

# **Sampling**

**VT WSMD Wastewater Program Lab Manual Section #5**

## Table of Contents

Sampling.....	2
The Importance of Good Sampling.....	2
Choosing A Sampling Location.....	2
General.....	2
Influent.....	2
Effluent.....	3
Types of Samples.....	4
Grab Samples.....	4
Composite Sample.....	4
Time-Flow Compositing.....	5
Sample Containers.....	6
TABLE I: Summary Chart with Required Containers, Preservation and Holding Times.....	8

## Sampling

### The Importance of Good Sampling

The collection of good, representative samples is probably the most important part of laboratory work and is often the most overlooked part. If the samples are not representative, no amount of care in analysis will produce accurate and precise values. If you do not collect samples properly, the time spent in analysis is wasted. Since the sample is a very small portion of the entire wastestream or basin, it is extremely important to select the sampling point, method, equipment, and time very carefully.

Quality samples are:

- Collected at a representative sampling point
- Stored and/or shipped at the appropriate temperatures (See [Table 1](#))
- Analyzed within the maximum recommended holding times

It cannot be stressed enough - without care in sampling, any values generated are not accurate or precise, leading to the data not being an accurate representation of the plant conditions at time of sampling.

### Choosing A Sampling Location

#### **General**

Again, the choice of a sampling location is an important decision that should be carefully considered. Samples should be taken in the middle of the flow in a well-mixed area. The sample should be taken from the middle depth (do not just skim the surface) to avoid floating wastes, etc. Eddies and backwaters should be avoided because of the settling that takes place there.

#### **Influent**

Influent samples should be taken after the comminutor or bar screen so as to avoid large solids and other such materials. Also avoid areas of settled grit and floating solids or grease because these are not truly representative of the whole stream. Influent samples must be collected at a point above any return flow such as RAS, etc. Leachate and septage must be included in the influent sample. In some cases due to facility design etc. this may be difficult or impossible. Under these conditions the sample must be taken at the source (septage truck, landfill leachate sampling point etc.) Required analyses must be performed on the leachate/septage sample. Using the best means of establishing the flow, the loading from the leachate/septage must be calculated in pounds. This result must be added to the influent results for reporting purposes (an example is included below). Samples must be collected before aerated grit chambers. If the facility has a fine screen grit removal system, the sample may be collected before or after the screen with the understanding that: **if collected downstream of the fine screen the sample collection point can NOT be used as an excuse for failing to meet the 85% removal requirement.**

Example of leachate/septage loading calculation (when it can't be collected in influent sample):

## Sampling

Leachate from a Hazardous Materials site is piped directly to the wastewater facility but enters the system downstream of the influent sampling site. A composite sample is collected at the sample port located at the HazMat site. Flow is determined by the number of times the tank discharges. (500-gallon leachate tank is emptied 5 times over the composite period). The BOD result from the leachate sample yields a result of 250 mg/L

Loading from the leachate is calculated using the pounds formula:

$$Flow (MGD) * BOD \left( \frac{mg}{L} \right) * 8.34 = Pounds (lbs) BOD$$

In our example:

$$0.0025 MGD * 250 \left( \frac{mg}{L} \right) * 8.34 = 5.2125 lbs BOD$$

This result is then added to the calculated influent loading to establish the "total" influent loading.

For example, if the influent loading was calculated to be 1000 lbs, the Total influent loading including the leachate would be 1005.2 lbs.

## Effluent

### BOD, pH and Solids Samples

Generally, it is best to collect effluent samples at the "final" discharge point, after all treatment processes including chlorination and if applicable dechlorination.

### Chlorine Residual Samples

The sample to be analyzed for total chlorine residual must be collected at a point beyond chlorine contact, at the end of the contact tank. If the effluent is dechlorinated before final discharge, the sample must be collected post dechlorination as well as post chlorination to establish the effectiveness of the dechlorinating agent. **Read your permit carefully.** Note that the permit may specify the days the *Escherichia coli* (*E. coli*) samples are to be collected, and that the sample for chlorine residual analysis must be collected at the same time and location as the *E. coli* sample.

### E. coli

Effluent samples collected for the analysis of fecal coliform or *E. coli* must be collected at a point beyond chlorination. If some form of dechlorination is used at the facility, these samples must be collected beyond the point where dechlorination takes place. \*\*

\*\* If a large discrepancy is observed in results between samples collected after chlorine addition and those collected after the addition of the dechlorinating agent, it may be wise to determine what source of feed water is being used to deliver the dechlorinating agent. On more than one occasion the feed water used to deliver the dechlorinating agent has been found to be the source of coliform contamination.

## Types of Samples

### **Grab Samples**

A grab sample is defined in Vermont NPDES permits as an individual sample collected in a period of less than 15 minutes. A grab sample represents the condition of the effluent, influent, or other matrix being sampled, for that specific time only.

Examples of parameters that must be collected as grab samples include pH, chlorine residual, dissolved oxygen, *Escherichia coli* bacteria, and FOG.

Be sure to use the appropriate sample collection device/bottle for the parameter being analyzed. For example, coliform samples MUST be collected directly into properly treated sterilized bottles and cannot be transferred from one bottle to another. The effluent sample collection bottles/devices should be kept separate from the influent sampling bottles/devices. It's a good idea to always collect samples from "cleanest to dirtiest" to help avoid contamination. (i.e., final effluent is sampled prior to influent)

### **Composite Sample**

A composite sample as defined in Vermont NPDES permits is a sample consisting of a minimum of one (1) grab sample per hour collected during a 24-hour period (or lesser period as specified in the section of the permit on Monitoring and Reporting) and combined proportionally to flow over that same time period. Collection of a 24-hour composite is required unless stated otherwise in the NPDES/Pretreatment permit, as it allows for representation of discharges from industries/workplaces with 24-hour shifts, variations in loading etc. Composite samples collected at industries should be representative of the entire working day. If the industry is running a single shift, an eight-hour composite is sufficient. If however, two or three shifts are operating, the composite should be representative of sixteen or twenty-four hours, respectively. For municipal wastewater treatment facilities in Vermont the minimum compositing frequency and duration is eight samples, one per hour for eight (8) hours. Eight-hour composite samples must be collected between the hours of 6:00 a.m. and 6:00 p.m. This eight-hour frequency is mainly reserved for lagoon systems.

Examples of parameters that are generally collected as composite samples include: Biochemical Oxygen Demand (BOD), Total Suspended Solids (TSS), Total Kjeldahl Nitrogen (TKN), Total Phosphorus (TP), the nitrogen series, and most metals.

List of Metals Usually Collected with Composite Samples

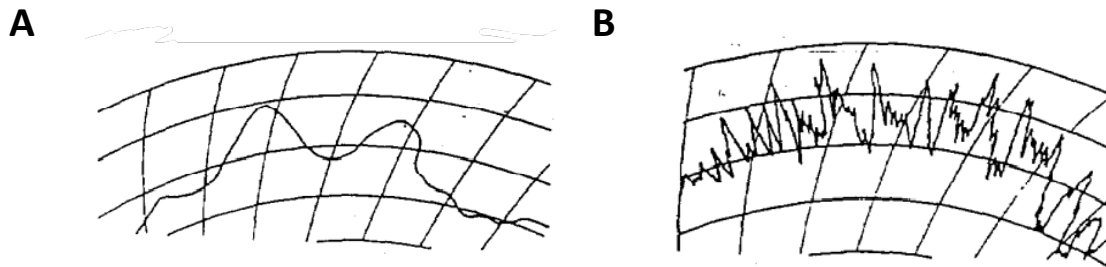
Aluminum	Boron	Copper	Manganese	Selenium	Tin
Antimony	Cadmium	Iron	Mercury	Silver	Titanium
Arsenic	Calcium	Lead	Molybdenum	Sodium	Vanadium
Barium	Chromium	Lithium	Nickel	Strontium	Zinc
Beryllium	Cobalt	Magnesium	Phosphorus	Thallium	

There are several different methods of compositing: straight or time compositing, flow compositing and time-flow compositing. If the flow during the day is very constant, i.e., it varies less than 10% during the day (for example, the effluent from an aerated lagoon), the samples may be time composited. In a time composite, the same volume is taken every hour and put together for the composite. If the flow is not

## Sampling

constant (for example, the effluent for a sequencing batch reactor), a flow-proportional compositing method must be used. In flow compositing, the same volume is taken at certain flow intervals. For example, 100 mL of sample might be taken every time 1,000 gallons passes over the weir for the duration of the sampling period. This type of compositing is used in automatic sampling but would be inconvenient for manual sampling. Time-flow compositing is used for manual sampling of flows that vary by more than 10% during the sampling period. In this method of sampling, samples and flow measurements are taken at specific time intervals, most often hourly, and the composite made by adding together amounts of each hourly sample varying with the flow passing through during that hour. Depending on the flow pattern in the plant, either the chart or the integrator readings will be used to flow proportion the sample.

If the flow pattern is fairly even, as in Chart A below, the instantaneous flow readings can be taken directly from the chart at the time of sampling. If the flow varies considerably during the sampling period due to pumping patterns, etc., and the chart looks like B below, the flow reading must be taken from the integrator or totalizer. In order to get a flow for a specific sample, for example the 9:00 a.m. sample, the flow reading at 8:30 a.m. must be subtracted from the 9:30 a.m. reading. This is because we have chosen the 9:00 a.m. sample to describe the flow for an hour period centered on 9:00 a.m.



Once the sampling period is over, the flow proportioning scheme can be calculated. If the integrator readings were used, flows must be generated by subtracting each reading from the one preceding it.

### Time-Flow Compositing

1. Add flows together.
2. Divide the size of the composite jug (remember to allow yourself a little head room) by the total of the flows.
3. Multiply the factor obtained above by each hourly flow for the number of milliliters (mL) to use from each hourly sample.

In the following example, the integrator readings are given, and a flow proportioning scheme is then calculated.

## Sampling

TIME	INTEGRATOR	DIFFERENCE	FACTOR	mL
7:30	77340	16		
8:30	77356	20		432
9:30	77376	24		540
10:30	77400	18		648
11:30	77418	16	x 27 =	486
12:30	77434	16		432
1:30	77450	12		432
2:30	77462	18		324
3:30	77480	—		486
		140		

Factor determination: For a 4 L jug, use the equation 3800 mL divided by 140 (Total Difference) = 27.14  
(We use 3800 mL in this equation in order to leave headroom in the jug for shaking the sample.)

Another method, probably more representative of measuring flows from a flow chart, is to get an hourly flow. Some flow charts even have breaks within the lines at every quarter hour. This would be more accurate than the hourly flows taken off the chart when a flow is erratic.

### Sample Containers

The type of sample containers used is dependent upon the parameters or tests the samples are being analyzed for. Some samples such as those for pH, DO, and chlorine residual analysis are affected by exposure to air. Gases in the samples and in the atmosphere may exchange and alter the levels in samples before they can be measured. For this reason, the samples must be collected carefully, with very little agitation into air-tight bottles, such as 300 mL DO bottles, and analyzed immediately. Chlorine residual samples are also affected by sunlight which dissipates the chlorine residual. These samples should be shielded from sunlight and analyzed quickly after collection.

BOD and TSS samples can be taken from the same four-liter (gallon) composite jug. This jug should be thoroughly washed with a chelating detergent, such as a 2% Micro solution or with Alconox, to remove any trace of organic matter; rinse the jugs thoroughly after washing. Distilled H<sub>2</sub>O should be used for the final rinse(s).

Most metals samples are collected in bottles that have been washed with 20% nitric acid solution (HNO<sub>3</sub>). Five hundred (500) mL should be sufficient sample size unless such metals as hexavalent chromium (Cr+6) or mercury (Hg) are being analyzed. Your lab will then direct you as to special sample collection procedures. Be sure to check preservation requirements for individual parameters.

Coliform sample bottles must be washed and sterilized. A 250 mL bottle should be of sufficient size. For chlorinated samples, the bottle must contain a chlorine neutralizing agent, usually sodium thiosulfate. As the effluent is discharged to the river, its chlorine residual is diluted by the receiving water and is no

## Sampling

longer an effective disinfectant. The presence of thiosulfate in the sample bottle simulated this effect, giving a better picture of the coliform count in the effluent when it reaches the receiving water.

Containers for Total Kjeldahl Nitrogen (TKN) testing should be 500 mL plastic or glass bottles for everything but river samples which should be taken in one-liter containers. The samples can be poured from the composite or grabbed.

Total phosphorus is best taken in a 250 mL glass bottle. Again, samples are either poured off the composite or grabbed.

Table I gives a summary of the above, along with recommended preservation methods and the maximum recommended holding times from the Federal Register. For valid data, these preservation methods and holding times must be adhered to.



Sampling

**TABLE I: Summary Chart with Required Containers, Preservation and Holding Times**

Parameter	Sample Type	Container*	Preservation	Maximum Hold Time	Note
<b>METALS</b>					
PRIORITY POLLUTANTS					
Group 1: (arsenic, selenium, mercury)	Water	P, 500 mL	HNO <sub>3</sub> to pH <2	6 months 28 days	b
Group 2: (cadmium, chromium, copper, lead, nickel, zinc)	Water	P, 500 mL	HNO <sub>3</sub> to pH <2	6 months	b
Group 3: (antimony, beryllium, silver, thallium)	Water	P, 500 mL	HNO <sub>3</sub> to pH <2	6 months	b
MISCELLANEOUS					
Group 4: (aluminum, calcium, magnesium, potassium, sodium)	Water	P, 250 mL	HNO <sub>3</sub> to pH <2	6 months	b
*Group 5: (molybdenum, tin, strontium, vanadium)	Water	P, 500 mL	HNO <sub>3</sub> to pH <2	6 months	b
†Group 6: (cobalt, iron, manganese)	Water	P, 500 mL	HNO <sub>3</sub> to pH <2	6 months	b
Group 7: (hexavalent chromium)	Water	P, 500 mL	<b>DO NOT ACIDIFY</b> Cool, 6°C	24 hours	b
Group 8: (titanium)	Water	P, 500 mL	HNO <sub>3</sub> to pH <2	6 months	b
*Group 5 can be combined with Group 3, total volume of 500 mL					
†Group 6 can be combined with Group 2, total volume of 500 mL					
SOLIDS					
Groups 1 through 8 (from above)	Soil	P, 500 mL	0 - 6°C	6 months	
Groups 1 through 8 (from above)	Liquid, Sludge	Two - P, 500 mL	0 - 6°C	6 months	
<b>MICROBIOLOGY</b>					
Coliform, Fecal	Water	P, 250 mL sterile	0 - 6°C	6 hours	c, d
Coliform, Total	Water	P, 250 mL sterile	0 - 6°C	6 hours	c, d
E Coli	Water	P, 250 mL sterile	0 - 6°C	6 hours	c, d
<b>NUTRIENTS</b>					
Chloride	Water	P, 50 mL	none required	28 days	

Sampling

Parameter	Sample Type	Container	Preservation	Maximum Hold Time	Note
<b>NUTRIENTS</b>					
Chloride-[Ion Chromatography] (chloride, nitrate, nitrite, sulfate in 1 container)	Water	P, 50 mL	0 - 6°C	28 days	
Nitrogen (Nitrate + Nitrite)	Water	P, 250 mL	0 - 6°C, H <sub>2</sub> SO <sub>4</sub> to pH < 2	28 days	c
Nitrogen (Nitrate)	Water	P, 50 mL	0 - 6°C, Filtered	48 hours	
Nitrogen (Nitrite)	Water	P, 50 mL	0 - 6°C, Filtered	48 hours	c
Nitrogen (Ammonia)	Water	P, 250 mL	0 - 4°C, H <sub>2</sub> SO <sub>4</sub> to pH < 2	28 days	e
Total Phosphorus	Water	G, 250 mL	none required	28 days	
Phosphorus-Ortho	Water	G, 75 mL tubes	Filter immediately, 0 - 4°C	48 hours	c
Silica	Water	P, 50 mL	Filter immediately for dissolved, 0 - 4°C	28 days	
Sulfate [Ion Chromatography]	Air	P, 50 mL	0 - 4°C after extraction	28 days	
Sulfate [Ion Chromatography] (chloride, nitrate, nitrite, sulfate in 1 container)	Water	P, 50 mL	0 - 4°C, filter	28 days	
<b>ORGANICS</b>					
Pesticides & PCBs & Semi-Volatiles	Water	G, 2.6 L amber, Teflon lined cap	0 - 4°C, Pesticides and PCBs need to be pH 5-9	7 days to extraction, 40 days after	d
Pesticides & PCBs & Semi-Volatiles	Solids	G, 500 mL amber, Teflon lined cap	0 - 4°C	7 days to extraction, 40 days after	
Volatile Organics	Water	G, 2-40 mL vials	0 - 4°C, HCl to pH < 2	14 days	
Volatile Organics	Solids	G, 2-40 mL vials	0 - 4°C	14 days	

Sampling

Parameter	Sample Type	Container	Preservation	Maximum Hold Time	Note
<b>WET LAB</b>					
Alkalinity	Water	P, 250 mL	Cool, 4°C	14 days	
BOD Carbonaceous 20 days	Water	P, 2 L	Cool, 4°C	48 hours	e, f
BOD 5-Day	Water	P, 2 L	Cool, 4°C	48 hours	c, f
Chlorophyll-a	Water	Glass fiber filter, Whatman GF/A, stored in black jar	Freeze filter, dark	21 days	
COD	Water	P, 250 mL	Cool, 4°C, H <sub>2</sub> SO <sub>4</sub> to pH <2	28 days	c
Conductance	Water	P, 250 mL	Cool, 4°C, filtered	28 days	
Cyanide, Total	Water	P, 2 L, amber	Cool, 4°C, NaOH to pH > 12	14 days	g
Dissolved Oxygen, Probe	Water	G, 300 mL DO bottle	none required	analyze immediately	
Dissolved Oxygen, Winkler	Water	G, 300 mL DO bottle	MnSO <sub>4</sub> , I-/Azide, dark	8 hours	h
Ignitability	Solid Liquid	G, 250 mL	Cool, 4°C		
Nitrogen, Total Kjeldahl	Solid	P, 250 mL	Cool, 4°C	28 days	
Nitrogen, Total Kjeldahl	Water	P, 250 mL	Cool, 4°C, H <sub>2</sub> SO <sub>4</sub> to pH <2	28 days	e
Oil & Grease	Soil	G, 250 mL freon rinse, Teflon lined caps	Cool, 4°C	28 days	
Oil & Grease	Water	G, 1 L freon rinsed, Teflon lined caps	Cool, 4°C, HCl to pH <2	28 days	i
pH	Water	P, 250 mL	none required	analyze immediately	
Phenols	Water	G, 1 L, amber	Cool, 4°C, H <sub>2</sub> SO <sub>4</sub> to pH <2	28 days	
Solids - Total Dissolved	Water	P, 250 mL	Cool, 4°C	7 days	
Solids - Total Suspended	Water	P, 1 L	Cool, 4°C	7 days	
Solids - Total Volatile	Water	P, 250 mL	Cool, 4°C	7 days	
TCLP	Solid	G, 250 mL, amber	Cool, 4°C	Extract ASAP	
Turbidity	Water	P, 250 mL	Cool, 4°C	48 hours	

## Sampling

\*G = Glass; P = High Density Polyethylene (HDPE)

### NOTES:

- a. Collect with minimum agitation. Leave no air space. Insert ground glass stopper into DO bottle.
- b. Approximately 0.5 mL concentrated  $\text{HNO}_3$  per 250 mL.
- c. Lab needs prior notice for this parameter.
- d. Chlorinated samples need to be collected in sample bottle containing a dechlorinating chemical, such as  $\text{Na}_2\text{S}_2\text{O}_3$ .
- e. Approximately 0.5 mL concentrated  $\text{H}_2\text{SO}_4$  per 250 mL.
- f. Hold time is from end of sample collection period.
- g. Test for chlorine and sulfides in the field **PRIOR** to preservation.
- h. Samples must be fixed in field, stored in the dark and analyzed within eight (8) hours.
- i. Approximately five (5) mL 1:1 HCl.
- j. Add five (5) drops 1:1 HCl to each vial