preserve with Nitric Acid
Watch for sampling interferences (tobacco use)
Zn and Cu can be high in domestic background samples

Organics

- Two (2) major groups
  - Semi-volatile (SVOCs) and Volatile (VOCs)
  - Semi-volatiles have two other broad categories:
    - Acid Extractables (phenol species)
    - Base Neutrals (phthalates, naphthalene, etc...)

Why do you use glass container to collect SVOCs?

GC/MS

Volatile Organic Compounds (VOCs)

- Special vials (normally two 40 ml vials)
- No air bubbles (zero headspace) in samples. Why?
- VOCs, as name implies, can change; sometimes rapidly.
- VOC Case Scenario – chloroform
  - The industry may not list a specific pollutant on their BMR, however by-products and break down of some other organics can form particular pollutants.

Quality ensured by

- Proper planning
- Sampler cleaning, clean containers
- Representative samples
- Proper handling and preservation
- Appropriate chain-of-custody and sample identification procedures
- Adequate QA/QC

QA/QC – validate the quality

- Equipment blanks – automatic sampler, some set up sampler to pull DI water for 24 hour period and then pour up for analysis.
- Trip blanks - VOCs
- Duplicate samples – collect two grab samples
- Split samples – one sample poured up in two containers. Note: For a 10 L sample container, recommend to pour up in one gallon container then split sample.

Preventative sampler maintenance

- Pump tubing replacement
- Suction line replacement
- Container replacement
- Diagnostic routines
- Volume calibration

Avoid sampler problems by:

- Always try to keep suction line as short and vertical as you can (do not coil excess tubing around sampler)
- Use fresh, fully charged battery for each set of samples taken
- Change pump tubing and suction line when needed
- Make sure strainer is covered with water and not pulling debris from bottom of channel

QA/QC – protect quality

- Sample from least to most contaminated sampling locations
- Wear gloves
- Do Not use tobacco products while sampling
- Proper preservation
- Do not exceed holding times

What to document

- Cleaning
- Calibration
- Equipment maintenance
- Preservation
- Chain-of-custody
- Date and time of samples
- Ambient field conditions
- Sampling personnel
- Field measurements (pH, temperature)
- Anything unusual that may effect sample (power outage, holding time exceeded).

Corrosion Control Monitoring

- Development & implementation of site-specific corrosion control measures (hydrogen sulfide or other corrosives)
- Monitoring program to evaluate corrosion control measures?
- Communication: work with sewer maintenance sections to identify problem areas.
- Performance measures, and mechanism to include corrosion control program in Information Mgt. System.

H2S – Hydrogen Sulfide

Industrial Corrosion

Industrial User Corrosion

- Corrosion impact may be further downstream than immediate downstream manholes.
  - Example: SIU initially discharges to 400 feet of PVC pipe, but then goes to concrete and iron pipe. Collapsed sewer resulted after 12 years of SIU discharge.
- Work with CCTV personnel to record sewer system impacts below IU's, especially those associated w/ dairy products, bottling operations, use of DI water & cleaners, metal finishers, etc... (scheduled CCTV)

Corrosion

- Hydrogen Sulfide-anaerobic decomposition of sulfate
  - FOG can contribute to sulfide formation in sewer pump stations and in collection system
  - Also, **<u>sulfate</u>** can react with calcium in concrete to form calcium sulfate, which can cause concrete to crack
- Chloride
  - Can cause decay and penetrate coatings
- Chlorine
  - HCl and HOCl can increase rate at which iron and steel corrode
- Nitrates and Nitrites
  - Can contribute to iron and steel corrosion
- Dissolved Salts
  - Electrolytic action on base material can corrode concrete, cement mortar
- Organic Compounds
  - Solvents will promote the dissolution of gaskets and rubber and plastic linings

Krispy Kreme pH adjustment system

Grease Interceptor deterioration, baffle wall collapse, leaking, and corrosion impact to public sewer

Other sources of corrosion

Sewer corrosion below a coffee shop

Food Service Establishments…

***Coffee Shops**

(coffee pH 4.6 to 5.1)

***Bakeries, FSEs with high sugar use**

Industrial Users: Dairy products, colas

Work with Support & Preventive Maintenance Personnel

Food Service Establishment Sampling & Analysis (from 325 FSEs)

- Average pH from Interceptor: 4.9 std. units (range 1.2 to 11.5)
  - Low pH: anaerobic conditions, sugars, cleaners, soft drinks
  - High pH: additives, cleaners, vent hood cleaning (NaOH)
- BOD5 from monthly pumped interceptor with all components can be 500 to 1,000 mg/L. What about facilities that do not have adequate grease control equipment or are not maintaining the equipment?
- O&G from 20 mg/L to 2,500 mg/L. Depends on time of day, type of restaurant, type of grease control equipment, etc...