Sample Handling – Things to Consider

Presented by: Kim Riddell-Furry

Alloway

Introduction

- The most precise and accurate analytical measurements are worthless and even detrimental if performed on a sample that was improperly collected and stored or was contaminated in the process (OEPA, 1978).

Introduction

- Field sampling defined
  - The process of obtaining a representative portion of an environmental matrix suitable for laboratory or field measurement or analysis

The NELAC Institute,

General Requirements for Field Sampling and Measurement

Introduction

- Four factors that affect quality of environmental data
  - Sample Collection
  - Sample Preservation
  - Analyses
  - Data Documentation
- Improper actions in any one area may result in:
  - Poor data
  - Leading to poor judgments

Introduction

Reliable performance begins with the foundation of an established program.

- A written sample-handling plan is essential before initiating any program. It will answer the following:
  - What parameters will be analyzed?
  - Frequency of collection and sample type?
    - Grab
    - Composite
  - What types of bottles?
  - What type of chemical preservation?
  - Is thermo preservation required (ice) ?
  - What is the holding time for each parameter?
  - What will be documented on the Chain of Custody?
  - How will samples be delivered to the laboratory?

Introduction

A sampling plan and the monitoring requirements are based on the permit that is issued.

- NPDES permit
- General permit
- Storm water permit
- Pretreatment permit
- Indirect Discharge Permit

Frequency Definitions

- Required frequency for sampling is typically listed in the permit and should be collected accordingly
  - Daily, Weekly, Monthly, Semi-Annually, or Annually
  - Depending on plant conditions and continuous monitoring, some of the analyses may be required more frequently.
  - ***All Samples taken according to proper protocol must be reported to the respective agency***

Types of Samples: NPDES Frequency Definitions

- **Weekly** sample collection requirements
  - OEPA defined weeks
    - Week 1 – days 1 thru 7
    - Week 2 – days 8 thru 14
    - Week 3 – days 15 thru 21
    - Week 4 – days 22 thru 28

Types of Samples: NPDES Frequency Definitions cont'd

- **Quarterly** (4 times per year)
  - March, June, August, December
- **Semi-annual** (2 times per year)
  - June & December
- **Annual** (1 time per year)
  - September

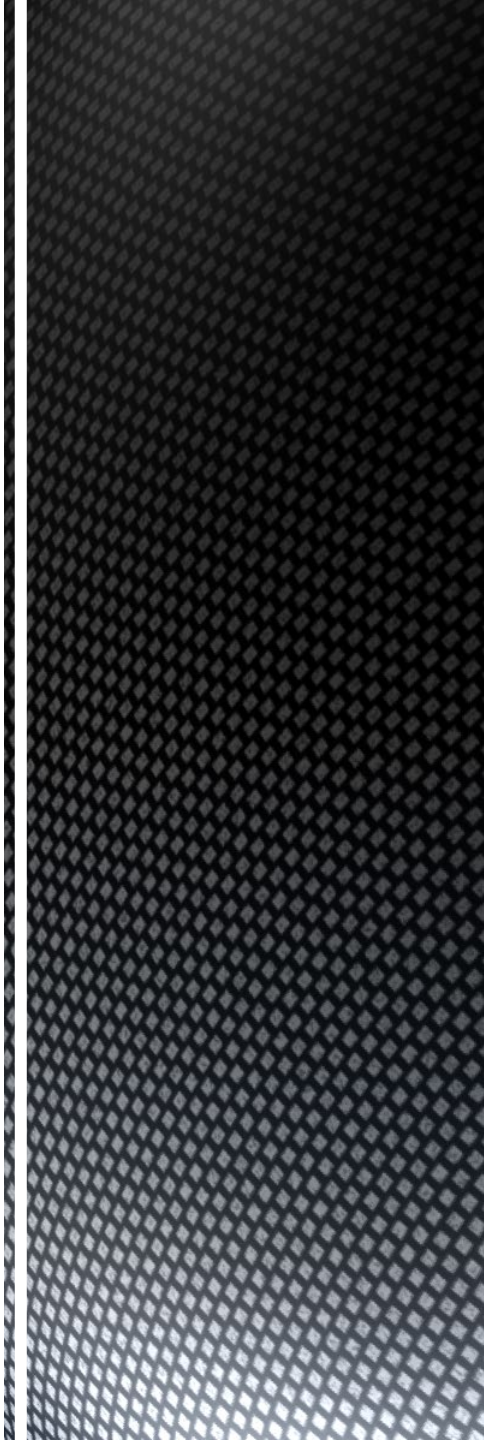
Part I, A. - FINAL EFFLUENT LIMITATIONS AND MONITORING REQUIREMENTS

2. During the period beginning on 12 months from the effective date of the permit and lasting until the expiration date, the permittee is authorized to discharge in accordance with the following limitations and monitoring requirements from the following outfall: 1PD00019001 . See Part II, OTHER REQUIREMENTS, for locations of effluent sampling.

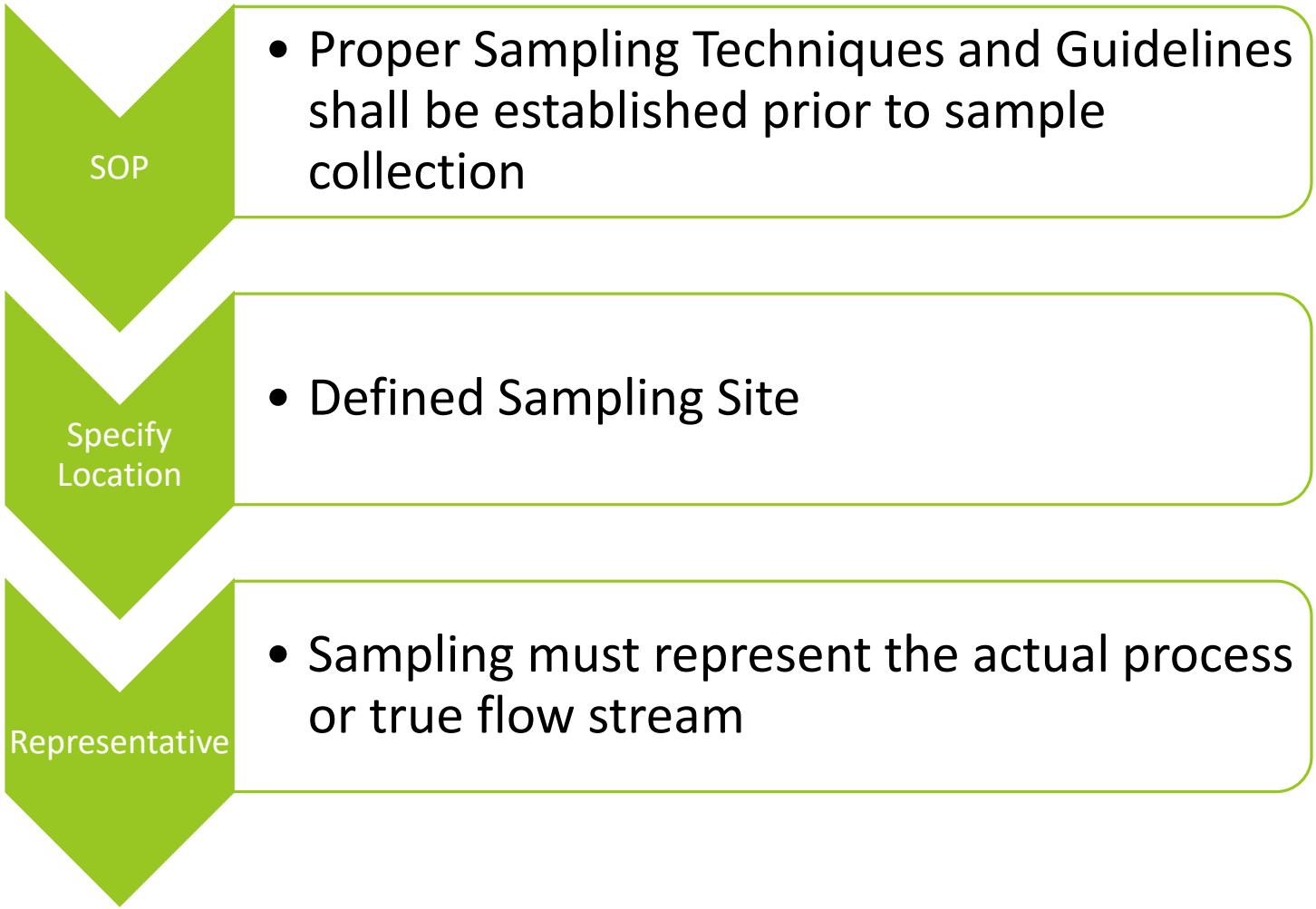
Table - Final Outfall - 001 - Final

Effluent Characteristic	Discharge Limitations							Monitoring Requirements		
	Concentration Specified Units				Loading* kg/day					
Parameter	Maximum	Minimum	Weekly	Monthly	Daily	Weekly	Monthly	Measuring Frequency	Sampling Type	Monitoring Months
00010 - Water Temperature - C	-	-	-	-	-	-	-	Continuous	Maximum Indicating Thermometer	All
00300 - Dissolved Oxygen - mg/l	-	5.0	-	-	-	-	-	1/Day	Continuous	All
00530 - Total Suspended Solids - mg/l	-	-	40	27	-	1060	715	3/Week	24hr Composite	All
00552 - Oil and Grease, Hexane Extr Method - mg/l	10	-	-	-	-	-	-	1 / 2 Weeks	Grab	All
00610 - Nitrogen, Ammonia (NH3) - mg/l	-	-	20	13	-	523	341	3/Week	24hr Composite	Dec. - Feb.
00610 - Nitrogen, Ammonia (NH3) - mg/l	-	-	12	7.8	-	307	204	3/Week	24hr Composite	Mar-May & Oct-Nov
00610 - Nitrogen, Ammonia (NH3) - mg/l	-	-	2.8	1.9	-	74.2	50.3	3/Week	24hr Composite	June - Sep
00625 - Nitrogen Kjeldahl, Total - mg/l	-	-	-	-	-	-	-	1/Month	24hr Composite	All
00630 - Nitrite Plus Nitrate, Total - mg/l	-	-	-	-	-	-	-	1/Month	24hr Composite	All
00665 - Phosphorus, Total (P) - mg/l	-	-	-	-	-	-	-	1/Week	24hr Composite	All
00719 - Cyanide, Free - mg/l	-	-	-	-	-	-	-	1/Quarter	Grab	Quarterly
01074 - Nickel, Total Recoverable - ug/l	-	-	-	-	-	-	-	1/Quarter	24hr Composite	Quarterly
01079 - Silver, Total Recoverable - ug/l	-	-	-	-	-	-	-	1/Quarter	24hr Composite	Quarterly
01094 - Zinc, Total Recoverable - ug/l	-	-	-	-	-	-	-	1/Quarter	24hr Composite	Quarterly
01113 - Cadmium, Total Recoverable - ug/l	-	-	-	-	-	-	-	1/Quarter	24hr Composite	Quarterly
01114 - Lead, Total Recoverable - ug/l	-	-	-	-	-	-	-	1/Quarter	24hr Composite	Quarterly
01118 - Chromium, Total Recoverable - ug/l	-	-	-	-	-	-	-	1/Quarter	24hr Composite	Quarterly
01119 - Copper, Total Recoverable - ug/l	-	-	-	-	-	-	-	1/Quarter	24hr Composite	Quarterly

Sampling Procedure



Sampling Procedure Guidelines



Sampling SOPs

- Documents outlining the procedures used by your facility
- SOPs need to be part of a controlled system
  - Log of all SOPs
  - One current version of each document
  - Revisions issued by QA or designated authority
  - SOPs should be numbered
  - SOPs need issue and revision dates

Defining the Procedures

Why is it Important?

- Ensures consistency from sample collector to sample collector
- Ensures method protocol is being met
- Integrity of sample
  - Minimizes Contamination
  - Holding time requirements
- Provides defensible data

Sampling Guidelines

- Accessibility and safety are also important factors when selecting a sampling site.
  - Do not choose a sample site that is difficult to get to or can result in falls and injuries.
- Flush or purge sample lines for an adequate time period before taking the sample
  - Replace sample lines regularly to avoid the possibility of sediment buildup, which could cause erroneous results.

Sampling Guidelines

- Avoid taking samples at points where solids settling occurs or floating debris is present.
  - These situations occur normally in quiescent areas where the velocity of the flow has decreased.
- Avoid sampling non-representative deposits or solids accumulated on channel or tank walls.

Sampling Guidelines

- Where samples are to be collected from flowing pipes, keep the sample lines as short as possible and with a minimum number of bends
- To ensure that the sample is representative, prevent settling by keeping samples thoroughly mixed throughout the collection and measurement procedure

Sampling Procedure

Eliminate Sample Contamination

- Field Blanks
- Trip Blanks
- Duplicates/Replicates
- Utilize Custody Seals on Sample Containers to Prevent Tampering
- Rinse Grab Samplers a Minimum of 3 times between sample location

Sampling Procedure

- ***ALWAYS CHECK SAMPLING SPECIFICS IN YOUR PERMIT***
- Grab Samples
  - Discreet
    - Collection not to exceed 15 minutes
  - Stormwater - Obtained during the first 30 minutes of a discharge
    - To determine max. concentration of a pollutant
  - Must be conducted for pH, temperature, cyanide, total phenols, residual chlorine, oil & grease, fecal coliform, E. coli

Grab Sampling

- A grab sample is defined as an individual sample collected over a period of time not exceeding 15 minutes
- Grab samples represent only the condition that exists at the time the sample is collected
- Typical grab sampling is required for parameters such as chromium hexavalent, cyanide, oil and grease, pH, total phenols, residual chlorine, bacterial analyses, and volatile organics

Composite Sampling

- Prepared by combining a series of grab samples over known time or flow intervals
- Shows the average composition of flow over a set time or flow period
- Can be collected manually and mixed together
- Can be collected by automatic sampling equipment
- All composite samples should be identified as to the method of sampling collection, duration of composite (e.g. 24 hours), and frequency of the sampling (e.g. every 2 hours)

Composite Sampling

- Twenty-four hour composite samples are to be used in NPDES compliance
- A twenty-four hour composite sample, using a minimum of four grab samples, must be used unless otherwise specified at 40CFR Part 136
- Typical composite sampling is required for parameters such as biochemical oxygen demand (BOD), suspended solids, ammonia, and total phosphorus

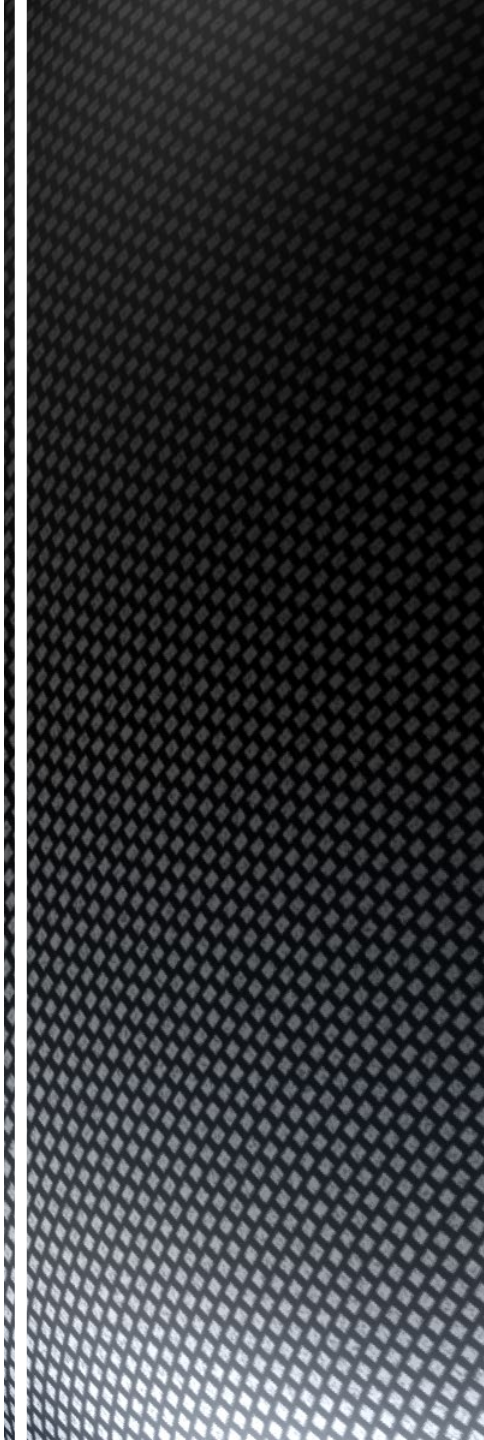
VOC Sampling Guidelines

- Samples collected for the analysis of volatile organic compounds (VOC) should be taken from areas of low turbulence to reduce the amount of entrapped air in the sample.
- VOCs could be driven off to the atmosphere (as outgas) in turbulent sections of the flow stream
- The “no head space” requirement for VOC sample containers, meaning no air space in the container, is important to ensure that all VOCs are kept in solution for proper analysis

Sampling Procedure

- Collect Samples for non-volatiles constituents at points where the sample stream or tank is well mixed
  - One-third the liquid depth from the channel between the point of maximum turbulence and the edge

Sampling Equipment



Sampling Equipment

- The most accurate data on a waste stream would be obtained by collecting and analyzing the entire flow from a discharge point.

Sampling Equipment

Samples Collected Shall Be:

- Representative to the total discharge
- Sufficient volume to represent the source but small enough to be handled in the laboratory
- Collected in accordance to the defined sampling plan
  - Quality of sampling is ensured by trained sampling personnel

Sampling Equipment

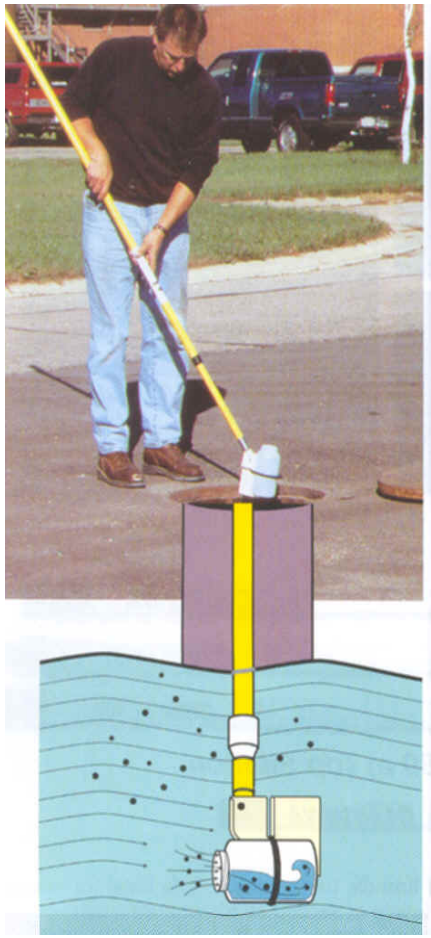
Two types of sampling equipment:

- Manual Collection
- Automatic Collection
  - Uniformity ensures samples collected were consistently and accurately collected
    - Collected by same method
    - From same point
    - Programmed time intervals
  - Reflect the condition in the source

Sampling Equipment

Manual

- Versatile, inexpensive, and simple to use
  - Bottle Samplers
    - Dippers
    - “Jar on a Rope”
    - Swing Samplers®
      - Allows collection at various angles, including 90° (*Nasco*)
    - Weighted Bottle Samplers
      - Glass bottle, weighted sinker, bottle stopper, line to lower and raise the container



Sampling Equipment

Manual

- Sampling equipment shall be kept clean using detergents, acid soaking, and thorough rinsing
- Rinsed with material being sampled before the sample is collected
- Ideally, sampling equipment should be designated and labeled for each location

Sampling Equipment

Automated

- More than 100 different automatic sampling devices available commercially
  - Portable
    - Easily transported to various sites
    - Fit into small sampling structures (i.e. manholes)
  - Refrigerated
    - Accommodate larger composite containers
    - Permanent sampling needs
  - Special
    - Flow-through sampler
      - Dipper mechanism

Sampling Equipment QA/QC

Quality Control for All Field Equipment

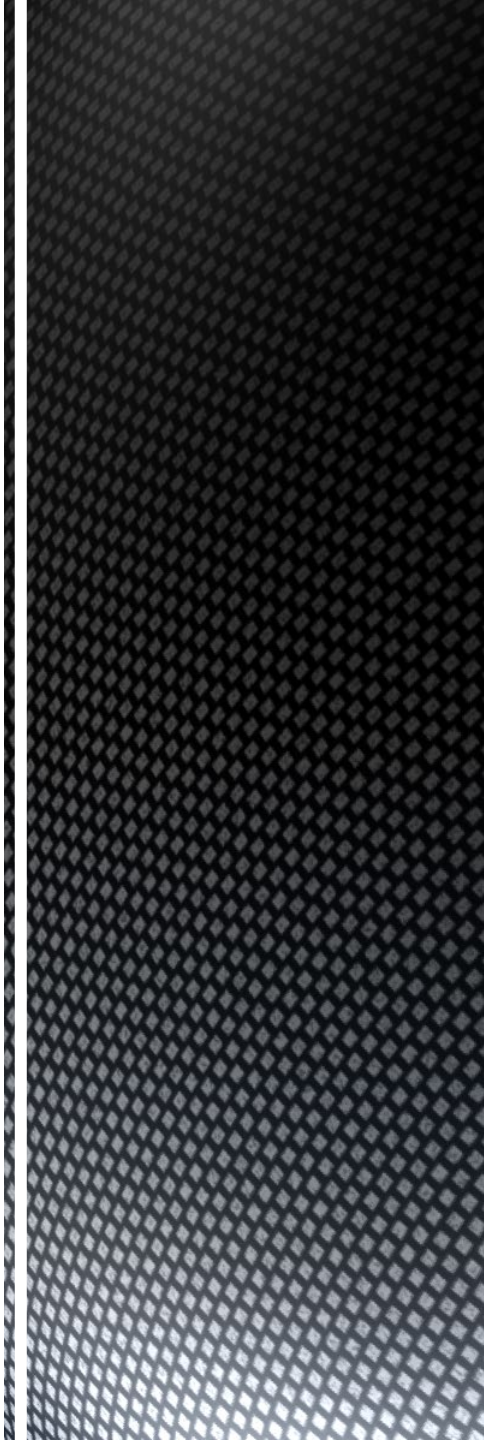
- Field blank
  - Identify and control errors resulting from interferences and contamination
  - Handled in the exact manner as any other environmental sample
  - Identical Sampling devices, sampling protocol, storage containers, shipping procedures, and preservation techniques should be used

Sampling Equipment QA/QC

Develop Format for Field Logbooks

- Date of Calibration
- Quality Control Data
- Sampling Date
- Sampling Location
- Result

Preservation & Containers



Sample Preservation

- Reference 40 CFR 136 *Table II – Required Containers, Preservation Techniques, and Holding Times*
- Complete preservation is impossible
- Minimize the deceleration of the **physical**, **chemical**, and **biological** changes by awareness of nature of changes
  - The effect of one will ultimately have an effect on all!

Sample Preservation

Nature of Changes (Physical):

Physical: Sample Environment has been altered

- **Sampling Equipment**
  - Introduce contaminants from outside
- **Sample Containers**
  - Residue from previous samples
  - Certain cations are subject to adsorption on, or exchange with, cations in the walls of both glass and plastic **containers**
    - Plastic: Al, Cd, Cu, Cr, Fe, Pb, Mn, Zn and Ag
    - Glass: Na, Bo, Si

Sample Preservation

Physical Changes (con't)

- Elevated Temperature
  - Solubilize precipitated material
  - Increase decomposition of organic materials
    - Affect the NO_3, NO_2, NH_3, BOD, Phenol, etc.
- Headspace
  - Zero headspace for volatile organic compounds
  - Microbiological samples should have air space for aeration and mixing

Sample Preservation

- Nature of Changes (Chemical):

  Chemical

  Algae creates photosynthetic activity

  - Affects DO, pH, and various other chemical equilibria

  Metals can precipitate or solubilize, leach from container walls, or be reduced or oxidized

  - Affects the color, odor, or turbidity

Nature of Changes (Biological):

Biological

Temperature

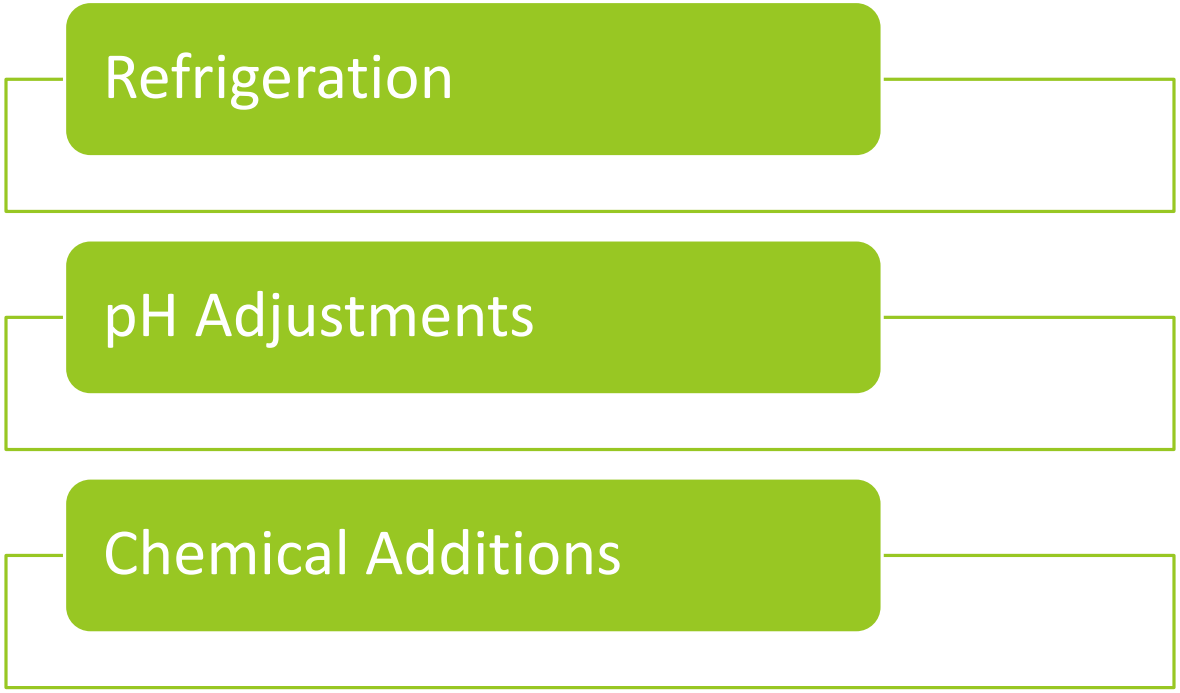
- Decreased
  - Generally retard biological changes (ideal!)
- Increased
  - Changes chemical composition
  - Increased decomposition

Biological Changes (con't)

- Changes in the dissolution of gases
- Consumption of organic material
- Production of cellular matter
- Formation of chemical byproducts (CO_2, NH_3, and H_2O)

Sample Preservation

3 primary methods of preservation:



Sample Preservation

Refrigeration

pH Adjustment

- Decreases biological and chemical activity
  - i.e. H_2SO_4
    - Combined with refrigeration it preserves and pretreats oil & grease
    - Retards bacterial action
      - COD, TOC, etc.

Sample Preservation

- May alter the composition of the original sample
- Avoid adding chemicals that contain elements for which the sample will be analyzed
  - HNO_3 preserved sample shall not be analyzed for nitrogen containing compounds
  - H_2SO_4 preserved sample shall not be analyzed for sulfate

Sample Preservation

- Care shall be taken when dispensing chemicals into sampling containers
  - Dispensing equipment should be designated
- Containers containing preservative should be clearly identified
- Preserve each sample with 15 minutes of collection
  - Ideally, sample container shall be preserved prior to collection

Sample Handling

- Procedures to be developed
  - Transportation
  - Receipt
  - Handling
  - Protection
  - Storage
  - Retention
  - Disposal
- Protects integrity of sample
- Protects interest of client and laboratory

Sample Handling

- Develop procedures to avoid:
  - Sample deterioration
  - Contamination
  - Loss or damage to sample during storage
- Procedures Implemented to:
  - Monitor and document storage conditions
    - Refrigerator temperature
    - Ensure samples stored in designated locations separate from reagents and standards

Sample Storage

- Volatile Organics maintained at 0-6°C and in separate unit than volatile standards
- Semi-Volatile Organics maintained at 0-6°C and in separate unit than semi-volatile standards
- Metals can be stored with or without cooling. Analyst should confirm acid preservation
- BOD, COD, phosphorus, and nitrogen form samples maintained at 0-6°C

Sample Storage

Composite Samples

- Automated samples shall be refrigerated at or below 6°C
- Manual samples shall be preserved with each collection

Sample Hold Times

Composite

- Set of grab samples composited in the field or laboratory
  - Holding time begins at the time the last grab was collected
- Sample collected with an automated sampler
  - Holding time begins at the time the last sample was collected

- Grab
  - Begins at the time of collection

Sample Hold Times

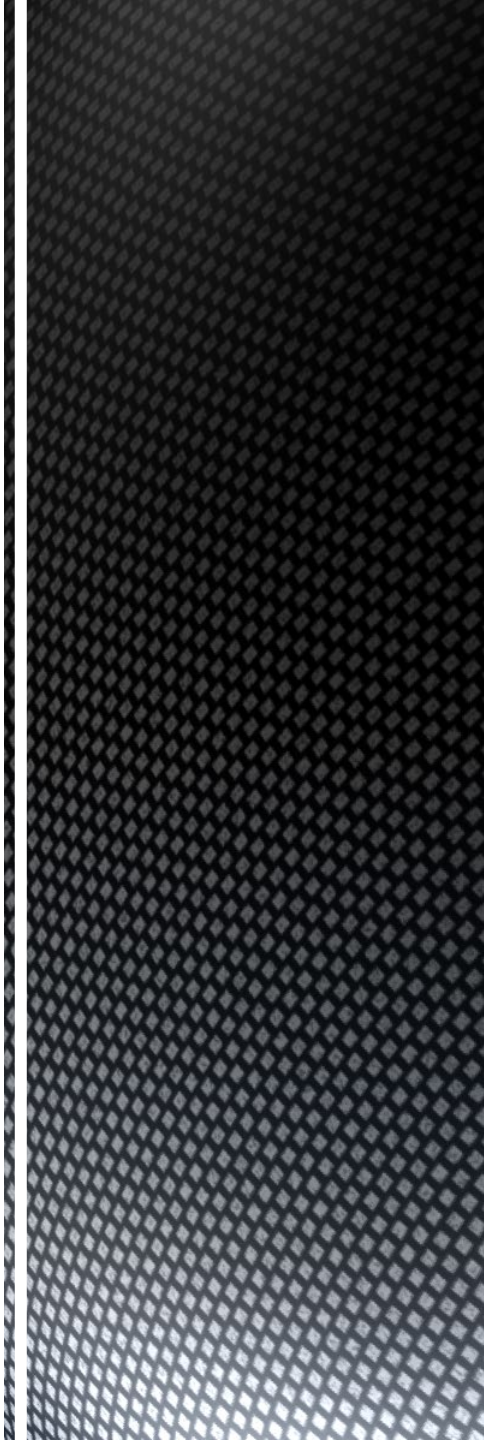
- Sample should be analyzed as soon as possible after collection
- Times listed are the maximum times the samples can be held before the start of analysis and still considered valid
- Term “Analyze Immediately” usually means within 15 minutes or less after sample collection

Sample Handling

- **Specified in 40 CFR 136.3 for NPDES**

Analyte	Bottle Type	pH Preservation	Temp	Holding Time
BOD or CBOD	Plastic or Glass	NONE	Cool, <6˚C	48 Hours
TSS	Plastic or Glass	NONE	Cool, <6˚C	7 days
Metals (Except Hg and Cr^6)	Plastic or Glass	HNO_3 pH < 2	NONE	6 months
NH_3	Plastic or Glass	H_2SO_4 pH < 2	Cool, <6˚C	28 Days
NO_3/NO_2	Plastic or Glass	H_2SO_4 pH < 2	Cool, <6˚C	28 Days

Documentation



Sample Documentation

- Successful implementation depends on capability to produce valid data and to demonstrate such validity
  - Sample identification procedures are needed
  - Chain of custody procedures are needed
- Evidence gathered must be controlled

Sample Documentation – Chain of Custody

- A sample is under custody if:
  - It is in your possession, or
  - It is in your view, after being in your possession, or
  - It was in your possession and then you locked it up to prevent tampering, or
  - It is a designated secure area
- A field sampler is personally responsible for the care and custody of the samples collected until they are transferred

Sample Documentation – Chain of Custody

- Samples that will leave the premises for analysis need a chain of custody
- Samples obtained from locations outside the facility (pretreatment monitoring) need a chain of custody

Sample Documentation – Chain of Custody

Samples obtained from the facility that will be analyzed in the facility's laboratory may not need a chain of custody

- If COC is not used, information must be supplied on controlled document such as a sample receipt log
  - Sample location
  - Date collected
  - Time collected
  - Preservation
  - Person performing collection

Sample Documentation – Chain of Custody

During transfer of possession of samples the involved persons relinquishing and receiving must:

- Sign
- Date
- Note time of transfer on Chain of Custody

Sample Documentation – Chain of Custody

Consider Establishing a Sample Acceptance Policy

- Documentation of sample condition
- Examine shipping containers and sample containers for damage or evidence that samples might be compromised
- Document temperature blanks if supplied
  - Limits generally are from 0 to 6 degrees Celsius
- Procedures established to notify customers or industries of noncompliance issues
- Outline the circumstances which samples are accepted or rejected

Conclusion

- Planning
  - Observe the outfall/discharge
  - Obtain samples first week of month
  - Know the parameters
- Correct sampling procedures
  - Calibration of field equipment
  - Obtain sample appropriately
  - Grab vs. Composite
- Documentation
  - Field Log
  - Chain-of-custody
- Shipping or transportation of samples
  - **Ice**

THANK YOU!

800-436-1243
kim.riddell@alloway.com
www.alloway.com

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