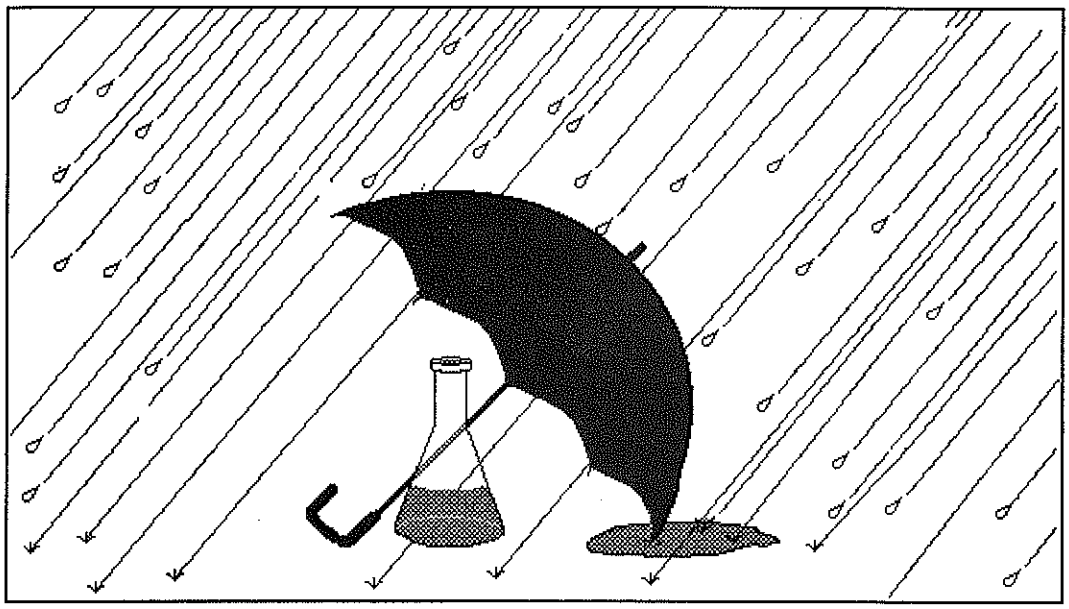
WISCONSIN'S GUIDANCE FOR INDUSTRIAL STORM WATER SAMPLING



Wisconsin Department of Natural Resources
Bureau of Wastewater Management
Municipal Wastewater Section - Storm Water Unit
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Prepared by:
Richard Dodds

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This document is based on the U.S. Environmental Protection Agency's NPDES Storm Water Sampling Guidance and has been modified to meet the chemical specific monitoring requirements of Tier One Type General Permit coverage under s. NR 216.23(1), Wis. Admin. Code.

Thanks to Ron Arneson of WDNR Technical Services for contributing Section 2.3 "Selecting a Laboratory for Storm Water Analysis".

CHAPTER 1 INTRODUCTION TO STORM WATER SAMPLING

1.1 PROGRAM HISTORY

The 1972 Federal Water Pollution Control Act (P.L. 92-500), commonly known as the Clean Water Act, prohibits the discharge of any pollutant to United States waters from a point source unless the discharge is authorized by a National Pollutant Discharge Elimination System (NPDES) permit. As a result of this legislation, the federal government, through the U.S. Environmental Protection Agency (US EPA), assumed the dominant role in directing and defining a national program for water pollution control. For the past couple of decades, efforts to improve water quality under the EPA have focused primarily upon reducing pollutants in industrial wastewater discharges and from municipal sewage treatment plants. Previous efforts to address storm water discharges through the NPDES program have generally been limited to certain industrial categories, using effluent limitations as a general permit condition.

In recognition of the need for more comprehensive controls on storm water discharges, the 1987 Congress enacted amendments to the Clean Water Act that require the US EPA to establish NPDES requirements for storm water associated with industrial and construction site activities. In response to these amendments, US EPA published the storm water rule on November 16, 1990 (55 Fed. Reg. 47990). In this rule, US EPA established the initial scope of the storm water program by requiring that 11 categories of industries obtain permits to discharge "storm water discharge associated with industrial activity".

The Wisconsin Department of Natural Resources (WDNR) has the authority to issue storm water discharge permits under ch. 147, Wis. Stats. The WDNR issues general WPDES permits to broad classes of industrial dischargers that include a set of general provisions to protect the environment. The WDNR has the authority to issue general permits for the discharge of storm water to waters of the state such as discharges from : 1) construction sites which disturb over 5 acres; 2) certain industrial sites and 3) certain municipalities.

Under ch. NR 216, Wis. Admin. Code, the state's administrative code for storm water regulation, the general storm water permits require regulated industries to reduce storm water pollution through the development and implementation of a Storm Water Pollution Prevention Plan (SWPPP). The WDNR has designed the program so that by minimizing the potential sources of pollution available to storm water, an industry will also minimize its chemical monitoring and reporting requirements. Ch. NR 216, Wis. Admin. Code, creates a multi-tiered system of permitting for industrial storm water discharge. Heavy industries and bulk storage facilities covered under a Tier 1 type general permit must perform chemical monitoring for pollutants expected to remain in their storm water runoff following the implementation of "source area" controls. This manual addresses the chemical specific

monitoring requirements of a Tier 1 type general permit for the discharge of storm water associated with industrial activity, as specified under s. NR 216.28(4), Wis. Admin. Code.

1.2 PURPOSE AND ORGANIZATION OF THIS MANUAL

This manual is for Tier 1 type facilities that discharge storm water associated with industrial activities. It is primarily designed to help you, as the operators/owners of an industrial site, in planning for and fulfilling the WPDES storm water discharge sampling requirements.

This manual is arranged to guide you through the stages of designing a sampling program, sampling your storm water, and submitting the resulting data to the WDNR. However, you should be aware of all of the subjects discussed in this manual before sampling to avoid mistakes in sampling or sample handling that may waste your efforts. Chapter 2 addresses the safety of sampling personnel and the selection of additional subjects to be considered before sampling storm water, such as the selection of a certified chemical laboratory for the analysis of storm water. Chapters 3 and 4 provide guidelines for planning and implementing your storm water sampling. There are discussions in these chapters on an acceptable rainfall event, the sampling procedures, and the equipment needed to collect a simple, time weighted composite sample. Chapter 5 describes the procedures for storm water sample analysis and submitting reports.

This manual is intended to assist you in meeting your storm water sampling requirements. You should note that you must make an honest effort to collect and report data that represents your storm water discharge. The intentional misrepresentation of discharge characteristics is unlawful.

Note: This manual does not include procedures for collecting flow weighted composite samples. An indepth discussion of flow sampling procedures are available in the US EPA's NPDES Storm Water Sampling Guidance Document (Publication Number EPA 833-B-92-001).

1.3 BENEFITS FROM SAMPLING

The characterization of storm water discharges is valuable to the WDNR and to you for several reasons. Storm water sampling provides a means to evaluate the environmental risk of the storm water discharge by identifying the types and estimating the amounts of pollutants leaving a site. The WDNR will also gain information on the effectiveness of both new and established best management practices (BMPs). Evaluating these data helps the WDNR staff to understand the need for the development of additional BMPs.

Storm water sampling also offers benefits to you in a variety of ways. As previously mentioned, data can be used to evaluate the general effectiveness of the BMPs currently in place. Sampling results also can uncover hidden sources of contaminants that can then be either eliminated or controlled by amendments to the SWPPP and changes to BMPs. Sampling and quarterly visual inspections allow you to note specifically where changes might be necessary in your SWPPP. Good pollution prevention can reduce the costs associated with wasted chemicals, avoid problems of site contamination, and reduce the risk of water quality impairment.

CHAPTER 2 PREPARATION FOR STORM WATER SAMPLING

This chapter presents background information and guidance for the period prior to sampling. Specifically, it covers the following areas:

- staffing considerations
- safety considerations
- selecting a laboratory for sample analysis
- when industrial activities must be sampled

2.1 STAFFING CONSIDERATIONS

The time it will take you to complete your sampling depends on the number of sample locations, the size of the area to be sampled, the type of sampling required, the sampling technique used, the number of samples to be taken (depending on the number of parameters to be analyzed), and safety considerations. To minimize accidents that could injure sampling personnel and interfere with sampling, all members of the sampling team must be trained in all aspects of the sampling program, including safety procedures. Also, be certain ahead of time that your sampling personnel are capable of taking accurate measurements and performing any calculations needed.

2.2 SAFETY CONSIDERATIONS

In the design of a storm water sampling program, the most important consideration is safety. All members of the sampling team need to be aware of the potential dangers. At most sites, these dangers may occur because of factors associated with your industry and the weather. You may wish to prepare a site storm water sampling safety plan. You should consider sampling hazards, safety training, and safety equipment when planning for storm water sampling.

2.2.1 SAMPLING HAZARDS

Storm water sampling often occurs when the sampling environment and/or storm water discharges create hazardous conditions. These conditions may include:

- physical hazards (i.e., traffic, falling objects, sharp edges, slippery footing, and the potential for lifting type injuries from opening or removing access panels and utility access hole covers, etc.).
- confined space hazards (i.e., utility access holes)
- chemical hazards
- weather hazards (i.e., flooding, tornadoes, lightning, etc.)
- biological hazards (i.e, bees, rodents and snakes)

It is essential that sampling personnel be aware of these hazards. Sampling personnel must be trained to evaluate hazardous situations and develop techniques for handling them. Sampling hazards can be life threatening, so safety must be the highest priority for all sampling personnel.

Physical hazards. Many physical hazards may exist, such as traffic hazards, sharp edges, falling objects, and slippery footing. If you are collecting the sample from a utility access hole in a street or driveway, traffic control is an important consideration. Besides traffic cones, markers, warning signs, and barricades, a vehicle or a heavy piece of equipment can be placed between the working area and oncoming traffic to increase the protection of sampling personnel. Flashing warning signals should be used to alert both drivers and pedestrians. Orange safety vests should be worn by personnel stationed on the surface when the utility access hole is in a vehicular traffic area. Depending upon your situation, you may also want to be certain that members of your sampling team wear steel toed boots and hard hats to reduce the chance of injury.

Open all access covers with the appropriate methods and tools. Remove utility access hole covers with a hook or pick axe. Exercise care to prevent dropping covers on hands or toes and keep all loose items away from the opening of the sampling area. Remember that tools, sand, gravel, and other objects can fall into the sampling space and cause injury to personnel or damage sampling equipment.

Confined space hazards. A confined space is any space not intended for continuous occupancy by personnel, with a limited means of entry and exit, and with possible accumulation of either an actual or potentially hazardous atmosphere. At your facility, confined spaces could include manholes, catchbasins, and storm sewers. In confined spaces a hazardous atmosphere probably poses the greatest safety threat to sampling personnel. A qualified person should judge whether the sampling space is safe. This can be accomplished using direct or remote sampling instruments to test for oxygen and carbon monoxide levels, and the potential for flammable and toxic materials. Since these materials may be heavier than air, tests on the atmosphere must be conducted beginning at the bottom of the confined space.

Personnel must not enter a confined space unless trained in confined space entry techniques.

CHAPTER 2 PREPARATION FOR STORM WATER SAMPLING

Confined spaces training covers hazard recognition, the use of respiratory equipment and atmospheric testing devices, lockout and tagging procedures, use of special equipment and tools, and emergency and rescue procedures. In addition, facilities that are planning to sample in confined spaces should establish a rescue team, with at least one member of the team certified in basic first aid and Cardiopulmonary Resuscitation (CPR). Annually, this team should practice removing victims through openings of the same size, configuration, and accessibility as potential rescue situations.

Never enter a confined space unless a qualified person has ensured the following actions:

- all pumps or lines carrying flammable, injurious, or disabling substances into the space have been disconnected, blinded, double blocked and bled, or effectively isolated by other means to prevent the development of dangerous levels of air contamination or oxygen deficiency within the space.

- all fixed mechanical devices in the space that can cause injury are turned off and locked out.

- all electrical equipment, excluding lighting, is turned off and locked out (padlocked) or, where this is impossible, properly tagged.

- the space has been emptied, flushed, or otherwise purged of flammable, injurious, or incapacitating substances.

When sampling in a confined space, an attendant should be stationed immediately outside the space within sight of the personnel in the confined space. Do not sample if a hazardous atmosphere exists.

You should develop and carry out a written entry "permission" system which includes a written entry procedure. This entry procedure should provide, at a minimum, the following:

- information on the minimum environmental conditions that are acceptable for entry and work in a confined space.

- in the cases where an attendant is required, keep a record of atmospheric test results conducted prior to entry and during the confined work.

- the last calibration date for the oxygen and combustible gas detectors.

- the signature of the qualified person responsible for securing the entry permit and reviewing conditions before entry.

- a written description of the location and type of work done that has the time and date of both the entry and exit (should carry an expiration time of 12 hours).

In private industry, employee activities in confined spaces is currently regulated by the Department of Labor Occupational Safety and Health Administration (OSHA) under 29 CFR 1910.146. The National

Institute of Occupational Safety and Health has developed a manual entitled "Working in Confined Spaces" that should be consulted before entering a confined space.

Chemical hazards. The storm water discharge may contain industrial wastes such as corrosive or toxic materials. Sampling personnel should always be aware of possible hazards that may be encountered and take all necessary safety precautions. All skin contact with the storm water runoff should be avoided. Sampling personnel should wear rubber gloves and safety glasses. Use a long-handled sampler (discussed in Section 3.4) that will keep you a safe distance away from potentially dangerous storm water flow conditions or if the immediate area of the flow is potentially hazardous. Avoid sampling under hazardous chemical circumstances.

Besides exposure to hazardous runoff substances, personnel should practice care when using potentially hazardous sample preservatives. Any internal or external contact with these chemicals should be avoided. Skin and eyes may be irritated if exposed to either the chemicals or the sample itself. Each team member should wear rubber gloves and safety glasses when collecting or pouring off samples. If an exposure to these chemicals occurs, flush the exposed area with large amounts of water. All samples should be proportioned into appropriate containers in a well-ventilated area to avoid the potential for the inhalation of chemical fumes.

Weather hazards. Good judgement is the primary requirement for maintaining safety in storm water sampling. Never sample during lightning storms, high winds, or unsafe flooding conditions. Also, the decreased visibility from heavy rain can pose additional risks where the sampling is close to vehicle traffic. A less hazardous storm event should be sampled when the weather poses less extreme conditions.

Biological hazards. A wide variety of insects, rodents, snakes, and other animals may inhabit the sampling area. The sampling personnel should remain alert to these hazards. Sampling equipment, for certain locations, should include insect/rodent repellant and a first aid kit.

2.2.2 SAMPLING AND SAFETY TRAINING

The training of sampling personnel is critical to the success of storm water discharge characterization and to the safety of facility personnel. All training of personnel should be done before the sampling event. Using untrained personnel can increase the potential for health risks related to storm water sampling. In addition, sampling conducted by untrained personnel may result in data that is unrepresentative of the facility's storm water discharge.

2.2.2.1 SAFETY EQUIPMENT

Precautions should be taken to insure personnel safety including proper equipment and appropriate operational techniques, sufficient time to accomplish the task, training on potential hazards, and

emergency procedures. Table 2-1 contains a list of safety equipment that may be applicable depending on the characteristics of the sampling site. For entry into utility access holes, all of the listed equipment should be used and the sampling personnel must be trained in confined spaces entry.

TABLE 2-1. LIST OF SAFETY EQUIPMENT	
Flashlight (non-sparking)	18-inch traffic cones
Meters (for oxygen and explosive toxic gas)	Insect/rodent repellant
Ladder	Ventilation equipment
Safety harness (and tripod, if necessary)	50 feet of 1/2-inch nylon rope
Hard hat	Safety shoes
Safety goggles	Rain wear
Coveralls	Gloves (rubber)
Respirator	First aid kit
Reflective vests	Self-contained breathing apparatus
Source: Adapted from NPDES Compliance Monitoring Inspector Training: Sampling, U.S. EPA, August 1990.	

2.2.2.2 RESCUE OPERATIONS AND FIRST AID

If your sampling crew will be collecting samples under potentially hazardous conditions, members of sampling crews should be taught first aid/CPR methods. One person in each group should always remain in a safe location and observe the work.

2.2.2.3 ACCIDENT REPORTING

Generally, facility policy will dictate that a report is completed for all accidents, whatever the extent of injury. If available, use a standard accident form and contact the sampling team coordinator, when possible. The coordinator should use this information to evaluate the conditions that cause accidents and, if possible, eliminate them.

2.3 SELECTING A LABORATORY FOR STORM WATER ANALYSIS

These are a number of considerations involved in selecting a laboratory for storm water analyses. By not requesting the specific service needed, you may run the risk of having to resample and reanalyze. It is your responsibility to decide if a laboratory is providing you with acceptable service.

Considerations when selecting a laboratory include:

- accuracy and precision of results
- approved methods
- sampling instructions, bottles and preservatives
- reporting results
- turnaround time on results
- holding time before analysis
- certification status
- experience/qualifications
- detection limits
- price

Accuracy and precision of results. Since the sample results will be used to determine the effectiveness of your site management, the results should be as accurate and precise as possible.

Approved methods. There are approved analytical methods for most contaminants. Be certain to tell the laboratory that the samples will be submitted as part of the Wisconsin Pollutant Discharge Elimination System (WPDES) storm water discharge permit program. In addition, be certain to pass information on to the laboratory concerning sampling methods required by the permit.

Sampling instructions, bottles and preservatives. The laboratory should provide the sample bottles, necessary preservatives, and written instructions on preserving the samples. Many directions needed for these analyses are in this manual. However, it is always best to check with the laboratory about sample preservation before sample collection. It is important to note that not all preservation techniques work for every parameter. In some situations it may be desirable to contract out the sampling too. Ch. NR 219, Wis. Admin. Code, and Appendix C list many of the parameters, their necessary preservative, bottle type, and holding time. You should consult with ch. NR 219, Wis. Admin. Code, directly for a list of approved analysis methods.

Any sample that has not been preserved properly may result in questionable results and must be qualified as such when reporting the results. Having the laboratory supply the bottles will help insure the correct type of bottle and minimize the mistaken use of a contaminated bottle.

Reporting results. The report that you receive from the laboratory should include:

- results with concentration units (milligrams or micrograms per liter)
- definitions for abbreviations used
- date and time sampled
- date and time analyzed
- method used
- detection limits
- sampling location or sample ID # (sample identification information)
- any special problems encountered during analyses (interferences, insufficient sample, etc.)

If you plan to have a sample analyzed for many parameters, it is appropriate to specify the report format. For example, the report could be alphabetical by organic fraction or in the order given on the Storm Water Discharge Monitoring Report (DMR) form you will receive from the WDNR.

Accuracy of the report is also important. If you see frequent problems (such as improperly place decimal points, calculation errors, or improper units) of poor data handling, notify the laboratory that this is not acceptable, and consider changing laboratories.

Turnaround time on results. If the laboratory results are required by a specific date to complete and mail the annual report, be certain to specify this to the laboratory.

Holding times before analysis. The sample "holding time" is the amount of time from when a storm water sample is collected to when it is analyzed. Your samples holding time must not exceed the time given in s. NR 219 Table F, Wis. Admin. Code. Be certain to inform the laboratory of the date and time that your sample(s) was collected, in order for the laboratory to accurately schedule their workload. If your sample exceeds the holding time, the results of the sample analysis are not valid and may not be considered as acceptable by the WDNR. Be certain to submit a short explanation for any sample results for samples that exceeded their holding time.

Certification status. The WDNR requires you to use a WDNR certified or registered laboratory for the analysis of all storm water samples that you will submit to fulfill the permit requirements for annual analytical testing. However, laboratory certification does not guarantee good quality data or service. What laboratory certification does is to make information available about analytical data quality. This information can be used to help make the selection of a qualified laboratory. Be certain that when contracting for laboratory services, the laboratory is certified for the required parameters in conformance with ch. NR 149, Wis. Admin. Code.

Be aware that many laboratories subcontract work to other laboratories when they cannot provide the complete service or because of workload. Laboratories can subcontract analyses to another certified laboratory, but the contracting laboratory should ensure the performance of the required quality control and record keeping. The potential danger in this for the client is that samples may get lost in the shuffle or holding times may be exceeded.

Experience/qualifications. Check with the laboratories to see how much experience they have in analyzing this type of sample. Industrial storm water runoff may contain such a variety of contaminants that the presence of one may influence the detection of another, experience is very helpful when dealing with these types of complex samples. Also, ask for references and contact those references for their opinions concerning what they think about the laboratory. Be sure to look at the laboratories reports to see if they are they easy to read and make sense.

Detection limits. The laboratory will need to **know what detection limits are necessary** to meet the permit requirements. To get the service needed, be certain to give the laboratory the information the WDNR supplies (e.g., sampling requirements, methods, detection limits, etc.).

The WDNR suggests a method because that particular method has the needed limit of detection. If there are interferences present, all method steps should be followed to remove the interferences (ie.

sample clean-up or standard addition). Many laboratories charge extra for sample clean-up and will only do it if requested.

If the detection limits on the submitted data do not meet the WDNR needs, you may be asked to test an additional storm, unless a satisfactory explanation accompanies your data submittal.

Price. The price may vary widely for laboratory services. When asking for quotes or bids be certain to request all of the needed services. There may be hidden costs (ie. additional cost for sample clean-up, standard addition, confirmation, or reporting of quality control results), so be sure to ask about these costs ahead of time. The lowest price may not save money if you needs to retest because of questionable results or if the detection limits are not low enough. Similarly, the highest price may not be associated with the highest quality service.

2.4 WHEN INDUSTRIAL FACILITIES MUST SAMPLE

Information that you generate through sampling is a tool to evaluate the types and presence of pollutants remaining in your storm water discharge after the implementation of your SWPPP. For the purposes of storm water sampling in Wisconsin, the composite sample is collected during the initial period of storm runoff. This sample method is different from the EPA's composite sample procedure because you only composite sample aliquots collected from the first 30 minutes of storm water runoff rather than the entire duration (not exceeding 3 hours) of the runoff. We are requiring this type of composite because it is a useful and inexpensive indicator of the effectiveness of your facility SWPPP. Chapters 3 and 4 discuss the collection and compositing of your samples.

Tier 1 permittees are required to sample one storm event per year for two years. If you collect and analyze samples from additional representative storms, the data representing each event may be reported. Storm water sampling should be conducted during periods of normal operating procedures (day or night), and, not when the facility was closed for an extended period (such as extended weekends, holidays, shutdowns, etc.) unless the contaminants that you are testing for are as a direct result of that shutdown (ie. outdoor storage of equipment or materials). If your industry is engaged in seasonal type production (ie. vegetable and fruit canneries, etc.) you should collect storm water samples only during your heavier production periods or periods of greater outdoor activity which could directly contribute to storm water runoff contamination.

CHAPTER 3 ESTABLISHING A STORM WATER SAMPLING PROGRAM

This chapter contains information on sampling procedures and special sampling requirements to help you meet your permit obligations. However, the quality of storm water discharges and the logistical needs for sampling may be different for many industries and, as a result, specific sampling requirements may vary.

In preparation, you need to plan your sampling strategy well in advance of the actual sampling event. This should include walking the site to find appropriate sampling locations, becoming familiar with local rainfall patterns, training sampling staff in procedures and safety, consulting with a laboratory, and collecting all the equipment and supplies to be used throughout your sampling. Hopefully, chemical monitoring will be minimal, if you have done a good job of source area contaminant control.

3.1 LOCATING SITE OUTFALLS

The location of the storm water outfalls at your facility should already be clearly defined on the site map prepared in your SWPPP. Remember that you must plan to collect samples from every storm water discharge outfall that is associated with your industrial activity which may contain significant amounts of contaminants after the implementation of your SWPPP. These outfalls include discharges of storm water from:

- areas where raw materials or finished product are exposed to storm water,
- roof areas where storm water may come into contact with contaminants from vents from industrial processes,
- areas where runoff from an industrial area has mixed with water from a non-industrial area, such as lawn, parking, and non-industrial roof areas.

Note: Section 3.2 of this manual discusses provisions under s. NR 216.28(4)(b), Wis. Admin. Code, which allows a facility to sample fewer outfalls.

Ideally, the samples of your storm water runoff should be collected directly from a storm water discrete conveyance, such as a pipe or channel. Also included in the definition of storm water outfall is the storm water from an industrial facility that enters, and is discharged through, a municipal separate storm sewer. In short, most storm water discharges can be defined as outfall discharges, since the flow will ultimately enter some kind of conveyance (e.g., a channel or swale) or into the waters of the State of Wisconsin, which includes ground water. Any industrial storm water is subject

to permit coverage when it leaves your site by any means other than by entering a municipal sanitary sewer or combined sewer system.

Storm water should be sampled at a location as close as is practical to where the flow leaves your property. Your sampling location should be easy to reach on foot and in a location that will not result in hazardous sampling conditions. Ideally, the sampling site should be on your property; if not, be sure to obtain permission from the owner of the property where the discharge outfall is located. Typical sampling locations may include the discharge at the end of a pipe, a ditch, or a channel, but could also include areas where runoff concentrates into a wide flow path and may need to be concentrated still further for sampling.

For more information on locating outfalls, consult the guidance manual entitled Industrial Storm Water Pollution Prevention Planning available from the Wisconsin DNR Storm Water Section address in Appendix A.

3.2 WHAT MUST BE SAMPLED

As a Tier 1 type facility under ch. NR 216, Wis. Admin. Code, you must collect and analyze a time based composite sample from the storm water outfall(s) with significant concentrations of contaminants after the implementation of your SWPPP. Outfalls should be sampled during the same representative storm event, if possible. Descriptions of each storm event and the outfalls sampled should be included with your data submittal (see section 4.2). Remember that you do not need to sample storm water runoff from employee parking lots, administration buildings, and landscaped areas that do not mix with storm water associated with industrial activity.

In addition, s. NR 216.28(4)(b), Wis. Admin. Code, allows you to sample the discharge of fewer storm water outfalls, if and when a facility:

> *has more than one outfall which have storm water discharges substantially similar based on consideration of industrial activity, significant materials, and management, one outfall may be selected to represent the group of similar outfalls provided that this strategy has been clearly stated in the facility monitoring plan and that the representative outfall is clearly identified as such on the drainage base map.*

In many cases, this might allow you to select one outfall that is representative of the discharge from all of the outfalls at your facility. Your SWPPP should contain a discussion of your intention to sample less outfalls, as well as a discussion of why these outfalls can be considered "similar". Samples collected from this outfall must be analyzed for all of the contaminants expected to be present in your runoff as a result of industrial activity, according to those specified in your facility SWPPP.

3.3 SAMPLING EQUIPMENT NEEDS

In the determination of your sampling equipment needs, remember that procedures outlined in s. NR 216.28(4)(e), Wis. Admin. Code, require that storm water samples:

shall be representative of either:

1. The "first flush" of storm water runoff from the outfall. Composite samples are required for all pollutants except those for which analytic techniques require grab samples. The composite sample shall be collected during the first 30 minutes of runoff. At least 3 separate samples shall be collected for compositing, and the collection of samples shall be evenly spaced throughout the sampling period, or

2. The storm water discharged from a detention pond that has greater than a 24 hour holding time for a representative storm. A grab sample is required for all pollutants. The grab sample shall be representative of the storm water discharge from the pond outfall.

Note: the first flush sample called for in the Wisconsin permit language is a composite sample, generally not a grab sample.

Either type of composite sample called for in the permit will satisfy the sampling procedural requirements for most contaminants. The following subsection on "The Basic Storm Water Sampling Kit" explains the equipment that you will probably need to fulfill the chemical monitoring obligations of your permit. The subsection "Determining Your Sampling Type and Technique" provides the information for you to decide what kind of composite sample you should collect and the additional equipment that you may need. The final subsection on the "Decontamination of Sample Equipment Containers", describes the procedures that you, or preferably your laboratory, should use to clean and care for your sampling bottles. These subsections will help you to gain an understanding for the equipment that you will need for sampling at your facility.

3.3.1 THE BASIC STORM WATER SAMPLING KIT.

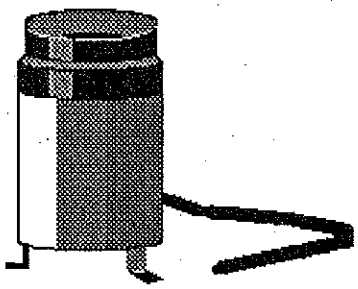
Each storm water sampling technique has certain equipment in common that is necessary to secure a sample and the necessary additional information. These items are:

- rain gauge
- sampling bottles
- laboratory transport bottles
- watch (hours/minutes)
- field sampling notebook
- latex gloves
- pH meter (see below)

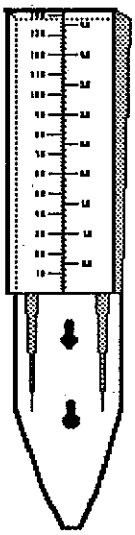
Rain gauge. The two most common types of gauges are the "standard" and the "recording" rain gauge. The standard rain gauge will provide all of the rainfall measurements required by the general permit. A standard rain gauge collects the rainfall so that the amount of rain can be easily measured. The standard gauge for the National Weather Service (NWS) has a collector that is 8 inches in diameter, but many suitable inexpensive standard gauges are available from local hardware stores and come in different diameters that will perform adequately. The rain gauge selected also must allow you to read the depth of rainfall to 0.1 inches.

Standard rain gauges are simple and inexpensive; however, with a standard gauge, there is no way to record changes in the intensity of the rainfall without making frequent observations of the gauge during the storm. Recording rain gauges collect information on rainfall intensity, as well as total

Figure 3-1. Types of rainguages. (not to scale)



Automatic
(tipping bucket)



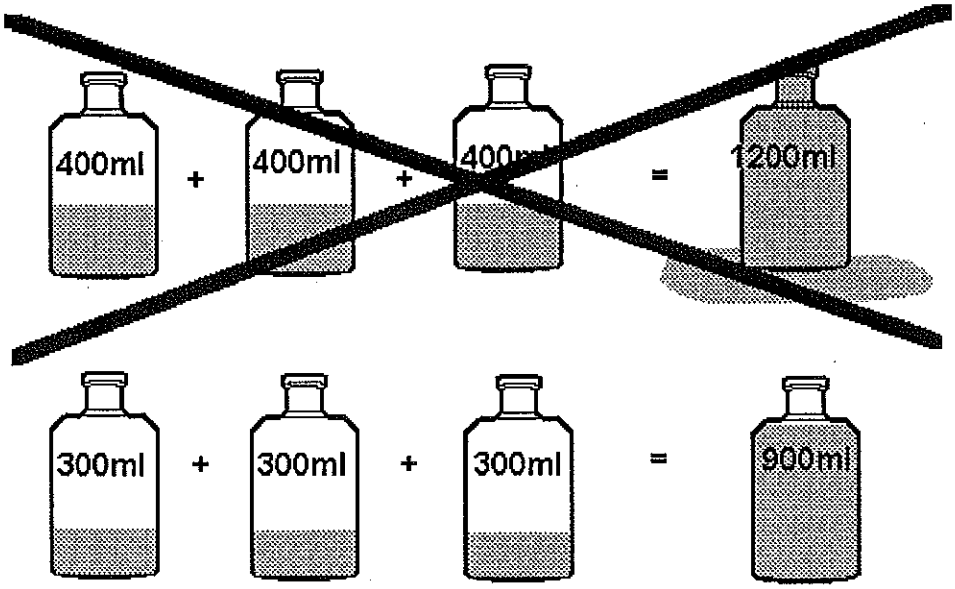
Manual

depth, and is often far more expensive and complicated than the standard rain gauge. In some very select instances, recording rain gauges may be necessary to obtain information to fulfill the special requirements of an individual type storm water permit rather than a general.

All rain gauges can be subject to error. However, most errors will be minimized by placing the gauge on a level surface that is not windswept and is away from trees and buildings that might interfere with the path of rainfall. Also, an additional source of error in rainfall measurements is mistakes in reading the scale of the rain gauge.

Sample collection bottles. You will need different types of bottles for sample collection and for the sample delivery to a laboratory. At least four bottles, with covers, will be needed per outfall for sample collection. Three of these four should be the same size and will be used for the collection of the individual grab samples. You will use the fourth bottle to mix all of the grab samples collected, so it will need to be large enough for the task. You will need to decide the size of these bottles by considering the amount of water that you will need for sample analysis (Figure 3-2). In addition, you can use the information found later in Table 4-1 to make a rough determination of the amount of sample that you will need to collect for the laboratory to perform the chemical analysis.

Figure 3-2 Be certain that the sample bottles you choose will fit all of the sample.



Laboratory sample delivery bottles. Once you have composited the samples, you will need to split the resulting mixture into the discrete subsamples for the each desired analysis (discussed in Chapter 4). These subsamples will need to be in separate bottles for sample delivery. It is common that a laboratory will supply precleaned bottles and the preservatives necessary to preserve subsamples (previously discussed in Chapter 2).

Check in Appendix C or with your laboratory to determine whether the contaminant to be analyzed must be contained in glass or plastic. Plastic bottles can absorb certain contaminants that may be present in the sample and produce an inaccurate representation of the storm water sample analyzed. However, you may prefer to use plastic, if possible, because its durability.

pH meter. The pH should be determined just after compositing the sample aliquots. The pH of a sample can change with time after collection, so it is important that it is checked as soon as possible. The accuracy of the pH technique that you choose should have no more than a ±0.1 pH units.

Additional equipment. Depending upon the conditions at your particular site, you may need any of the following:

- clean funnel
- clipboard and pencils
- paper towels

Be certain to check the list of safety equipment in Chapter 2 for any equipment that you will need during sampling.

3.3.2 DETERMINING YOUR SAMPLING TYPE AND TECHNIQUE

Before choosing the equipment to collect a composite sample, it is important to understand the two basic aspects of storm water sampling:

- sample type (i.e., grab versus flow or time weighted composite)
- sample technique (i.e., manual versus automatic)

Sample type. "Sample type" refers to the kind of sample that must be collected--either flow or time weighted composite or grab sample. It is very important to understand these "types", because they have different procedures.

time weighted composite sample: prepared by collecting fixed volume aliquots at specified time intervals and combining into a single sample for analysis.

flow weighted composite sample: combines discrete aliquots (subsamples) of a sample collected over time, based on the total flow of runoff sampled.

grab sample: a discrete sample collected from the runoff on a one-time basis with no regard to flow or time.

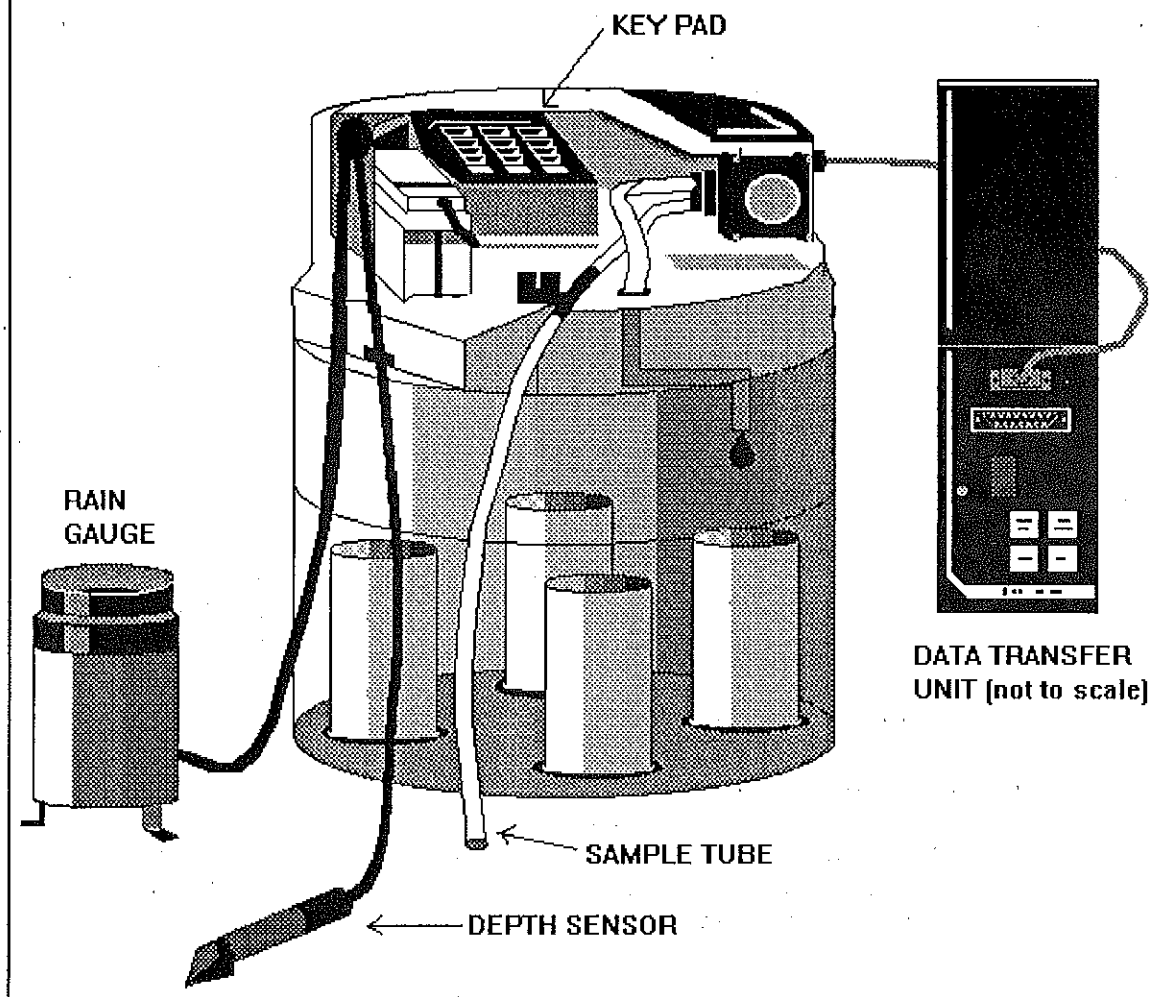
As previously stated, ch. NR 216, Wis. Admin. Code, requires a Tier 1 type facility to collect a time weighted composite sample for the majority of contaminants. The time weighted sample type is often the easiest of the composite sample types because it is based on collecting the same size sample aliquots as a function of time. Flow weighting a sample is much more complex because you must monitor the flow of the runoff to estimate the size of the aliquots to composite. This procedure takes additional equipment and expertise. This manual is focussed primarily upon the time weighted composite sample because it is the required procedure under s. NR 216.28, Wis. Admin. Code. However, an indepth discussion of techniques for collecting a flow weighted composite sample can be found in the US EPA's NPDES Storm Water Sampling Guidance Document (Publication Number EPA 833-B-92-001).

Grab sampling specific requirement. In keeping with federal regulations [40 CFR 122.21(g)(7)], grab sampling is required to analyze for certain pollutants. Monitoring by grab sample must be conducted for:

- cyanide
- residual chlorine
- oil and grease
- fecal coliform
- volatile organic compounds (VOCs)
- total phenols
- chromium (VI)
- sulfite
- fecal streptococcus

If the sampling plan in your Storm Water Pollution Prevention Plan includes any of these contaminants you will need to collect an additional single grab sample (over and above your composite sample for other contaminants) within the first 30 minutes of runoff. Composite samples are not

Figure 3-3. An Automatic Sampler



appropriate for these parameters due to their tendency to transform to different substances or change in concentration after a short period. Such transformations may be particularly likely in the presence of other reactive pollutants.

Sample technique. It is important to consider the differences between manual and automatic sample collection techniques. You can collect samples manually by placing a sampling bottle directly into the storm water runoff, while automatic samplers are powered devices that collect runoff samples

according to preprogrammed criteria. Figure 3-3 shows a typical automatic sampler configuration. For most pollutants, either manual or automatic sample collection will conform with the sampling requirements.

Manual and automatic techniques have many comparable advantages and disadvantages to consider before deciding which to use in your sampling program. Ultimately, it is up to you to decide which sampling technique to use at your site. Frequently, manual sampling presents the simplest technique for sampling your storm water discharge. Manual sampling is generally less expensive than purchasing or renting an automatic sampler. Also, manual sampling will often allow you to tailor your collection technique quickly to changing conditions and have fewer problems with incompatible sampling materials than with automatic sampling. However, a disadvantage of manual sampling can be that sampling from a remote discharge site may put personnel into direct contact with the hazards associated with storm water sampling.

Automated sampling can often be more convenient depending upon the demands of sampling at your facility. The advantage of automated samplers is the ability to collect a sample at anytime, whereas the personnel needed for manual sampling often restricts it to sampling only those storms that occur during business hours. Also, the automated technique allows personnel into outfall areas during safer, dryer, daylight hours for installation of the sampler, so that it will be ready prior to the storm. Most automated systems are also available in models that will record all of the significant information concerning the depth and intensity of precipitation, runoff flow, and sampling frequency. Unfortunately, it may take one or two lost sampling opportunities to accurately calibrate the collection of storm water runoff with an automatic sampler.

Table 3-4 presents a comparison of advantages and the disadvantages of the both manual and automatic sampling types. Be certain to familiarize yourself with the section on sampling hazards (Chapter 2) and compare these to your own site during a large storm before making a commitment of which sampling technique to use at your site.

In addition, some restrictions on sample collection techniques (such as container type and preservation) can be determined through the information provided in Appendix C or by consulting the approved analytical methods listed in ch. NR 219, Wis. Admin. Code. Chapter 2 provides additional information on sample handling, holding times, and preservation methods.

Several pollutants should not be collected using an automatic sampler. Oil and grease requires teflon coated equipment to prevent clinging to the sampling equipment and so automatic equipment costs can be quite high. In addition, your sample must be collected from an area of maximum mixing so that the sample represents the actual concentration found in the runoff because oil and grease rise to the surface of the water column. Constituents such as fecal streptococcus, fecal coliform and chlorine must be analyzed quickly because they have very short holding times (i.e., 6 hours or less), so the usefulness of automatic nighttime sampling may be diminished.

TABLE 3-4. COMPARISON OF MANUAL AND AUTOMATIC SAMPLING TECHNIQUES

Sample Method	Advantages	Disadvantages
Manual Grabs	• Appropriate for all pollutants • Minimum equipment required	• Labor-intensive • Environment possibly dangerous to field personnel • May be difficult to get personnel and equipment to the storm water outfall within the 30 minute requirement • Possible human error
Manual Flow or Time Weighted Composite (multiple grabs)	• Appropriate for all pollutants • Minimum equipment required	• Labor-intensive • Environment possibly dangerous to field personnel • Human error may have significant impact on sample representativeness • Requires flow measurements taken during sampling (only if collecting flow based samples)
Automatic Grabs	• Can potentially minimize labor requirements, once calibrations are completed • Low risk of human error • Reduced personnel exposure to unsafe conditions • Sample may be triggered remotely or initiated according to present condition	• Samples collected for O&G may not be representative • Automatic samplers cannot properly collect samples for VOCs analysis • Costly if many sampling sites require the purchase of equipment • Requires equipment installation and maintenance, may malfunction • Requires operator training • May not be appropriate for pH and temperature • May not be appropriate for parameters with short holding times (e.g., fecal streptococcus, fecal coliform, chlorine) • Cross-contamination of aliquot if tubing/bottles not washed
Automatic Flow or Time Weighted Composites	• Minimizes labor requirements • Low risk of human error • Reduced personnel exposure to unsafe conditions • May eliminate the need for manual compositing of aliquots • Sampling may be triggered remotely or initiated according to on-site conditions	• Not acceptable for VOCs sampling • Costly if many sampling sites require the purchase of equipment • Requires equipment installation and maintenance, may malfunction • Requires initial operator training • Requires accurate flow measurement equipment tied to sampler (only for flow based samples) • Cross-contamination of aliquot if tubing/bottles not washed

Sampling for VOCs presents a particular case in which automatic samplers cannot be used, because VOCs will likely volatilize due to agitation during automatic sampler collection. If you must analyze for the presence of VOCs, be certain to get any special sampling and handling directions from the laboratory before collecting the sample. In addition, Chapter 4 contains a discussion of some special requirements for VOC sampling.

3.3.3 DECONTAMINATION OF SAMPLE EQUIPMENT CONTAINERS

Storm water sample containers should be cleaned and prepared for field use by:

1) nonphosphate detergent and tap water wash
2) tap water rinse
3) distilled or deionized water rinse
4) total air dry.

These procedures may be used for plastic or glass containers. In order to assure limited contamination, you may want any or all of these procedures done by the laboratory or container distributor.

After the cleaning procedures, the sampling containers should be capped or sealed with foil (not for samples to be analyzed for metals), and the sampling device should be protected and kept clean. It is a good idea to label your sample containers after cleaning. The laboratory should keep a record of the technician performing the cleaning procedure as well as the date and time. This record is essential to trace the sample integrity in the event that quality control checks reveal problems. Consequently, we suggest that the laboratory performing the analysis also perform the cleaning so as to avoid problems if contamination issues arise.

The laboratory should follow much the same cleaning procedures as you need to for your sampling containers. However, if the sample is to be analyzed for heavy metals, the tap water rinse of the laboratory sample bottles should be followed by a rinse with 10 percent nitric acid solution and then the distilled or deionized water rinse.

3.4 SPECIAL SAMPLING SITE CONSIDERATIONS

Storm water sampling is not always easy. Some sites may have physical characteristics that make sampling very awkward. Tables 3-5 and 3-6 give quick answers to possible sampling location problems. In addition, the following is a discussion of the more common sampling location problems and remedies. In situations where discharge points are too difficult to sample, you may have to just take the best sample possible and explain the conditions along with your submittal of sample results.

TABLE 3-5. SOLUTIONS TO SAMPLE LOCATION PROBLEMS	
Problem:	Sampling where storm water commingles with process or non-process water
Solution:	Attempt to sample the storm water discharge before it mixes with the non-storm water discharge. If this is impossible, you should collect the runoff sample from the outfall. Keep in mind that it may be helpful to sample the dry weather discharge later if it appears that it may be the source of contaminant levels, instead of the storm water runoff.
Problem:	Many small point discharges or shallow flow
Solution:	Impound channel or join together flow by building a weir or digging a ditch to collect discharge at a low point for sampling purposes. This artificial collection point should be lined with plastic to prevent infiltration and/or high levels of sedimentation. Or, if possible, collect samples of the runoff at several locations to represent a composite of the total outfall runoff.
Problem:	Inaccessible discharge point [examples include underwater discharges or unreachable discharges (e.g., out of a cliff)]
Solution:	Go up the pipe to sample (i.e., to the nearest utility access hole or inspection point). If these are not available, tap into the pipe or sample at several locations to best represent total site runoff.
Problem:	Managing multiple sampling sites to collect grab samples during the first 30 minutes
Solution:	Have a sampling crew ready for mobilization when forecasts suggest that a representative storm will occur or sample using several different representative events. Also, for most parameters, automatic samplers may be used to collect samples within the first 30 minutes triggered by the amount of rainfall, the depth of flow, flow volume or time.
Problem:	Commingling of parking lot runoff with discharge associated with industrial activity
Solution:	If you cannot sample just the runoff from your industrial area, be certain to specify in your report that the runoff is commingled with runoff from a parking area.
Problem:	Sampling from a storm water detention pond
Solution:	Collect your composite sample from the detention pond discharge. In order to help assess your pond as a part of your treatment system, be certain to select a storm that will be representative of its normal function. Try to avoid sampling too large a storm that may have washed out the pond bottom, resuspending contaminants, or too small a storm, where the discharge from the pond may not have accurately represented the average discharge quality. See also Section 3.3 on special sampling techniques for detention ponds.
Problem:	Runon from other property
Solution:	Provide a narrative discussion of the upstream site (e.g., is it developed, if so the type of facility, the types of pollutants that may be present on the site, etc.). It may be advisable to collect a runon sample if you believe that it is a major source of contamination to the storm water leaving your property.

Shallow flow. Shallow flow runoff may be present a sampling problem because it often does not appear to form any well defined channels, or even a easily discernible outfall, that would allow for a sample collection point where the runoff is well mixed. Sometimes you may find it convenient to use temporary structures to channelize and combine many small discharge points to create a single sampling point. When you have channelized the flow, collect a sample by using any of the normal techniques illustrated in this manual.

Utility access hole. Sampling through utility access holes (manholes) should be strongly discouraged if it involves entering into a confined space. Under current OSHA regulations, you will need training in confined space entry if any part of your body is to enter the utility access hole. In dry weather a storm sewer may have many confined space hazards, but during a storm these can be complicated by additional dangers from slippery surfaces and flowing water. To avoid sampling in hazardous conditions, you may want to collect your samples at the point where the storm

TABLE 3-6. LOGISTICAL PROBLEMS OF STORM WATER SAMPLING

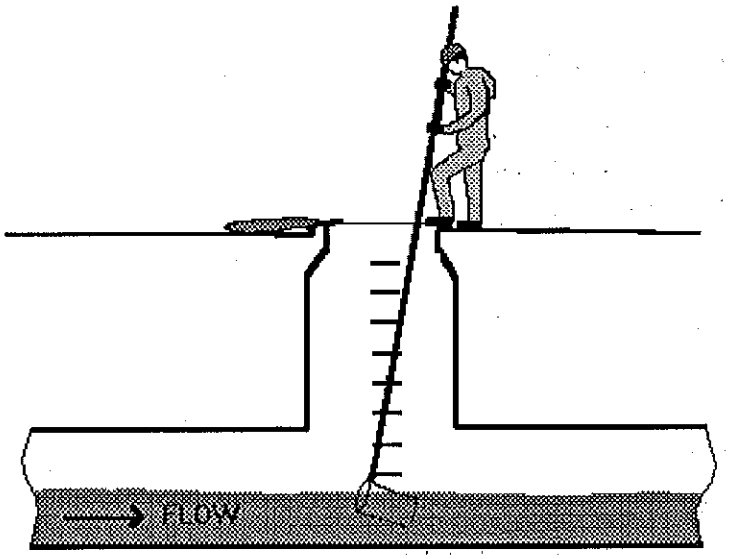
Problem:	Drought areas
Solution:	Submit a request for an extension, and submit the other information without sampling data by the due date with a certified explanation.
Problem:	Adverse weather conditions such as freezing, flooding, winds, tornadoes, electrical storms, and gully washes
Solution:	Sample another, less hazardous event.
Problem:	False starts
Solution:	Discard the sample if the volume is inadequate. Continue to monitor weather conditions and attempt to sample the next *acceptable storm* (defined in section 4.1).
Problem:	Stop/start rains
Solution:	Continue to sample in case the storm event turns out to be representative. If sample volumes are inadequate, continue to monitor weather conditions and attempt to sample the next acceptable storm.

water runoff from your site enters into the confined storm sewer system.

Safety is the key if you must sample through a utility access hole. Automatic samplers offer the safest sampling option because they can be set during dry periods. Also, many distributors of safety equipment sell sampling devices designed for limited access sampling. Manual sampling can be accomplished with a device called a "dipper", a collection cylinder connected to a telescoping handle (Figure 3-7). However, with a little ingenuity you can devise a manhole sampler consisting of just a pole and a firmly attached bucket or plastic jar.

Base flow. You should check the storm sewer during dry weather periods for "base flow". This is often present in storm sewers from either ground water infiltration through cracks in the sides of the sewer pipe or from the discharge of non-contact cooling water. If there is a base flow present, you should report it in your SWPPP. The presence of a large base flow makes accurate sampling very difficult because the presence of contaminants in the base flow can produce inaccurate results. If the dilution of the storm water runoff by the base flow will be significant, the results of the analysis of your storm water samples may not provide you with reliable information about the effectiveness of your SWPPP. You may need to collect your samples at a location where the storm water is unaffected by the base flow or have samples of the dry weather base flow analyzed to determine its potential for contaminant contribution to your total storm water and base flow discharge.

Figure 3-7. Manual sampling in a manhole.



3.5 SOURCES OF WEATHER INFORMATION

A member of your sampling team should be assigned to follow current weather conditions so that you will be prepared to collect samples. Several sources provide accurate local weather information that can aid you in predicting the occurrence of a storm. The National Weather Service (NWS) of NOAA can provide information on forecasted weather conditions. Local NWS telephone numbers can be obtained from the NWS Public Affairs Office at (301)713-0622. Your local telephone directory will generally contain a listing for the local weather service under "National Weather Service" or "Weather." In addition, NOAA runs the NOAA NWS Weather Radio that provides a continuous broadcast of the most current weather information and can be accessed with a weather band radio. Also, most NWS offices provide telephone recordings of weather conditions.

Cable TV weather stations and local airports can provide weather information that is continuously updated. The weather information provided by the local newspaper to TV stations should be used only if all of the more accurate weather services (as described above) are unavailable, since weather forecasts can change drastically within several hours.

CHAPTER 4 COLLECTING A STORM WATER SAMPLE.

The previous chapters have discussed the pre-sampling considerations necessary for storm water sampling. By this point, you should have an understanding for what you will need for a storm water sampling program, including safety policies, a sampling team, all the sampling equipment, and the sampling sites. This chapter presents the characteristics of the acceptable storm and the techniques for collecting a storm water sample. This chapter should also be helpful to understand what are the characteristics of an acceptable storm, how to keep records of storm characteristics, and the sampling procedures to collect a sample to fulfill the chemical monitoring obligations of your general storm water discharge permit.

4.1 THE ACCEPTABLE STORM

According to s. NR 216.28(4)(d), Wis. Admin. Code, a storm event must fulfill minimum criteria to produce a sample that will adequately represent the movement of contaminants from an industrial site. A storm must:

- *during the period of March through November,*
- *produce greater than 0.1 inch of rainfall,*
- *occur at least 72 hours after a previous rainfall of 0.1 inch or greater.*

Storms that do not fit these criteria are not acceptable for sample collection, so collect a sample from a different storm. Remember, you only need to sample once per year, so be patient and collect a good sample from an acceptable storm.

4.2 COLLECTING STORM INFORMATION

Your data submittal for storm water discharge must include an *estimate of duration of the rainfall event (in hours) and the total amount of precipitation falling during the rainfall event.* The measurement of total precipitation from a rainguage should be reported to the nearest 0.1 inches.

4.3 VOLUME OF SAMPLE NEEDED

Table 4-1 presents suggested sample volumes for specific parameters. Table 4-1 may not include all contaminants applicable to your site and is by no means intended to be a mandatory sampling list.

4-1. VOLUME OF SAMPLE REQUIRED FOR DETERMINATION OF THE VARIOUS CONSTITUENTS OF INDUSTRIAL WASTEWATER

Tests	Volume* (ml)
Physical	
Electrical conductivity**	25 to 500
pH, electrometric**	25 to 100
Chemical	
VOC's	120
Ammonia,*** NH_3	250 to 1,000
Hydrogen sulfide,*** H_2S	100 to 500
Sulfur dioxide,***free SO_2	100
Acidity and alkalinity	100 to 250
Bacteria (fecal coliform)	100 to 250
Bacteria (fecal strept)	100 to 250
Biochemical oxygen demand (BOD)	500 to 1,000
Carbon dioxide, total CO_2	200
Chemical oxygen demand (COD)	20 to 250
Chlorine, total residual Cl_2	200 to 1,000
Detergents	50 to 400
Hardness	25 to 250
Volatile and filming amines	500 to 1,000
Oily matter	1,000 to 2,000
Organic nitrogen	100 to 1,000
Phenolic compounds	100 to 1,000
Polyphosphates	50 to 100
Silica	50 to 1,000
Solids, dissolved	100 to 500
Solids, suspended	100 to 1,000
Tannin and lignin	100 to 200
Aluminum, Al	250 to 1,000
Ammonium,*** NH_4	100 to 1,000
Bromide, Br	50 to 250
Chloride, Cl^-	25 to 500

Tests	Volume (ml)
Physical	
Turbidity**	25 to 250
Chemical	
Cyanide, Cn	500 to 1000
Fluoride, Fl^-	30 to 250
Nitrate/Nitrite, NO_3/NO_2^-	50 to 100
Phosphate, Ortho, PO_4^{--}, HPO_4^{--}, $H_2PO_4^-$	50 to 250
Sulfate, SO_4^{--}, HSO_4^-	50 to 100
Sulfide, S^{--}, HS^-	100 to 1,000
Sulfite, SO_3^{--}, HSO_3^-	50 to 250
Antimony, Sb	250 to 1,000
Arsenic, As	250 to 1,000
Barium, Ba	250 to 1,000
Cadmium, Cd	250 to 1,000
Calcium, Ca	250 to 1,000
Chromium, Cr	250 to 1,000
Copper, Cu	250 to 1,000
Iron,*** Fe	250 to 1,000
Lead, Pb	250 to 1,000
Magnesium, Mg	250 to 1,000
Manganese, Mn	250 to 1,000
Mercury, Hg	250 to 1,000
Potassium, K	250 to 1,000
Nickel, Ni	250 to 1,000
Silver, Ag	250 to 1,000
Sodium, Na	250 to 1,000
Strontium, Sr	250 to 1,000
Tin, Sn	250, to 1,000
Zinc, Zn	250 to 1,000

* Volumes specified in this table are taken from information provided by several Wisconsin laboratories and should be considered as only a guide for the approximate quantity of sample necessary for a particular analysis. The exact quantity used should be consistent with the volume prescribed in the standard method of analysis, whenever a volume is specified.

** Aliquot may be used for other determinations.

*** Samples for unstable constituents must be obtained in separate containers, preserved as prescribed, completely filled, and sealed against all exposure.

Note: Only selected parameters will have to be analyzed from your facility, as stated in your SWPPP.

If the laboratory that you have selected has not provided this information, you can use the information in Table 4-1 to estimate the volume to collect for analysis of each pollutant. Many contaminants can be detected from the same sample, so be certain to get the information from your laboratory on how they would like you to split your composite sample.

4.4 COLLECTING SAMPLES

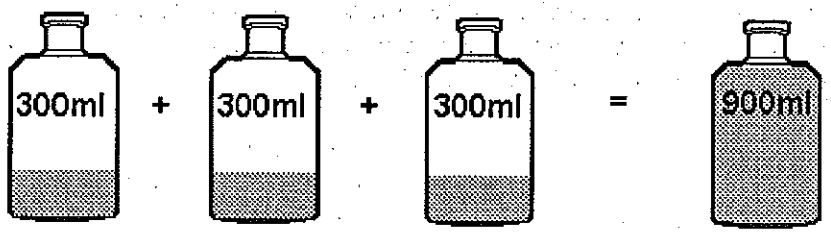
Prior planning is very important for collecting your storm water samples. Chapter 3 has a discussion of sampling types and techniques to consider before you undertake the task of sampling. All of the sampling equipment must be cleaned and prepared before sampling a storm event (in addition, see Chapter 3).

To collect a 30 minute time weighted composite sample of three subsamples:

- collect your first sample within 10 minutes from the time of first noticeable runoff,
- next sample should be collected within 10 minutes after the first,
- final sample should be collected after an additional 10 minutes.

These three samples will be combined (see Figure 4-2) to make a *first flush* time weighted composite sample that you will submit to a laboratory for analysis. These grab samples may be collected either manually or automatically, as discussed below.

Figure 4-2. Compositing three collected sample aliquots to make one sample.



4.4.1 MANUAL SAMPLES

Collect a manual sample by inserting a container under (or down) current of a discharge with the container opening facing upstream. Outfalls which are harder to reach may require the use of some ingenuity (such as those discussed in Chapter 3) to collect samples. The following procedures presented in Table 4-3 should be used to collect manual samples either as a part of your composite sample or as grab type samples.

Specialized equipment and monitoring procedures may be needed, particularly in situations where storm water discharges are inaccessible. For example:

- when sampling for oil & grease (O&G) and volatile organic compounds (VOCs), use equipment that safely and securely houses O&G bottles or VOC vials. This may be necessary because O&G will cling to containers and so it should not be transferred from one container to another. Excessive aeration during sample collection or transfer may result in the partial escape of VOCs.

- do not collect samples in containers that already contain preservatives. Take the sample in a separate container and transfer the water into the bottles containing preservative that will be sent to the laboratory. All equipment and containers that come into contact with the sample must be clean to avoid contamination. Additionally, sample collection equipment and container materials should be totally unreactive to prevent leaching of pollutants. The previous chapter discusses cleaning procedures in detail.

TABLE 4-3. RECOMMENDED PROCEDURES FOR COLLECTING MANUAL SAMPLES

- Label sample containers before sampling event
- Take a cooler with ice to the sampling site
- Collect the sample from the middle of the water column at the center of the channel
- Avoid stirring up bottom sediments in the channel
- Hold the container so the opening faces upstream
- Avoid touching the inside of the container to prevent contamination
- Keep the sample free from uncharacteristic floating debris
- Keep each sample separate and labelled clearly until compositing
- Use safety precautions (see Chapter 2)

4.4.2 AUTOMATIC SAMPLES

Samples can also be collected using preprogrammed automatic samplers. The programming is specific to the type of automatic sampler. Some samplers are portable and have been developed specifically to sample for storm water discharges. These samplers are frequently attached to rain gauge and/or a flow sensor and can be programmed to initiate sample collection by one or more of the following conditions: (1) depth of flow in a channel; (2) rainfall in inches; (3) flow rate; (4) time; and (5) external signal. A sample can be collected in separate containers and composited later, or it can be composited into a single sample container during sampling so as to save time and mistakes.

Planning is very important when using an automatic sampler. First, all equipment must be properly cleaned, particularly the tubing and the sample containers. There are several different types of tubing available, including rubber and Tygon tubing. Frequently, Tygon tubing is preferred since it generally does not leach contaminants. Deionized water should be drawn through the sampler to remove any remaining pollutant residuals before you collect samples. The tubing should be replaced periodically to avoid algae or bacterial growth.

Sampling personnel must use appropriate, well cleaned containers. Chapter 3 has information on cleaning procedures for all equipment. Samplers should be programmed, set up, and supplied with a source of power. Properly charged batteries should be readily available for portable samplers before a storm event and as a backup power supply in case of power failure. Automatic samplers that use battery power must have the battery charge checked routinely, as per the manufacturers instructions. In addition, most automatic samplers will need to be reset for each storm that you plan to sample. Finally, as previously discussed in section 4.4.1 of this chapter, although automatic samplers may be useful in most situations, several parameters are cannot be collected by automatic sampler. These pollutants include fecal streptococcus, fecal coliform, oil and grease and VOCs that should be collected using manual grab sampling procedures.

4.5 COMPOSITING SAMPLES

Be certain to use a container for compositing that will be large enough for the entire sample. It should also have volume measurement markings to be certain that the total volume of your composited samples exceeds the amount you will need for the analysis of all of the parameters to be analyzed (see Table 4-1).

Your samples are already collected on a time basis, so compositing your sample is a fairly easy procedure. To composite and split your sample, you should:

- Pour equal volumes of each individual sample into the compositing container,
- Gently mix the composite to allow for an even blend of the sample. (Be certain that whatever you choose to stir the mixture is clean and is constructed from none of the constituents for which you are sampling),

- The composite should be poured into the containers supplied by the bottles for delivery to the laboratory,

- Preservatives should be added as needed. (In some cases the laboratory bottles may already contain preservatives and this should be determined ahead of time).

As stated in the previous section, automatic samplers will often allow you to collect all samples into one container, so less of these directions will apply.

CHAPTER 5 ANALYZING A STORM WATER SAMPLE

Much of the information gathered before and during sampling, such as storm characteristics, will help you to decide if a sample is acceptable and if the sample should be submitted for analysis. This chapter focusses upon the steps to take after the collection of a sample. These post-sampling steps must be considered to ensure that the sample is suitable for analysis. These are:

- sample handling and preservation
- maximum holding times
- sample documentation, identification, and labeling
- packaging and shipping of samples

5.1 SAMPLE HANDLING AND PRESERVATION

Samples must be handled and preserved in accordance with the information in Appendix C or provided by your certified laboratory. This chapter describes acceptable analytical methods, including requirements regarding sample holding times, containers, sizes, and preservation requirements. For each pollutant or parameter to be analyzed, Appendix C includes information on:

- container types to be used to store the samples after collection
- procedures to preserve the samples
- the maximum holding time allowed for each parameter.

Most laboratories can provide clean sample containers, preservatives, sealing, chain-of-custody forms and can advise further on sample handling and preservation.

Preservation techniques ensure that the sample remains representative of the storm water discharge at the time of collection. Since many sampled pollutants are unstable (at least to some extent), the sample should be analyzed immediately or preserved to minimize changes during its holding time. You should preserve most samples, regardless of the time of analysis, because immediate analysis is not always possible.

Problems may be encountered when composite samples are collected. Sample deterioration can take place during the compositing process. It is necessary to preserve or stabilize the samples during compositing, in addition to preserving aggregate samples before shipment to the laboratory.

Preservation techniques vary depending on the pollutant parameter to be measured; therefore, consult with your laboratory to help you to understand proper preservation techniques. It is important to verify that the preservation techniques for one parameter do not influence the analytical results of another in the same sample.

Sample preservation techniques can consist of refrigeration, pH adjustment, and/or chemical fixation. An adjustment of the sample pH is necessary to stabilize the target analyte (e.g., addition of NaOH stabilizes cyanide); acidification of total metal samples ensures that metal salts do not precipitate. Samples must be put on ice or refrigerated to reduce the sample decomposition. **Do not use dry ice.** You should put ice in durable plastic bags which will help to avoid any damage of sample bottle labels prior to analysis. Icing or refrigeration should continue after the sample has been composited. And you will need to ice the samples during shipment to the laboratory. The analytical laboratory may provide chemicals necessary for preservation, or may tell sampling personnel where they can be purchased.

Although Appendix C provides information on required sample containers, preservation techniques, and holding times, some more commonly monitored parameters warrant additional discussion.

Cyanide. Cyanide is very reactive and unstable. You should contact your laboratory for their recommendations on sampling techniques and materials for preserving samples for cyanide. If the sample cannot be analyzed immediately, it must be preserved by pH adjustment after collection. However, if chlorine may be present, you must follow procedures to eliminate residual chlorine and sulfides prior to adjusting the pH. In such case, the sample should be tested for residual chlorine by using potassium iodide-starch test paper previously moistened with acetate buffer. If the sample contains residual chlorine (a blue color shows the need for treatment), ascorbic acid must be added 0.6 grams (g) at a time until the tests produce a negative result; then, an additional 0.6 g of ascorbic acid should be added to the sample.

For samples containing sulfides, the sulfides may be removed, in which case the maximum holding time is to 14 days. Sulfides must be removed as follows:

- Use lead acetate paper moistened with an acetic acid buffer solution to test for the presence of sulfide. Darkening of the lead acetate paper shows sulfide is present in the sample.
- Add cadmium nitrate to the sample in a manner similar to the ascorbic acid until the test is negative.
- Filter with a 0.45 micrometer (μm) filter and prefilter combination immediately after.

After eliminating chlorine and sulfide residuals, the sample pH should be adjusted to greater than 12.0 standard units (s.u.) and chilled to 4°C.

If you suspect that cyanide is present, the sampling personnel should bring all applicable materials mentioned above to the sampling location.

Volatile organic compounds (VOCs). Sampling for VOCs should be done by collecting a grab sample, not composite sample. In compositing a sample, the sampling personnel would have to mix it thoroughly and this mixing action would aerate the sample and cause volatiles to be lost and produce inaccurate results.

Sampling for VOCs requires the use of a glass vial. The vial should contain a teflon-coated septum seal. Volatiles will escape from the water to the air if you have entrapped any air in the container. Therefore, the sample should be collected so that after the screw cap and septum seal are applied, no air bubbles are in the container. The following procedures should be followed to ensure that the vial contains no air bubbles:

- Fill the vial until a reverse meniscus forms above the top of the vial
- Screw on the cap (the excess sample will overflow)
- Invert the vial to check for the presence of air bubbles
- If you can see air bubbles, the vial should be opened, emptied, then completely refilled, and the first three actions should be repeated.

Organics and pesticides. The procedures affecting organics and pesticides [base/neutral/acids and pesticide polychlorinated biphenyls (PCB's)] are less complex than VOC procedures. Glass containers must be used for sample collection purposes, amber glass should be used to eliminate the potential for reactivity caused by light. These samples should be maintained at 4°C during storage and shipment. If residual chlorine is present, add 0.008 percent sodium thiosulfate ($NA_2S_2O_3$) to the sample to preserve organic samples. You can use a small color indicator test kit to decide if chlorine is present. Eighty ml of ($NA_2S_2O_3$) per liter of sample must be added and mixed well until chlorine tests show a negative result. This procedure is according to methods 604 and 625 of s. NR 219 Table D., Wis. Admin. Code. Pesticide samples must be adjusted to a pH between 5 and 9.

Oil and grease (O&G). O&G tends to adhere to the surfaces that it touches. Therefore, it should not be transferred from one container to another; a 1-liter container should be used to take the sample. The container used for O&G must be made of glass and haave a teflon insert included in the container's lid. If teflon is not available, you may use aluminum foil that extends out from under the lid. Samples for O&G must be preserved by adding sulfuric acid (H_2SO_4) or hydrochloric acid (HCl) to a pH of less than 2 and stored at 4°C.

5.2 SAMPLE HOLDING TIMES

Appendix C gives the maximum holding time for a sample before analysis. The holding time is the maximum amount of time that samples may be held before analysis. Samples exceeding these holding times are invalid and sample collection may have to be repeated.

Additional considerations. Some pollutants have specific analysis requirements due to short holding times that you must consider. For example:

- requirements to analyze immediately (pH, total residual chlorine, temperature, sulfite, and dissolved oxygen)

- requirements to preserve immediately and analyze within 6 hours (fecal coliform and fecal streptococcus)

- requirements to analyze within 24 hours (BOD_5) after compositing.

Due to these requirements, you may find that you need to purchase, borrow, or rent field testing equipment for those parameters that may require field analysis. Remember, like many other parts of sampling, learning how to use this equipment during a storm event is seldom the best time, so read the directions and test the equipment prior to the sampled event. It would be a shame to waste your sample. In many cases analysis in the field may not be required if the laboratory is located nearby. Before you collect your sample, be certain that you get any specific directions from your contracted laboratory, especially any that concern preservation procedures.

Laboratories do not always operate in the evenings or on weekends. As result, you should avoid situations where you might exceed holding times for samples taken in the late afternoon or on a Friday. Close coordination with laboratories is necessary to prevent this from occurring. The latest date and time of delivery that the laboratory will accept should be understood to avoid collecting samples, only to discover they cannot be accepted because of problems with holding times.

5.3 SAMPLE DOCUMENTATION, IDENTIFICATION, AND LABELING

You should submit information to the laboratory with the sample to ensure proper handling by the laboratory. Figure 5-1 is an example form that can be used to document the following information.

- unique sample or log number. All samples should be assigned a unique identification number. If there is a serial number on the transportation case, the sampling personnel should add this number to the field records.

- date and time of sample collection. Date and time of sample collection (including notation of a.m. or p.m.) must be recorded. In composite samples, the sequence of times and aliquot size should be noted.

- source of sample, including facility name and address. Use the outfall identification number from the site map with a narrative description; include a diagram referring to the particular sampled outfall.

- name of sampling personnel. The names and initials of the persons involved with taking the sample must be included.

- sample type. Each sample should indicate whether it is a grab or composite sample. If the sample is a composite, the volume and frequency of individual aliquots should be noted.

FIGURE 5-1. FIELD SHEET FOR SAMPLE DOCUMENTATION		
Sample Source	Sample ID #	**Date:**
Facility Name		**Time:** **:** **a.m./p.m.**
Address	Person Performing Sampling	
Outfall ID #	Signature	
Description	Preservation Method	
Comments		
Visual Flow Description	Ship Via: Stable Shipping Paper/Manifest	
Analyses Required		

- preservation used. Any preservatives (and the amount) added to the sample should be recorded. The method of preservation (e.g., refrigeration at 4°C) should be shown.

- analysis required. All parameters for which the sample must be analyzed at the laboratory should be specified.

- date, time and documentation of sample shipment. The shipment method (e.g., air, rail, or bus) as well as the shipping papers or manifest number should be noted.

- comments. All relevant information about the sample or the sampling site should be recorded. Such comments could include the condition of the sample site, observed characteristics of the sample, environmental conditions that may affect the sample, and problems encountered during sampling.

Prior to collecting your sample, you may find it helpful to attach, a waterproof, gummed sample identification label or tag to each sample container. This label should contain relevant information for sample analysis, such as:

- facility name
- name of the sample collector
- sample identification number
- date and time of sample collection
- type of analysis required
- location of sample collection
- preservatives used
- type of sample (grab, or time or flow weighted composite).

Sample lids should be used to protect the sample's integrity from the time of collection to the time it is analyzed in the laboratory. The lid should contain the collector's name, the date and time of sample collection, and a sample identification number. Information on the seal must be identical to the information on the label. In addition, the lid should be taped shut so that the seal must be broken to open the sample container. Caution should be taken to ensure that glue from tape and label tag wires do not contaminate samples, particularly those containing volatile organics and metals. Also, waterproof ink should be used to avoid smearing on the label from melted ice used for cooling.

5.4 SAMPLE PACKAGING AND SHIPPING

If the samples cannot be hand-delivered to the laboratory or analyzed in an onsite laboratory, they should be placed in a transportation case (e.g., a cooler) along with the chain-of-custody record form, pertinent field records, and analysis request forms, and shipped to the laboratory. Glass bottles should be wrapped in foam rubber, plastic bubble wrap, or other material to prevent breakage during shipment. The wrapping can be secured around the bottle with tape. The container lid also should be sealed with tape. Samples should be placed in ice or a synthetic ice substitute that will maintain the sample temperature at 4°C throughout shipment. Ice should be placed in double-wrapped watertight bags so the water will not leak from the shipping case. Metal or heavy plastic ice chests make good sample transportation cases. Filament tape wrapped around each end of the ice chest guarantees that it will not open during transport. Sampling records (preferably laminated or waterproof) can be placed in a waterproof envelope and taped to the inside of the transportation case to avoid getting them wet in case a sample container or an ice bag leaks. You should also seal shipping containers to prevent tampering. In addition, keep a copy of all sampling records onsite in case they are requested by the WDNR.

Most samples will not require any special transportation precautions except careful packaging to prevent breakage and/or spillage. If the sample is shipped by common carrier or sent through the U.S. mail, it must comply with Department of Transportation Hazardous Materials Regulations (49 CFR Parts 171-177). Air shipment of hazardous materials samples may also be covered by requirements of the International Air Transport Association (IATA). Before shipping a sample, ask your laboratory if there are any special shipping requirements. Storm water samples are not generally considered hazardous materials, but in the event of a spill, leakage, etc., at the collection site hazardous materials may be present in the samples. Be aware, before sampling, of what hazardous materials may be in the discharge drainage area. If you suspect the presence of hazardous materials, do not sample unless properly trained.

NOTES

APPENDICES

APPENDIX A WHERE TO CALL FOR HELP.

Getting started at your industrial site is not always easy. Even after studying this manual, you still may be confused about some aspect of chemical monitoring. There are many engineering firms that can provide expert assistance with many aspect of industrial storm water, from sampling to pollution prevention. These firms are listed in the telephone yellow pages under "Environmental & Ecological Services", or a similar heading.

If you would like to discuss sampling problems, WDNR staff members are available at (608) 267-7694, or write:

Storm Water Section
Bureau of Wastewater
P.O. Box 7921
Madison, WI 53707-7921

APPENDIX B A SKELETON SAMPLING PROGRAM

This section should be an overview of the manual, touching on the highlights of sampling procedures.

Pre-sampling.

1. Determine the extent and type of sampling that you will need to perform.
   A. how many sampling points will you need?
   B. are there any outfalls substantially similar activities and runoff?
   C. how many pollutants do you feel will still remain in your runoff after the implementation of Storm Water Pollution Prevention Plan (SWPPP)?
   D. do any of the outfalls need non-typical sampling procedures?
   E. will you need additional personnel to sample your site or should you sample some of your outfalls in a different storm?

2. Contract with a laboratory for chemical determination services.

3. Obtain sampling equipment.
   A. rain guage (must measure to 0.1" of precipitation)
   B. sample collection bottles
   C. laboratory (transport) bottles
   D. safety gear

4. Train any sampling personnel needed.

Sampling.

1. Collect each of subsamples for compositing.

2. Read the rain guage (0.2" minimum needed).

3. Composite (mix) the subsamples.

4. Split the composited sample for the laboratory.

5. Add preservatives to the samples (if necessary).

6. Store samples at (or close to) 36°F. (4°C.).

Post-sampling.

1. Send samples to laboratory (keep them cold).

2. Transpose the results returned from the laboratory onto your Discharge Monitoring Results (DMR) sheet and mail the sheet to the WDNR.

APPENDIX C - REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES

REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES				
Parameter	Units	Container[1]	Preservative[2],[3]	Maximum HoldingTime[4]
Bacterial Tests				
Coliform, fecal and total	number per 100 mL	P, G	Cool, 4°C 0.008 %$NA_2S_2O_3$(5)	6 hours
Fecal streptococci	number per 100 mL	P, G	Cool, 4°C 0.008 %$NA_2S_2O_3$(5)	6 hours
Inorganic Tests				
Acidity (as $CaCO_3$)	mg/L	P,G	Cool, 4°C	14 days
Alkalinity (as $CaCO_3$)	mg/L	P,G	Cool, 4°C	14 days
Ammonia (as N)	mg/L	P,G	Cool, 4°C H_2SO_4 to pH < 2	28 days
Biochemical oxygen demand	mg/L	P,G	Cool, 4°C	48 hours
Bromide	mg/L	P,G	None required	28 days
Chemical oxygen demand	mg/L	P,G	Cool, 4°C H_2SO_4 to pH < 2	28 days
Chloride	mg/L	P,G	None required	28 days
Chlorine, total residual	mg/L	P,G	None required	Analyze immediately
Color		P,G	Cool, 4°C	48 hours
Cyanide, total and amenable to chlorination	µg/L	P,G	Cool, 4°C NaOH to pH < 12, 0.6g ascorbic acid (5)	14 days (6)
Fluoride	mg/L	P	None Required	28 days
Hardness (as $CaCO_3$)	mg/L	P,G	HNO_3 to pH < 2 H_2SO_4 to pH < 2	6 months
Hydrogen ion (pH)		P,G	None required	Analyze immediately
Kjeldahl and organic Nitrogen	mg/L	P,G	Coo, 4°C H_2SO_4 to pH < 2	28 days
Metals (7)				
Chromium VI	µg/L	P,G	Cool, 4°C	28 hours
Mercury	µg/L	P,G	HNO_3 to pH < 2	28 hours
Metals, except above	µg/L	P,G	HNO_3 to pH < 2	6 months
Nitrate (as N)	mg/L	P,G	Cool, 4°C	48 hours

REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES				
Parameter	Units	Container[1]	Preservative[2],[3]	Maximum HoldingTime[4]
Nitrate-nitrite	mg/L	P,G	Cool, 4°C H_2SO_4 to pH < 2	28 days
Nitrite (as N)	mg/L	P,G	Cool, 4°C	48 hours
Oil & Grease	mg/L	G	Cool, 4°C H_2SO_4 or HCl to pH < 2	28 days
Organic carbon	mg/L	P,G	Cool, 4°C HCl or H_2SO_4 to pH < 2	28 days
Orthophosphate	mg/L	P,G	Filter immediately Cool, 4°C	48 hours
Phenols	µg/L	G only	Cool, 4°C H_2SO_4 to pH < 2	28 days
Phosphorus (elemental)	mg/L	G	Cool, 4°C	48 hours
Phosphorus, total	mg/L	P,G	Cool, 4°C H_2SO_4 to pH < 2	28 days
Residue, total (Total solids)	mg/L	P,G	Cool, 4°C	7 days
Residue, filterable (Dissolved solids)	mg/L	P,G	Cool, 4°C	7 days
Residue, nonfilterable (T. Suspended solids)	mg/L	P,G	Cool, 4°C	7 days
Residue, settleable (Settleable solids)	mg/L	P,G	Cool, 4°C	48 hours
Residue, volatile (Volatile solids)	mg/L	P,G	Cool, 4°C	7 days
Silica	mg/L	P	Cool, 4°C	28 days
Specific conductance	µmhos/cm	P,G	Cool, 4°C	28 days
Sulfate (as SO_4)	mg/L	P,G	Cool, 4°C	28 days
Sulfide (as S)	mg/L	P,G	Cool, 4°C, add zinc acetate plus sodium hydroxide to pH > 9	7 days
Sulfite (as SO_3)	mg/L	P,G	None required	Analyze immediately
Surfactants	mg/L	P,G	Cool, 4°C	48 hours
Temperature	° C.	P,G	None required	Analyze immediately
Turbidity	NTU	P,G	Cool, 4°C	48 hours
Organic Tests (8)				
Purgeable halocarbons	µg/L	G, Teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$ (5)	14 days

REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES				
Parameter	Units	Container[1]	Preservative[2],[3]	Maximum HoldingTime[4]
Purgeable aromatics	µg/L	G, Teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$ (5) HCl to pH<2 (9)	14 days
Acrolein and acrylonitrile	µg/L	G, Teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$ (5) adjust pH to 4-5 (10)	14 days
Phenols (11)	µg/L	G, Teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$ (5)	7 days until extraction, 40 days after extraction
Benzidines (11)	µg/L	G, Teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$ (5)	7 days until extraction (13)
Phthalate esters (11)	µg/L	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Nitrosamines (11), (14)	µg/L	G, Teflon-lined cap	Cool, 4°C store in dark 0.008% $Na_2S_2O_3$	7 days until extraction, 40 days after extraction
PCBs (11) acrylonitrite	µg/L	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Nitroaromatics and isophorone (11)	µg/L	G, Teflon-lined cap	Cool, 4°C store in dark 0.008% $Na_2S_2O_3$ (5)	7 days until extraction, 40 days after extraction
Polynuclear aromatic hydrocarbons (11)	µg/L	G, Teflon-lined cap	Cool, 4°C store in dark 0.008% $Na_2S_2O_3$ (5)	7 days until extraction, 40 days after extraction
Haloethers (11)	µg/L	G, Teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$ (5)	7 days until extraction, 40 days after extraction
Chlorinated hydrocarbons (11)	µg/L	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
TCDD (11)	µg/L	G, Teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$ (5)	7 days until extraction, 40 days after extraction
Pesticides Tests				
Pesticides (11)	µg/L	G, Teflon-lined cap	Cool, 4°C pH 5-9 (15)	7 days until extraction, 40 days after extraction

(1) Polyethylene (P) or Glass (G).

(2) Sample preservation should be performed immediately upon sample collection. For composite chemical samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then chemical samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

(3) When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such

REQUIRED CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES				
Parameter	Units	Container[1]	Preservative[2],[3]	Maximum HoldingTime[4]

compliance. For the preservation requirements of Table II, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO_3 in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid H_2SO_4) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weights or less (pH about 12.30 or less).

(4) Samples should be analyzed as soon as possible after collection. The times listed are the maximum times the samples may be held before analysis and still be considered valid.

(5) Should only be used in the presence of residual chlorine.

(6) Maximum holding time is 24 hours when sulfide is present. Optionally all samples may be tested with lead acetate paper before pH adjustments in order to determine of sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

(7) Samples should be filtered immediately on-site before adding preservative for dissolved metals.

(8) Guidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

(9) Sample receiving no pH adjustment must be analyzed within seven days of sampling.

(10) The pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within 3 days of sampling.

(11) When the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times should be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4°C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting the pH to 6-9; samples preserved in this manner may be held for seven days before extraction and for forty days after extraction. Exceptions to this optional preservation and holding time procedure are noted in footnote 5 (re the requirement for thiosulfate reduction of residual chlorine), and footnotes 12, 13 (re the analysis of benzidine).

(12) If 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0±0.2 to prevent rearrangement to benzidine.

(13) Extracts may be stored up to 7 days before analysis if storage is conducted under an inert (oxidant-free) atmosphere.

(14) For the analysis of diphenylnitrosamine, add 0.008% $Na_2S_2O_3$ and adjust pH to 7-10 with NaOH within 24 hours of sampling.

(15) The pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $Na_2S_2O_3$. (5)

Source: NR 219 Wisc. Admin. Code

APPENDIX D GLOSSARY

Aliquot: A discrete sample used for analysis.

Base Flow: That portion of the water transported through a storm water conveyance system which is not a direct storm water contribution.

Best Management Practice (BMP): Structural devices or nonstructural practices that are designed to prevent pollutants from entering into storm water flows, to direct the flow of storm water or treat polluted storm water flows.

Biochemical Oxygen Demand (BOD): The quantity of oxygen consumed during the biochemical oxidation of matter over a specified period of time, usually 5 days.

Calibration: To check the precision or accuracy of measuring equipment.

Certified Laboratory: A laboratory which performs tests for hire in connection with a covered program and which receives certification under s. 144.95(7), Stats., or receives reciprocal recognition under s. 144.95(5), Stats.

Chain-of-Custody: Procedures used to minimize to possibility of tampering with samples.

Chemical Oxygen Demand (COD): Measurement of the oxydizable matter found in a runoff sample, a portion of which could deplete dissolved oxygen in receiving waters.

Conveyance: A channel or passage which conducts or carries water including, but not necessarily limited to, any pipe, ditch, channel, tunnel, conduit, well, or container.

Detection Limit: The lowest concentration level that can be determined to be significantly different from a blank for a particular analytical test method.

Detention Pond: A basin designed to temporarily hold storm water runoff to control peak discharge rates, and to provide gravity settling of pollutants.

Note: NR 216.28(4)(e)2 Wis. Admin. Code, allows a Tier 1 permittee to collect a grab sample from the discharge, rather than requiring a composite sample, for detention ponds with greater than a 24 hour holding time.

Discharge: Any addition of any pollutant to the waters of Wisconsin by any conveyance.

Effluent: Any discharge flowing from a conveyance.

Error: Difference between the true and the expected value and the measured value of a parameter.

General Permit: A permit for the discharge of pollutants issued by the Department under s. 147.023, Stats., which allows the Department to issue a permit applicable to a designated area of the state authorizing discharges from specified categories or classes of point sources, instead of issuing a separate permit to an individual point source.

Holding or Detention Time: The amount of time that a unit of water is actually present in the practice. Theoretical detention time for a runoff event is the average time a unit of water resides in the pond (BMP) over the period of release from the pond (BMP).

Infiltration: The penetration of water into and through the soil.

Outfall: Point source where an effluent is discharged into receiving waters.

pH: The negative logarithm of the hydrogen ion activity or the logarithm of the reciprocal of hydrogen activity, in a liquid solution.

Point Source: Under s. 147.015(12), Stats., means a source from either a discernible, confined and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, well, discrete fissure, container, rolling-stock, concentrated animal feeding operation or vessel or other floating craft from which pollutants may be discharged into the waters of the state or into a publicly owned treatment works, except for a conveyance that conveys only storm water.

Note: if your facility has or should have a permit for the discharge of storm water associated with industrial activity, the storm water is considered to be contaminated storm water, not *only storm water*.

Pollutant: Generally, any substance introduced into the environment that adversely affects the usefulness of a resource.

Precipitation: Any form of rain or snow.

Raw Material: Any product or material that is converted into another material by processing or manufacturing.

Runon: Storm water surface flow or other surface flow which enters property other than that where it originated.

Runoff: That part of precipitation that runs off the land into streams or other waters of the state. It can carry pollutants from the air and land into the receiving waters.

Sanitary Sewer: A system of pipes that carries domestic or industrial sewage to a treatment works plant.

Sedimentation: The process of depositing soil particles, clays, sands, and other sediments that were picked up by runoff.

Significant Materials: Under NR 216.002(26), Wis. Admin. Code, these are defined as being materials related to industrial activity that may contaminate storm water, including, but not limited to: raw materials; fuels; materials such as solvents, detergents and plastic pellets; finished materials such as metallic products; raw materials used in food processing or production; hazardous substances designated under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA); any chemical the facility is required to report pursuant to the Emergency Planning and Community Right-to-Know Act (EPCRA), also Section 313 of Title III of the Superfund Amendments and Reauthorization Act (SARA); fertilizers; pesticides; and waste products such as ashes, slag, and sludge that have the potential to be released to be released with storm water discharges.

Storm Water: Storm water runoff, snow melt runoff, discharged to the surface or ground waters of the state.

Storm Water Discharge Associated with Industrial Activity: Discharge from any conveyance which is used for collecting and conveying storm water which is directly related to those processes identified as industrial activity or bulk storage under NR 216.21(2) Wis. Admin. Code.

Subsample: A portion taken from a sample.

Toxic Materials: Substances that cause death, disease, and/or birth defects in organisms that ingest or absorb them.

Turbidity: Describes the capability of light to pass through water.