Chapter 4
WATER QUALITY MONITORING

This chapter provides guidance for collection of water quality samples for assessment of stormwater Best Management Practice (BMP) performance. It is intended to be used in conjunction with Chapter 2 Developing a Monitoring Plan and Chapter 3 Hydrologic and Hydraulic Monitoring. Topics addressed include: water quality parameters and analytical methods; selection of sampling locations; considerations for collecting discrete and composite samples, manual sampling, and automatic sampling; and field and laboratory QA/QC. Water quality monitoring is a multifaceted, complex topic that is the subject of many textbooks and manuals. For more information on specific topics, Exhibit 4-1 lists several references that provide more detail.

Exhibit 4-1. Resources for More Detailed Information on Water Quality Monitoring

Burton and Pitt. 2001. *Stormwater Effects Handbook: A Toolbox for Watershed Managers, Scientists, and Engineers*. http://www.epa.gov/ednnrmrl/publications/books/handbook/index.htm

Caltrans. 2003. *Caltrans Comprehensive Monitoring Protocols Guidance Manual*. CTSW-RT- 03-105.51.42. http://www.dot.ca.gov/hq/env/stormwater/special/newsetup/index.htm

EPA. 1992. *National Pollutant Discharge Elimination System Stormwater Sampling Guidance Document.* EPA 833-B-92-001. http://www.epa.gov/npdes/pubs/owm0093.pdf

EPA. 1997. *EPA Monitoring Guidance for Determining the Effectiveness of Nonpoint Source Controls.* EPA 841-B-96-004. http://nepis.epa.gov/EPA/html/Pubs/pubtitleOW.htm

Federal Highway Administration. 2001. *Guidance Manual for Monitoring Highway Runoff Water Quality*. http://www.fhwa.dot.gov/environment/h2o_runoff/index.htm

Granato et al. 2002. *National Highway Runoff Water-Quality Data and Methodology Synthesis, Volume I --Technical Issues for Monitoring Highway Runoff and Urban Stormwater*. http://ma.water.usgs.gov/fhwa/fhwaep.htm

Keith, L.H. (ed.). 1996. *Principles of Environmental Sampling*, 2nd ed. American Chemical Society.

Shaver et al. 2007. *Fundamentals of Urban Runoff Management: Technical and Institutional Issues*, Second Edition. EPA and North American Lake Management Society. http://www.nalms.org/Resources/PDF/Fundamentals/Fundamentals_full_manual.pdf

State Water Resources Control Board and the Southern California Stormwater Monitoring Coalition. 2004. *Southern California Coastal Water Research Project, Model Monitoring Program for Municipal Separate Storm Sewer Systems in Southern California*. Technical Report #419. ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/419_smc_mm.pdf

U.S. Department of Agriculture-National Resources Conservation Service. 1996. *National Handbook of Water Quality Monitoring.* 450-vi-NHWQM. http://www.wsi.nrcs.usda.gov/products/W2Q/water_qual/docs/wqm1.pdf

U.S. Geological Survey (USGS). (various dates). *Techniques of Water-Resources Investigations Reports*. Multiple chapters. http://pubs.usgs.gov/twri/

4.1 Water Quality Parameters and Analytical Methods

4.1.1 Selecting Parameters

Stormwater runoff may contain a variety of substances that can adversely affect the beneficial uses of receiving water bodies. To select the parameters to be analyzed for a given monitoring location, consider the following:

- Permit requirements (if any). Permit requirements often specify both the analyte and required analytical method.

- Land uses in the catchment area and associated pollutants. Sources such as the BMP Database (http://www.bmpdatabase.org) and the National Stormwater Quality Database (http://rpitt.eng.ua.edu/Research/ms4/Paper/Mainms4paper.html) have considerable information on pollutants associated with various land uses.

- Existing monitoring data (if any) for the catchment area. Previous monitoring data can be helpful in refining the parameter list; however, it is important to understand the purposes and methods of previous studies to place the data in context.

- Beneficial uses of the receiving water. Information on water quality within a stormwater drainage system often is used to indicate whether discharges from the system are likely to adversely affect the receiving water body.

- Anticipated pollutant removal mechanisms and targeted pollutants for BMP being monitored. When selecting analytes, it may be beneficial to include parameters associated with the targeted pollutant, as well as inexpensive parameters with similar characteristics to the target pollutant that can serve as surrogates. For example, if total phosphorus is the regulated parameter, it may also be beneficial to include orthophosphate since BMP effectiveness may be influenced by the portion of total phosphorus that is in the dissolved form. Additionally, inexpensive basic water quality characterization parameters such as temperature, conductivity, and pH among others should typically be included.

- Overall program objectives and resources. The parameter list should be adjusted to match resources (personnel, funds, time).

If program objectives require assessing a large number of parameters (based on a review of land uses, prior monitoring data, and so on), consider a screening approach where samples collected during the first one or two storms are analyzed for a broad range of parameters of potential concern. Parameters that are not detected, or are measured at levels well below concern, can then be dropped from some or all subsequent monitoring events. To increase the probability of detecting the full range of pollutants, the initial screening samples should be collected from storms that occur after prolonged dry periods.

A recommended list of basic constituents (along with recommended method detection limits enabling comparison of stormwater samples to water quality criteria) for BMP monitoring is

presented in Exhibit 4-2 below. The choice of which constituents to include as standard parameters is somewhat subjective and, ultimately, site-specific conditions and study objectives must be considered. It is important to note that not all of the parameters listed in Exhibit 4-2 are suitable for automatic samplers—some level of manual sampling would also be required to evaluate all of the listed parameters.

The following factors were considered in developing the recommended list of monitoring parameters:

- The pollutant has been identified as prevalent in typical urban stormwater at concentrations that could cause water quality impairment (EPA 1983; Pitt et al. 2004; and recent municipal National Pollutant Discharge Elimination System data).

- The analytical result can be related back to potential water quality impairment.

- Sampling methods for the pollutant are straightforward and reliable for a moderately careful investigator.

- Analysis of the pollutant is economical on a widespread basis.

- Some parameters are listed because they may affect the function of some BMPs or affect the toxicity of certain pollutants, even if the parameter itself is not a pollutant of concern. For example, temperature can affect the function of infiltration facilities; pH and temperature can affect ammonia toxicity to aquatic life; and hardness and pH can affect toxicity of certain metals.

A few practical comments regarding analyte groups include:

- Nutrients: Where budget constraints are an issue, total phosphorus and total nitrogen should be the minimum parameters to monitor, thereby avoiding additional filtration, preservation, and processing requirements associated with other forms of the analytes. Nutrients can repartition or be metabolized during storms. As with metals, the speciation of nutrients during stormflows may be less important than the post-discharge concentrations in receiving waters. For some types of BMPs, it may be more meaningful to characterize geochemical redistribution of nutrients within BMPs between storms than to focus on within-storm transport. For more information on nutrient monitoring, see Hem (1992) and EPA (2000). For regulatory background, see EPA's Water Quality Criteria for Nitrogen and Phosphorus Pollution website (http://www.epa.gov/waterscience/criteria/nutrient/).

- Organic Compounds: Organic compounds include polycyclic aromatic hydrocarbons (PAHs), other semi-volatiles, volatiles, herbicides, and pesticides. Sampling of these compounds is not addressed in detail in this manual. Nonetheless, there are a number of issues to be considered. For example, containers (metal and glass) and processing materials recommended for sampling organics are not recommended for sampling metals. Automatic samplers can increase volatilization by suction and by squirting samples into vented containers. Many organic compounds are commonly measured at or near detection

limits. Therefore, protocols are more sensitive to contamination and data are harder to analyze. As with metals, many organic compounds are associated with sediments. Whole-water sampling may be a better strategy for sampling organic compounds. See Shelton (1997) and Shelton and Capel (1994) for more information.

- Metals: There are a number of issues associated with metals sampling, which are discussed in Section 4.1.2.

- Suspended Solids and Gross Solids: Since the original release of this monitoring manual in 2002, substantial research has been conducted related to issues associated with monitoring suspended solids and gross solids. These topics are discussed in Sections 4.1.3 and 4.1.4. (Sampling of deposited sediments is discussed in Section 4.4.)

- Microbiology: At the time this manual was released, EPA was in the process of revising recreational water quality criteria, including considering whether alternative microbiological indicators of fecal contamination should be used. See EPA's Recreation Water Quality Criteria website (http://www.epa.gov/waterscience/criteria/recreation/) for the latest information on this effort. In the interim, Section 4.1.5 provides a brief discussion of some microbiological monitoring issues.

As a final note, researchers should also keep in mind that probe-measured parameters such as specific conductance, turbidity, and others can be used to augment information from limited water quality sampling efforts requiring laboratory analysis. For example, flow and specific conductance can be used to estimate annual inlet and outlet loads of chlorides. Specific conductance records can also provide a "free" tracer test. Continuous monitoring records from probes can also provide helpful context for data from sampled storms. For more information, see *Guidelines and Standard Procedures for Continuous Water-Quality Monitors: Station Operation, Record Computation, and Data Reporting* (Wagner et al. 2003, http://pubs.usgs.gov/tm/).

Exhibit 4-2.
Typical Urban Stormwater Runoff Constituents and Recommended Detection Limits

Parameter	Common Units	Target Detection Limit
Conventional		
pH	s.u.	N/A
Conductivity	µs/cm	N/A
Temperature	C	N/A
Turbidity	n.t.u.	5.0
Total Suspended Solids (TSS)	mg/L	5.0
Suspended Sediment Concentration (SSC)	mg/L	5.0
Total Hardness	mg/L	1.0
Chloride	mg/L	1.0
Bacteria[1]		
Fecal Coliform	MPN/100 mL	2
E. coli	MPN/100 mL	2
Enterococci	MPN/100 mL	2
Nutrients[2]		
Orthophosphate	mg/L	0.05
Total Phosphorus	mg/L	0.05
Total Kjeldahl Nitrogen	mg/L	0.1
Nitrate + Nitrite	mg/L	0.05
Ammonia Nitrogen	mg/L	0.1
Metals—Total Recoverable		
Cadmium	µg/L	0.2
Copper	µg/L	1
Lead	µg/L	0.2
Zinc	µg/L	1
Metals Dissolved		
Cadmium	µg/L	0.2
Copper	µg/L	1
Lead	µg/L	0.2
Zinc	µg/L	1
Organics		
Organophosphate Pesticides (scan)	µg/L	0.05 - 0.2
Hydrocarbons		
Total Petroleum Hydrocarbons	mg/L	0.5

Note: This list includes constituents found in typical urban stormwater runoff. Additional parameters may be needed to address site specific concerns. See Strecker (1994) and Urbonas and Stahre (1993) for additional guidance.

[1] The upper quantitation limit is typically more significant for bacteria in stormwater monitoring data, which are prone to be right-censored, as opposed to left-censored.
[2] Nutrient contamination of receiving waters such as lakes and the Gulf of Mexico is resulting in greater attention to the various forms of nutrients in runoff. For this reason, multiple forms of nitrogen have been included in this list.

4.1.2 Dissolved vs. Total Metals

Different metal forms (species) show different levels of toxic effects. In general, metals are most toxic in their dissolved, or free ionic form. Specifically, EPA developed revised criteria for the following dissolved metals: cadmium, chromium, copper, lead, nickel, silver, selenium, and zinc. Arsenic and iron are assessed based on total recoverable forms. Total mercury criteria were developed based on mercury residuals in aquatic organisms (food chain effects) rather than based on toxicity. For comparisons with dissolved metal water quality criteria, the dissolved metals fraction usually needs to be determined in some manner. This can either be determined by sample analysis, or in some cases through models.

Analysis results for "dissolved metals" should be reported in the context of type and nominal pore size of filter used in the laboratory analysis. This supplemental information helps the user to differentiate whether the metals are truly ionic or potentially colloidal and complexed. There are many important issues with "dissolved" metals, which are more appropriately characterized as "filtered" metals (Clark 2009). In actuality, only a small proportion of the metals in a filtered water sample may be in the dissolved state as the majority are adsorbed to colloids or bound to humic or fulvic compounds. Other problems include sample contamination, adsorption, desorption, digestion issues, pre- and post-processing holding times, under-acidification, over-acidification, sample splitting procedural problems, and so on. Dissolved metals can partition and repartition within the time required to collect and process a stormflow sample. Dissolved metal sampling artifacts can also significantly affect measured concentration. Because many trace elements are associated with solids, there are more detection-limit issues with filtered metals (Granato et al. 2002).

Other factors to consider with regard to the distribution of pollutants between the dissolved and particulate phases includes where in the system the sample is collected. Runoff collected in pipes with little sediment will generally have a higher percentage of pollutants present in the dissolved form. Runoff collected in receiving waters will generally have a higher percentage of pollutants present in particulate form due to higher concentrations of suspended solids that act as adsorption sites for pollutants. It is difficult to determine how much of the dissolved pollutants found in storm system pipes will remain in the dissolved form when they are mixed with suspended sediments in receiving waters. As a result, it is difficult to determine the ecological significance of moderate levels of dissolved pollutants present within the conveyance system. In addition, hardness and pH values for receiving waters are often different than those for stormwater. For example, in some areas, hardness of runoff appears to increase as it travels across concrete surfaces; therefore, the chemical composition of the drainage system may also have an impact on total versus dissolved metals concentrations (Clark 2009). Hardness and pH affect the bio-availability of heavy metals, further complicating prediction of the ecological impact of dissolved heavy metals. If loads to the receiving waters are of concern (e.g., discharge to a lake known to be a water quality limited water body), it may be desirable to determine total recoverable metals to assess the relative load from different sources. Total recoverable metals data can also be used to assess potential issues involving metals in sediment.

An alternative to dissolved metals analysis is modeling of geochemical speciation of the metals in the runoff, in the BMP, and in the receiving water. If sediment, pH, alkalinity, major ions, hardness, and dissolved organic compounds (DOC) are sampled, models can be used to estimate

metals partitioning. For example, EPA has adopted a biotic ligand model for copper, and WERF is working on biotic ligand models for nickel and other metals. The cost and effort required for collecting pH, major ions, and DOC for a biotic ligand model are much less than the cost for ultra clean (high purity) sampling (e.g., Teflon® equipment, high purity filters, high purity acid, extra samplers for clean-hands-dirty-hands sampling) (Granato 2009).

On a related note, researchers conducting work in multiple locations should be aware that dissolved metals data are less transferable than whole-water metals data because of the previously discussed data quality issues, the varying geochemical conditions that will occur at a given site from storm-to-storm and season-to-season, and the varying geochemical conditions that will occur from site-to-site and region-to-region. For these reasons, researchers should strongly consider collection of whole-water metals and related geochemical data, as an alternative to dissolved metals monitoring. The geochemical data may ultimately be more transferable because this information can be used with geochemical or biotic ligand models to examine conditions that may mobilize metals. With regard to BMP selection, geochemical redistribution of metals within BMPs between storms may be more important to characterize than within-storm transport (Granato 2009).

Finally, if monitoring objectives and site-specific conditions necessitate dissolved metals analysis, researchers should consider ultra-clean sampling procedures. Although ultra-clean monitoring protocols are not necessary for whole-water metal sampling, they have been shown to be very important for filtered-water sampling, even in contaminated waters. Much more operator and sample-processing equipment contact with the sample is needed to obtain a filtered water sample. Even if sampling artifacts are similar for filtered and whole-water samples, the artifacts will have a greater effect on the lower concentrations typically measured for filtered metals. Although ultra-clean monitoring protocols may not be practical in all monitoring studies, researchers should be aware of the issues associated with filtered metals results and carefully weigh the costs and benefits of ultra-clean sampling techniques (Granato 2009).

For more information on issues associated with dissolved versus total metals sampling, see the references in Exhibit 4-3.

Exhibit 4-3. Supplemental Information on Dissolved and Total Metals Monitoring

EPA. 1994. *The Biotic Ligand Model: Technical Support Document for Its Application to the Evaluation of Water Quality Criteria for Copper*. (EPA 822R03027). http://yosemite.epa.gov/water/owrccatalog.nsf/0/e693bcf79893c3e085256e23005fcd3b?OpenDocument

Granato et al. 2002. *National Highway Runoff Water-Quality Data and Methodology Synthesis, Volume I--Technical issues for monitoring highway runoff and urban stormwater*. FHWA-EP-03-054. http://ma.water.usgs.gov/fhwa/fhwaep.htm

Horowitz et al. 1994. *U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water*. OFR 94-539. http://pubs.er.usgs.gov/usgspubs/citfor/ofr/ofr94539?currow=6

Water Environment Research Foundation (WERF). 2004. *Development of a Biotic Ligand Model for Nickel: Phase I*. http://www.werf.org/AM/CustomSource/Downloads/uGetExecutiveSummary.cfm?FILE=ES-01-ECO-10T.pdf&ContentFileID=7450

4.1.3 Measurement of Suspended Solids Concentration

A variety of methods have been employed in stormwater quality studies for quantifying sediment concentration in the water column. The most frequently cited parameter is "TSS" or total suspended solids; however, this label is often generically used to refer to more than one sample collection and sample analysis method, including:

- EPA Method 160.2: Total Suspended Solids (TSS) (Gravimetric, Dried at 103-105ºC). (USEPA 1999).

- American Society for Testing and Materials (ASTM) Method D3977-97(B): Standard Methods for Determining Sediment Concentration in Water (ASTM 1997). The USGS employs this suspended sediment concentration (SSC) method. SSC data are often described as TSS data, although results from the two methods may be significantly different in many cases.

- Standard Method (SM) 2540D: This TSS analytical method originated in wastewater analysis and is promulgated by the American Public Health Association in *Standard Methods for the Examination of Water and Wastewater* (APWA et al. 2005).

Differences in nominal filter pore size, sample mixing, aliquot size and method of aliquot collection, as summarized in Exhibit 4-4, can result in significantly different results from these methods (Clark and Siu 2008). Guo (2007) conducted tests to determine the relationships between the various test methods and found that SSC (using ASTM D3977-97(B)) results were very close to the true concentration of solids in laboratory tests, whereas the EPA Method 160.2 TSS measure was well correlated with SSC, but TSS using SM 2540D was not well correlated with SSC. The study also found that the difference between the SSC and EPA TSS results were

well correlated with particle size, with increasing differences as particle size increased. Clark and Siu (2007) also concluded that correlations between the results and the known sample concentration could be established for TSS samples, dependent on the sample's particle size distribution and on the aliquot collection technique. These results emphasize the need to report not only the analytical method but also the particle size information on the solids in stormwater runoff.

Exhibit 4-4. Comparison of Three TSS/SSC Analytical Methods (Clark and Siu 2008)

Method Requirements	USEPA TSS (160.2) and ISO (11923)	SM TSS (2540D)	ASTM SSC (D3977-97 (B))
Filter Nominal Pore Size	not specified	<2.0 µm	1.5 µm (recommended)
Sample Mixing	shake vigorously	stir plate	decant supernatant and flush bottle with DI water
Aliquot Size	not specified	not specified	entire sample
Method of Aliquot Collection	pour aliquot into graduated cylinder	pipette at mid-depth in bottle; midway between wall and vortex	vortex pour from original bottle

One of the key differences between methods is sample size—the SSC method analyzes the entire sample, whereas the TSS method uses a sub-sample. The process of collecting a representative sub-sample containing larger sediment particles is problematic because large sediment particles (e.g., sand) often settle quickly. Differences between the results obtained from SSC and TSS analytical methods become apparent when sand-sized particles exceed 25 percent of the sample sediment mass (Gray et al. 2000). Gray demonstrates that at similar flow rates, sediment discharge values from SSC data can be more than an order of magnitude larger than those from TSS data (USGS 2001), due primarily to larger particles that are often missed in the TSS method. For this reason, the USGS's stated policy on the collection and use of TSS data is that TSS concentrations and resulting load calculations of suspended material in water samples collected from open channel flow are not appropriate (USGS 2001).

Another critical factor affecting comparability of data is the filter's nominal pore size. Analytical laboratories use filters with varying pores sizes obtained from various manufacturers. More complete documentation on the method type, filter size, and sample processing procedures is needed in many cases. In some cases, labs may use hybrid approaches from these methods, which necessitates better documentation for each component of the analysis.

To resolve potential interpretation issues regarding suspended sediment, it is recommended that both TSS (for comparison to existing data sets) and SSC be measured, when budgets allow. One of the reasons that this issue has received much attention is that various state and local regulations and technology verification protocols have chosen to use TSS as a performance measure, so a clear understanding of the TSS method and procedure used is important to performance evaluations.

Regardless of the analytical methods used, the sampling methodology often introduces the largest bias to sediment data. Properly installed autosamplers appear to be capable of collecting suspended sediment up to about 250 μm, but may have only about a 50 percent recovery for larger particles up to about 2 mm. If other sample fractions are desired, then bedload and floatable samples should compliment autosampler collection (Clark et al. 2009).

The discrepancies in sampling and analysis methodologies currently employed in the field highlight the importance of particle size distribution (PSD) analysis as an essential component of any BMP monitoring study to serve as a common denominator for comparing different analytical methods for sediment in runoff (Clark and Siu 2008). PSD data provide the information necessary to meaningfully interpret the ability of a BMP to remove suspended materials. PSD methods are varied and include (USGS 2001):

- Dry sieve
- Wet sieve
- Visual accumulation tube (VA)
- Bottom withdrawal tube
- Pipette (typical method)
- Microscopy
- Coulter counter
- Sedigraph (x-ray sedimentation)
- Brinkman particle size analyzer
- Laser diffraction spectroscopy
- Light-based image analysis

Another source of variability in suspended solids sample results is the lack of a standard protocol for sample preparation for particle size fractionation and analysis. For this reason, Pitt and Clark (2009) developed a sample preparation protocol to assist research laboratories in documenting a standardized protocol for sample preparation and testing so that performance results can be more appropriately compared. This protocol addresses gaps in guidance to produce a repeatable sample preparation technique, including these steps:

1) Set up a cone splitter for the desired number of subsamples, up to a maximum of 10, considering the needed analytical volumes for each subsample.

2) Place a 1200-μm cleaned mesh screen on top of the cone splitter and pour the entire sample through the mesh. The material retained on the mesh should be dried, weighed and saved for further analyses.

3) Split the remaining samples according to the required analyses with approximately half of the samples screened through a 250-μm sieve in order to characterize the fraction in the larger range (below the mesh size) that cannot be quantified as easily by a Coulter Counter Multisizer 3.

4) For samples requiring both TSS and SSC, set aside the appropriate subsamples. For verification protocol testing, this requires four aliquots: TSS unsieved; TSS sieved to less than 250 μm; SSC unsieved; and SSC sieved to less than 250 μm.

5) Filter TSS/SSC samples through the appropriate filter – either glass-fiber (if metals analyses are not required) or membrane (if metals analyses are required).

Specific gravity (SG) of sediments is also an important component in determining the settleability of sediments and is recommended for sediment analysis by ASTM (1997). For BMP studies where PSD data are being collected, SG provides additional useful information about the ability of a particular BMP to remove sediment. Settling velocities of sediments are highly important and can be either measured directly or calculated theoretically from SG and PSD data. Settling velocities give the most useful information for quantifying BMP sediment removal efficiency; however, historically, this information has not been frequently reported in typical stormwater BMP monitoring studies.

4.1.4 Measurements of Gross Solids

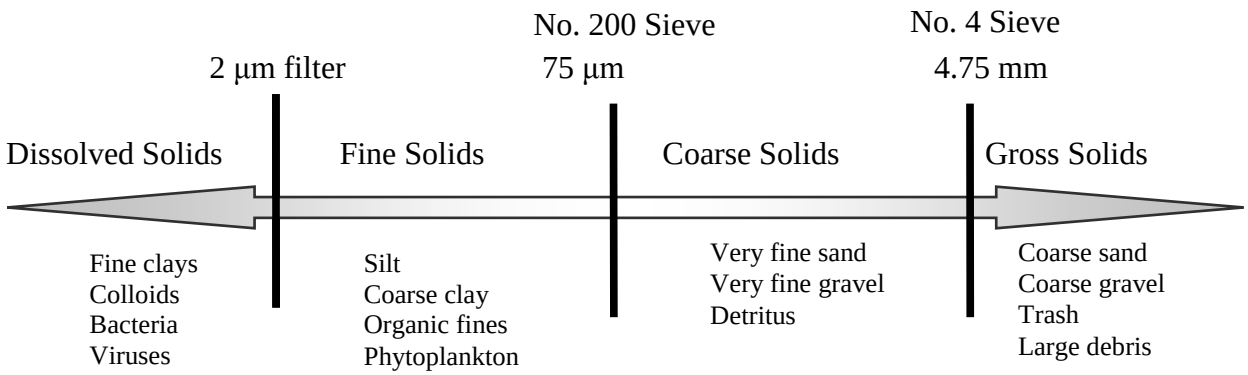
Closely related to measurement of TSS and SSC is the measurement of gross solids. Gross solids are the litter, trash, leaves, and coarse sediment that travel either as floating debris or as bedload in urban runoff conveyance systems. A variety of BMPs are designed to remove gross solids, including sediment basins, baffle boxes, hydrodynamic separators, oil/grit separators, modular treatment systems, and inlet traps, among others (EPA 2009). In 2009, the "ASCE Guideline for Monitoring Stormwater Gross Solids" was released by the Environmental and Water Resources Institute's Urban Water Resources Research Council Gross Solids Technical Committee (Rushton et al. 2009), defining three gross solids categories as summarized in Exhibit 4-5. The gross solids guideline was developed for many reasons, one of which is that EPA has identified sediment as a cause of widespread impairment of the Nation's rivers and streams. Additionally, an accurate quantification and characterization of all particle sizes, including gross pollutants, is needed for testing and evaluating BMPs in order to facilitate proper BMP design, as well as maintenance requirements and schedules. Furthermore, most gross solids cannot be sampled by traditional automatic samplers and have been ignored in studies evaluating the impact of storm water runoff on receiving waters (Rushton et al. 2009). The purpose of the ASCE guideline is to standardize data collection procedures used in evaluating the removal of gross solids by BMPs and also to allow for direct comparison of field data from separate studies by using the same collection methodologies.

Exhibit 4-5. Gross Solids Categories (*Source: ASCE Guideline for Monitoring Stormwater Gross Solids*, Rushton et al. 2009)

Category	Description
Litter	Human derived trash, such as paper, plastic, Styrofoam, metal and glass greater than 4.75 mm in size (#4 sieve)
Organic Debris	Leaves, branches, seeds, twigs and grass clippings greater than 4.75 mm in size (#4 sieve)
Coarse Sediments	Inorganic breakdown products from soils, pavement, or building materials greater than 75 microns. It also includes fragments of litter and organic debris not included in the other two categories. (#200 sieve).

Exhibit 4-5 builds upon solids classification work completed by Roesner et al. (2007), as summarized in Exhibit 4-6.

Exhibit 4-6. Solids Size Classification Diagram
(Source: Roesner et al. 2007)



The ASCE monitoring guideline for gross solids addresses a variety of factors, which vary according to the objectives of the monitoring program. The guideline should be referenced for more detail. An overview of the general topics included in the guideline based on monitoring program objectives is provided in Exhibit 4-7. The guideline also provides recommendations on sample collection techniques, contamination prevention, and sample compositing. Approaches to sampling include compositing sampling techniques developed by EPA (2006) and procedures for complete analysis of all samples by Roesner et al. (2007) and Sansalone and Kim (2008).

Exhibit 4-7.
Overview of ASCE Guideline for Gross Solids Monitoring
—Program Level Summary
(Source: Rushton et al. 2009)

Level 1 Minimal Monitoring (Screening Evaluation)	Level 2 Detailed Monitoring (Performance Evaluation)	Level 3 Advanced Monitoring (Research and Design)
1. Rainfall amount 2. Time interval since last cleaning 3. Volume and weight of material captured in each chamber 4. Separation of large litter from coarse sediment and organic debris 5. At least two samples for chemical analysis of sediment/debris mixture 6. Percent organic matter of sediment/debris sample 7. Percent solids	1. Rainfall characteristics 2. Separation of organic debris from coarse sediment 3. Mass and weight of debris 4. Mass and weight of sediment 5. Sediment particle size distribution using sieve analysis 6. Chemical analysis for two debris samples per chamber 7. Chemical analysis for two sediment samples per chamber 8. Percent organic matter of sediment sample in each chamber 9. Water quality sampling using standard methods 10. Flow measurement for storm duration including bypass & baseflow	1. Sediment chemical analysis for each sieve size and whole sample 2. Additional chemical analysis for special parameters 3. Subdivide litter and debris into special categories 4. Baseflow measurement and chemical analysis 5. Leachate analysis 6. Mass balance 7. Other analysis as needed

4.1.5 Microbiological Sampling

Microbiological sampling has become increasingly important to stormwater managers because many streams throughout the country do not attain recreational water quality criteria established by EPA. As of publication of this monitoring manual, EPA was in the process of revising its Ambient Recreational Water Quality Criteria (EPA 1986); therefore, recommended microbiological sampling may change in the future. In the interim, communities undergoing the Total Maximum Daily Load (TMDL) process for non-attainment of recreational criteria will often monitor one or more indicator bacteria such as *E. coli*, *Enterococci*, or fecal coliform. While historically fecal coliform was typically monitored, *E. coli* or *Enterococci* are recommended as pathogen indicators for recreational criteria under current EPA criteria. *E. coli* is a bacterium found exclusively in the feces of humans and other warm-blooded animals and is

used as an indication of fecal pollution and the possible presence of enteric pathogens. A limitation of *E. coli* as an indicator is that it can be present due to natural sources at levels that exceed stream standards and does not necessarily represent controllable sources of contamination of human origin.

A variety of microbiological methods are available following ASTM, IDEXX, Standard Methods and EPA methods. A discussion of each method is beyond the scope of this manual, however, the National Environmental Methods Index website (http://www.nemi.gov), can be referenced for more detailed information on over 30 current methods, including key information such as:

- General method information
- Media
- Method source (e.g., Standard Methods, ASTM)
- Brief method summary
- Scope and application
- Applicable concentration ranges
- Method download (links to websites)
- Interferences from other constituents
- QC requirements
- Sample handling
- Maximum holding time
- Relative cost/effort
- Sample preparation method(s)
- Precision descriptors
- Detection level notes

Representative challenges associated with microbiological sampling of stormwater include:

- Sample should be analyzed within six hours after sampling and within two hours from receipt of sample in lab for compliance monitoring or within 24 hours for routine monitoring (Standard Methods, 20th ed., Section 9060B); however, a six hour holding time for all samples is highly recommended (Myers and Sylvester 1997).

- Sample preservation requirements include chilling to 1 to 4 degrees C.

- For membrane filtration methods, sources of interference include: high turbidity, toxic compounds, or large numbers of non-coliform (background) bacteria, and organisms damaged by chlorine or toxic compounds. For example, samples with high levels of colloidal or suspended materials can clog the membrane filter pores and prevent filtration.

4.1.6 Analytical Methods

After the parameters have been selected, the analytical methods to be used to measure them must be chosen. Select analytical methods that will provide results of sufficient quality to support the intended uses of the data. To determine the quality of data necessary for a program, consider the following:

- Appropriate analytical levels: EPA guidance suggests tailoring the analytical level to the intended use of the data. EPA has defined five analytical levels:

  1) Field screening and analysis using portable instruments.

2) Field analysis using more sophisticated portable analytical instruments, possibly set up in a portable laboratory at the site.

3) Analysis performed at an off-site analytical laboratory using EPA Contract Laboratory Program (CLP) or equivalent methods, but without the validation or documentation procedures required for CLP.

4) CLP routine analytical services and complete data reporting packages.

5) Analysis by non-standard methods (to achieve very low detection limits or measure a specific parameter not included in standard methods).

Stormwater samples are generally analyzed using Levels I, II, or III. Levels IV and V are not used very often for stormwater projects because these levels are intended for situations requiring low detection limits and high confidence, such as human or ecological risk assessments or Superfund/MTCA investigations.

- Appropriate methods for the chemicals of concern: Chemicals of concern are the most significant contributors to human health or environmental risk and are generally the most toxic, mobile, persistent, and/or frequently occurring chemicals found at the site. Commonly occurring chemicals of concern in stormwater runoff include metals (cadmium, copper, lead, and zinc), PAHs, and organo-phosphate insecticides (e.g., diazinon and chloropyrifos). Other chemicals (e.g., organochlorine pesticides and PCBs) should be included if there is reason to believe they are present. Note that the potential toxicity of some metals in freshwater systems is affected by the hardness of the water; thus, water quality standards for cadmium, copper, chromium, lead, nickel, silver, and zinc are calculated based on water hardness. For this reason, total hardness should be measured if metals are measured at sites where fresh water quality standards may apply. Examples of Level V monitoring may include particle size distribution analysis and sample extraction methods for organics.

- Level of concern: This term refers to the chemical concentration that is of concern. Typically, state or federal water quality criteria for protection of aquatic life or human health are used as the default level of concern for water sample results, and sediment quality criteria are used as the level of concern for sediment sample results. For pollutants that do not have state or federal water or sediment quality standards, the Risk-based Concentration Table developed by EPA Region III (EPA 1994a,b) can be used as levels of concern for water and soil sample results.

- Required detection limit/practical quantification limit: The level of concern directly affects the data quality requirements because the sampling and analysis methods used must be accurate at the level of concern. Sampling variability is often difficult to control, especially in stormwater. The relative accuracy of most laboratory methods decreases as concentrations approach the detection limits. For these reasons, the practical quantification limit (5 to 10 times the detection limit) should be below the level of concern, if possible.

If the objective is to conduct a screening study to identify chemicals that appear to be present at levels of concern, consider analyzing for a wide range of constituents using analytical methods with low detection limits. An initial screening analysis can generally reduce the number of chemicals analyzed in subsequent studies by eliminating those that were detected below their corresponding levels of concern.

In cases where it is known that there is a high degree of correlation between the concentration of the target pollutant(s) and some other parameter (e.g., fine particles, TSS, total organic carbon), then it may be possible to use less costly monitoring approaches to track the substitute, or "proxy" parameter(s). Although this approach can introduce some uncertainty because it does not track the target pollutants, it is still worthy of consideration. If the correlations are known to be strong and the cost differences pronounced, this strategy may provide a way to obtain much more data (i.e., more frequent observations during more storm events and/or at more locations). Such improvements in data quantity could more than offset the uncertainties introduced by imperfect correlations.

There are many precedents for using proxy parameters as indicators. For example, *E. coli* or fecal coliform are typically used as indicators for pathogens and fecal contamination. Total organic carbon and COD are sometimes used as proxies for biochemical oxygen demand (BOD). Turbidity is commonly used as a proxy for suspended solids, which in turn, is sometimes used as a proxy for other pollutants of concern (e.g., metals, PAHs).

In many BMP monitoring programs, there are opportunities to obtain additional information at little or no incremental cost (e.g., temperature or pH data). Such information may turn out to be valuable to the overall stormwater program at some time in the future and/or to others programs.

4.2 Sampling Location

The location of a permanent sampling station is probably the most critical factor in a monitoring network that collects water quality data. If the samples collected are not representative of the flow conditions, the frequency of sampling and data interpretation approach are inconsequential. The representativeness of a water quality sample is a function of the uniformity of the sample concentrations in a flow path's cross-sectional area. Wherever the concentration of a water quality variable is independent of depth and lateral location in a flow path's cross section, the flow path at that point is completely mixed and could serve as a desirable sampling location (Saunders 1983). Extensive discussion on this subject can be found in Fischer et al. (1979).

To assess BMP performance, sampling locations typically include an upstream and downstream location and, in some cases, one or more intermediate locations within the BMP or the BMP system, as described below.

4.2.1 Upstream

Monitoring stations established upstream of a BMP can give results that reveal the influent concentration or load of pollutants before they flow through the BMP. Upstream water quality is indicative of concentrations and pollutant loads that would be observed downstream if no BMP were implemented. It is important to monitor only waters that flow into the BMP to be able to

use the resultant data to compare upstream water quality with downstream locations. Upstream monitoring locations can also be useful to determine bypass water quality. Where bypass is present, accurate flow measurement is highly important. Where sufficient funds are available and the physical layout of the control structures allow, bypass and flow to the BMP should be monitored directly. In situations where direct measurement is not practical, modeling of bypass flows can be substituted, particularly where the hydraulics of the bypass structure are well known or can be calibrated to flow rates. Typically, a mass balance approach is used to model bypass flow rates and volumes.

Upstream monitoring stations should be located far enough away from the BMP to ensure that samples are independent of the BMP. Immediately upstream from a BMP, contributing runoff could be affected by backflow, slope, vegetation, etc.

4.2.2 Downstream

Monitoring stations established downstream of a BMP are used to monitor water quality of flows that are treated by the BMP. Downstream monitoring is essential for establishing:

- Whether the BMP provides a measurable and statistically significant change in water quality.
- Whether the BMP provides effluent of sufficient quality to meet water quality criteria.
- Whether the BMP's effluent concentrations are comparable to similar BMPs to assess whether the BMP is achieving typical effluent water quality.

Monitoring stations should be located immediately downstream of the BMP so that BMP effluent is sampled before it is introduced into the receiving waters or is exposed to factors that may affect constituent concentrations. Where bypass is present and one wants to understand the efficiency of the BMP system, it is important to monitor water quality of the bypass flows prior to mixing with the effluent from the BMP. In many cases, BMP influent data can be used to estimate bypass water quality; however, accurate estimates of bypass flow rates and/or volumes from monitoring or flow modeling will still be needed. In some cases, bypass flows may be very difficult to separate from treated effluent (e.g., in hydrodynamic devices).

4.2.3 Intermediate Locations

BMPs are sometimes designed as a group of devices or chambers that target specific processes. For example, a media filter might have a settling chamber to quickly remove large settleable solids before flowing into the filter media chamber. A treatment train approach is sometimes taken to combine various practices in order to maximize removal of specific constituents. Intermediate monitoring locations in the interior of the BMP are useful for investigating how various sections of the facility are working. Monitoring stations are also useful in between treatment train practices to assess effectiveness of each individual component in addition to monitoring upstream/downstream stations to determine overall BMP efficiency. (In this case, the intermediate monitoring location is the effluent from the upstream BMP and the influent to the downstream BMP.)

For interior monitoring, such as in the middle of a wetland or detention pond, stations should be established in a location that is representative of the facility. When selecting intermediate monitoring locations, it is important to have a clear understanding of the hydraulic/hydrologic features of the system to avoid “dead zones”. For example, monitoring within a wetland should be done in the middle section, where the slopes, vegetation, channel width, and so on are uniform and similar to the rest of the wetland, avoiding any microcosms of unique vegetation, basins, or slopes. Additionally, intermediate sampling location results have different implications, depending on whether the system processes operate as a plug flow reactor or a continuously stirred tank reactor. In the case of a system that operates more like a plug flow reactor, an intermediate sample location would represent the mid-point of the reactions.

To monitor in between treatment train practices, stations should be established to capture effluent from the upstream BMP or inflow to the downstream BMP, or both. Monitoring should not be conducted in a place where backflow or mixing occurrs, as these processes do not allow for isolated sampling of direct BMP discharge or inflow. During high flow conditions, this may be difficult because many BMPs overflow, reducing the distinction and separation between BMPs. Intermediate treatment train BMP monitoring stations need to be carefully evaluated to determine if samples taken during high flows are representative of water quality of flow between the BMPs and not backflow or some other phenomena.

Other intermediate monitoring locations sometimes associated with Low Impact Development (LID) studies that rely on infiltration may include soil moisture or groundwater monitoring at various depths. Similarly, some grass swale and buffer studies may incorporate monitoring at various distances along the flow path. Researchers must balance study complexity and cost associated with additional monitoring stations with the expected benefits of additional stations such as better characterizing the effectiveness of various treatment system components.

4.3 Water Quality Sample Collection Techniques

Regardless of whether manual or automated sampling techniques are used, it is critical to select sampling locations that are well mixed and will yield relatively homogenous samples (Clark et al. 2009). Basic guidance and references for grab sample and automated sample approaches follow.

4.3.1 Grab Samples

The term “grab sample” refers to an individual sample collected within a short period of time at a particular location. Analysis of a grab sample provides a "snapshot" of stormwater quality at a single point in time. The results from a single grab sample generally are not sufficient to develop reliable estimates of the event mean concentration (EMC) for the pollutant or pollutant load because stormwater quality tends to vary dramatically during a storm event. Nevertheless, grab sampling has an important role in many stormwater monitoring programs for the following reasons:

- A single grab sample collected during the first part of a storm can be used to characterize pollutants associated with the "first flush." The first part of a storm often contains the highest pollutant concentrations in a storm runoff event, especially in small catchment

areas with mostly impervious surfaces, and in storms with relatively constant rainfall. In such cases, the first flush may carry pollutants that accumulated in the collection system and paved surfaces during the dry period before the storm. Thus, the results from single grab samples collected during the initial part of storm runoff may be useful for screening-level programs designed to determine which pollutants, if any, are present at levels of concern. However, this strategy may be less effective in areas subject to numerous low-intensity, long duration storms with short inter-event times, because "first flush" effects are less obvious under such weather conditions.

- Some measurable parameters, such as temperature, pH, total residual chlorine, phenols, volatile organic compounds (VOCs), and bacteria transform or degrade so rapidly that compositing can introduce considerable bias. (Note: Grab sampling is the typical method for VOCs because VOCs can be lost through evaporation if samples are exposed to air during compositing. Although automated VOC samplers have been used in the past, they are no longer recommended.)

- Some pollutants, such as oil and grease and total petroleum hydrocarbons, tend to adhere to sample container surfaces so that transfer between sampling containers must be minimized. (If program objectives require characterization of the average oil and grease concentration over the duration of a storm, obtain this information from a series of grabs analyzed individually.)

To estimate EMCs or pollutant loads, a series of grab samples at short time intervals can be collected throughout the course of a storm event. There are several different approaches for obtaining information from a series of grab samples. One approach would be to analyze each grab sample individually. If the samples are analyzed individually, the results can be used to assess the rise and fall of pollutant concentrations during a storm and to estimate EMCs of pollutants. This approach can be particularly useful if the monitoring objective is to discern peak pollutant concentrations or peak loading rates for assessing short-term water quality impacts. Analyzing each grab separately adds significantly to laboratory costs; consequently, this approach is rarely used except when program objectives require detailed information about changes in constituent concentrations over the course of a storm.

4.3.2 Composite Samples

Another sampling approach is to combine appropriate portions of each grab sample to form a single composite sample for analysis, but this is generally impractical if there are more than a few stations to monitor. Moreover, manual monitoring can be more costly than automated monitoring if the monitoring program encompasses more than a few storm events. For these reasons, many monitoring programs have found that the use of automated monitoring equipment and methods are more appropriate for compiling composite samples than manual monitoring. If detecting peak concentrations or loading rates is not essential, composite sampling can be a more cost-effective approach for estimating EMCs and pollutant loads. A composite sample is a mixture of a number of individual sample "aliquots." The aliquots are collected at specific intervals of time or flow during a storm event and combined to form a single sample for laboratory analysis. Thus, the composite sample integrates the effects of many variations in stormwater quality that occur during a storm event. Composite samples are suitable for most

typical stormwater quality parameters, but are unsuitable for parameters that transform rapidly (e.g., *E. coli*, residual chlorine, pH, VOCs) or adhere to container surfaces (e.g., oil and grease).

The two basic approaches for obtaining composite samples are referred to as time-proportional and flow-proportional. A time-proportional composite sample is prepared by collecting individual sample aliquots of equal volume at equal increments of time (e.g., every 20 minutes) during a storm event, and mixing the aliquots to form a single sample for laboratory analysis. Time-proportional samples do not account for variations in flow; pollutant concentrations in sample aliquots collected during the portion of the storm with lower flows are given the same "weight" as sample aliquots collected during higher flows. Consequently, time-proportional composite samples generally do not provide reliable estimates of EMCs or pollutant loads, unless the interval between sample aliquots is very brief and flow rates are relatively constant.

Flow-weighted composite samples are more suitable for estimating EMCs and pollutant loads. A flow-weighted composite sample can be collected in several ways (EPA 1992):

1) Constant Time: Volume Proportional to Flow Rate. Sample aliquots are collected at equal increments of time during a storm event and varying amounts of each aliquot are combined to form a single composite sample. The amount of water removed from each aliquot is proportional to the flow rate at the time the aliquot was collected. This type of composite sample can be collected using either manual or automated techniques.

2) Constant Time: Volume Proportional to Flow Volume Increment. Sample aliquots are collected at equal increments of time during a storm event and varying amounts from each aliquot are combined to form a single composite sample. The amount of water removed from each aliquot is proportional to the volume of flow since the preceding aliquot was collected. This type of compositing is generally used in conjunction with an automated monitoring system that includes a continuous flow measurement device. It can be used with manual sampling in conjunction with a continuous flow measurement device, but this combination is uncommon.

3) Constant Volume: Time Proportional to Flow Volume Increment. Sample aliquots of equal volume are taken at equal increments of flow volume (regardless of time) and combined to form a single composite sample. This type of compositing is generally used in conjunction with an automated monitoring system that includes a continuous flow measurement device.

Select the flow-weighted compositing method most suitable for the program based on the monitoring technique (manual or automated) and planned equipment. Compositing Methods 2 and 3 are more accurate than Method 1 because Methods 2 and 3 both use the total volume of flow based on continuous flow measurement to scale the sample volume. In contrast, Method 1 uses a single instantaneous rate measurement to estimate the flow over the entire sampling interval. However, for manual methods, compositing Method 1 is generally the most practical choice. If automated equipment is to be used, Method 3 is generally preferred because it minimizes the need for measuring and splitting samples, which are activities that can increase the chance for sample contamination. If automated methods will be used, the equipment

manufacturer's specifications and instructions should be reviewed to select the compositing method most appropriate for that particular make and model.

Storm events affect stream flows for variable lengths of time depending on the storm duration and antecedent conditions and catchment characteristics. Runoff may persist for a period of a few hours to one or two days. This suggests runoff rarely persists long enough to be considered comparable to chronic exposure duration. Discrete sampling over the course of the storm event will provide concentration information that can be used to determine how long water quality criteria were exceeded during the storm. Alternatively, discrete samples can be composited on a time-weighted basis over time scales comparable to the acute and chronic water quality criteria exposure periods (one hour and four days, respectively). However, the latter would likely include dry-weather flows since few storms last four days. For catchments which are relatively small (a few acres), it is recommended that one or more one-hour composite samples be collected during the first few hours of flow by collecting and combining three or more grab samples.

Flow-weighted composite sampling can be used for comparison with water quality objectives (for example, if flow-weighted composites are collected to measure loads). However, it should be recognized that a flow-weighted sample contains more water from peak flows than from the initial part of the storm. Results from Santa Clara Valley Nonpoint Source Monitoring Program indicated that for a large watershed with significant suspended sediment concentrations (200 - 400 mg/L), peak total metals concentrations are generally 1.5 times the flow-weighted composite concentrations (WCC 1993). Results from monitoring a smaller, highly impervious industrial catchment with lower suspended sediment concentrations were more variable, and no conclusions could be drawn as to the relationship between flow-composite concentrations and grab samples due to difficulties in grab sampling runoff that only occurred during precipitation.

4.3.3 Automated Sampling

Automated monitoring involves sample collection using electronic or mechanical devices that do not require an operator to be on-site during actual stormwater sample collection. It is the preferred method for collecting flow-weighted composite samples. Automated monitoring is generally a better choice than manual monitoring at locations where workers could be exposed to inadequate oxygen, toxic or explosive gases, storm waves, and/or hazardous traffic conditions. Automated samplers can be set so that sampling operations are triggered when a pre-determined flow rate of storm runoff is detected. Conversely, manual monitoring relies on weather forecasts (and considerable judgment and good luck) to decide when to send crews to their monitoring stations. It is very difficult to predict when stormwater runoff is likely to begin; consequently, manual monitoring crews may arrive too early and spend considerable time waiting for a storm that begins later than predicted, or they may arrive too late and miss the "first flush" from a storm that began earlier than predicted. If the automated equipment is set to collect flow-weighted composite samples using the constant volume-time proportional to flow method, it reduces the need to measure samples for compositing.

If field-measured "indicator" parameters (e.g., turbidity, conductivity, dissolved oxygen, pH) are sufficient for meeting monitoring objectives, electronic sensors and data loggers may be useful.

Electronic sensors and data loggers can provide near-continuous measurements of indicator parameters at reasonable cost.

BMP monitoring can be an especially useful application for some automated systems (e.g., continuous flow recorders, auto samplers, continuous monitoring probes) for the following reasons:

- Automated systems can provide data covering virtually the entire volume of runoff that passes through the BMP (i.e., they are not likely to miss or leave out small events and the beginnings and ends of other events).

- Automated systems are well suited to providing data sets that are useful (recognizing that performance evaluations are generally based on the differences between inlet and outlet concentration data sets, both of which are inherently noisy).

- The information obtained from good performance monitoring programs can be very valuable by protecting against inappropriate BMP applications. Therefore, the cost of using automated systems is often justifiable.

4.3.3.1 Automated Sampling Equipment

An automated sampler is a programmable mechanical and electrical instrument capable of drawing a single grab sample, a series of grab samples, or a composited sample, in-situ. The basic components of an automated sampler are a programming unit capable of controlling sampling functions, a sample intake port and intake line, typically a peristaltic pump (although vacuum/compression pumps may also be used), a rotating controllable arm capable of delivering samples into sample containers and a housing capable of withstanding moisture and some degree of shock. Additionally, inexpensive first-flush sampling equipment for specific regulatory purposes is also now available.

An automated sampler can be programmed to collect a sample at a specific time, at a specific time interval, or on receipt of a signal from a flow meter or other signal (e.g., depth of flow, moisture, temperature). The sampler distributes individual samples into either a single bottle or into separate bottles which can be analyzed individually or composited. Some automated samplers offer multiple bottle configurations that can be tailored to program objectives.

Important features of automated samplers include:

- Portability

- Refrigeration

- Alternative power supplies

Exhibit 4-8. Programming an Automatic Sampler

Portable samplers are smaller than those designed for fixed-site use, facilitating installation in confined spaces. If a suitable confined space is not available or is undesirable (e.g., because of safety issues), the sampler can be housed in a secure shelter at the sampling site. Portable samplers can use a 12V DC battery power supply, solar battery, or AC power.

Several manufacturers produce automatic sampling equipment that can refrigerate samples as they are collected. For non-refrigerated samplers, ice may be added to the housing of some units to preserve collected samples at a temperature as close to 4°C as possible. The objective of this cooling is to inhibit pollutant transformation before the sample can be analyzed.

It is important to be aware that some common sampler heads do not function at subfreezing temperatures without retrofit. After-market heater and thermostats can be purchased to enable year round continuous monitoring in cold climates. Similarly, data logger failure due to cold temperatures can result in data loss.

In typical installations for BMP sampling, for each of the types of samplers described above, an intake line is bracketed to the channel bottom. The intake tubing should be mounted as unobtrusively as possible, to minimize disturbance of the site hydraulics. Generally, the optimum position for the intake is to the channel bottom. However, if high solids loadings are expected and potential deposition could occur, the intake can be mounted slightly higher on one side of the channel wall. Typically, a strainer is attached to the intake to prevent large particles and debris from entering the tubing. The strainer is usually installed so that it faces upstream, into the flow. This configuration minimizes the development of local turbulence that could affect representative sampling of constituents in the particulate phase.

Two types of pumps are incorporated into automated samplers for typical water quality sampling: peristaltic and vacuum/compressor.

Peristaltic Pump

A peristaltic pump creates a vacuum by compressing a flexible tube with a rotating roller, drawing a sample to the pump that is then pushed out of the pump. Field experience with peristaltic pumps has shown that their reliability in drawing a consistent sample volume is greatly reduced as the static suction head (i.e., distance between the flow stream surface and the sampler) increases. It may be possible to increase the efficiency of these samplers by placing the pump closer to the sample source, reducing the suction head. In addition, changing the tubing from the peristaltic pump on a regular basis will improve consistency. In general, the sampler itself should be installed no more than 6 meters (20 feet), and preferably less, above the channel bottom. If the sampler is to be installed at greater than 20 feet above the channel invert, it may be necessary to use a remote pump that is placed closer to the flow stream to ensure reliable sample collection.

The degree to which sampler lift affects the concentration of TSS and other pollutant parameters, especially coarser materials, is not well known. That is, the mean transport velocity achieved by the peristaltic pump is sufficient to draw suspended solids; however, the pulsed nature of the flow may allow suspended solids to settle back down through the pump tubing during transport. There have been improvements in capabilities of pumps for automated samplers over the past five years enabling collection of larger/heavier particles with fewer problems. In work performed by the USGS (FHWA 2001), it was found that suspended solids concentrations did not vary with pumping height (0 to 24 ft); however, sample volumes delivered to sample bottles did vary from sample to sample at high lift heights for some of the older sampler models.

Another concern with peristaltic pumps is their incompatibility with Teflon®-lined tubing in the pump assembly. Compression of the intake tubing by the rollers tends to create stress cracks and small recesses in the lining where particles can accumulate. Under these circumstances, some pollutant concentrations could be underestimated and the cross-contamination of samples can occur. Although Teflon®-lined tubing is preferable because it reduces the potential loss of pollutants through surface interactions, this advantage cannot be accommodated with a peristaltic pump.

Vacuum/Compressor Pump

A vacuum/compressor pump draws a sample by creating a vacuum. Although less commonly present in currently available equipment, this type of pump can create a higher transport velocity in the intake tube and provide more steady and uniform discharge than a peristaltic pump. However, the higher intake velocity can scour sediments in the channel near the sampler intake, resulting in disproportionately high concentrations of suspended solids.

After a sampler is installed, it must be programmed to collect the desired sample size. Calibration of peristaltic pumps is achieved by one of two methods: automatic or timed. In automatic calibration, the actual volume of sample drawn is measured using a fluid sensor located at the pump and the known pump speed. In timed calibration, the volume is determined from the number of revolutions of the peristaltic pump and the time taken for the sample to travel from its source to the sample container. Calibration by this latter method is site specific and incorporates the pump speed, the head (vertical distance above the sample source), and the length

and diameter of the intake tubing. The Manning and Epic samplers, which employ vacuum pumps, permit adjustment for specific sample volumes via a fluid level device in a chamber. This chamber can cause sample cross-contamination, as it cannot be flushed like the tubing can.

4.3.3.2 In-Situ Water Quality Devices

The concentration of most pollutants in stormwater runoff is likely to vary significantly over the course of a given storm event. Some of this variability can be captured through the collection of multiple samples. The ideal data set would contain not just multiple samples, but also a continuous record of constituent concentrations throughout a storm, capturing both the timing and magnitude of the variations in concentration. Given the availability of other continuous data, this approach might allow better correlation with potential causative factors. Unfortunately, the laboratory costs for even a near-continuous data set would be prohibitive. USGS determined that between 12 and 16 individual samples resulted in a mean that was within 10 to 20 percent of the actual event mean concentration (FHWA 2001). In-situ monitoring devices offer a possible solution to obtaining a continuous record of water quality; however, at this time, they are only practical for a limited set of parameters.

In-situ water quality probes have been adapted from equipment developed for the manufacturing and water supply/wastewater industries. In-situ water quality monitors attempt to provide the desirable near-continuous data set described above at a relatively low cost, eliminating (or reducing) the need for analysis of samples in the laboratory.

In general, water quality monitors are electronic devices that measure the magnitude or concentration of certain specific target constituents through various types of sensors. Discrete measurements can be made at one minute or less intervals. Most monitors use probes that provide a controlled environment in which a physical and/or electrochemical reaction can take place. The rate of this reaction is typically driven by the concentration of the target constituent in the flow. The rate of reaction, in turn, controls the magnitude of the electrical signal sent to the display or a data-logging device. Probes to detect and measure the following physical and chemical parameters are currently available for practical use in the field:

Physical Parameters

- Temperature
- Turbidity

Chemical Parameters

- pH
- Oxidation-reduction potential (redox)
- Conductivity
- Dissolved oxygen
- Salinity
- Nitrate (not currently recommended)
- Ammonia (not currently recommended for remote/unattended operation)
- Resistivity
- Specific conductance
- Ammonium

There are some potential probes for heavy metals, but given the complexities associated with highly variable solids concentrations and other factors, studies have found that they are not practical for field application (FHWA 2001). Instruments can be configured to measure the concentrations of several of these parameters simultaneously (i.e., multi-parameter probes) and provide data logging and PC compatibility.

In many cases, the electrochemical reaction that drives a probe's response is sensitive to changes in temperature, pH, or atmospheric pressure. Where appropriate, monitors are designed to simultaneously measure these associated properties. Data on the target constituent are then corrected through a mathematical routine built into the probe's microprocessor (e.g., dissolved oxygen probes are compensated for temperature and atmospheric pressure, pH probes for temperature. and ammonia probes for pH), or are adjusted in a spreadsheet after downloading to a personal computer. As of publication of this manual, nitrate probes are not recommended, but improvements in technology may occur in the future. Similarly, ammonia probes currently require frequent calibration, which limits their use from a practical perspective.

Despite the advantage of these instruments for measuring near-continuous data, they require frequent inspection and maintenance in the field to prevent loss of accuracy due to fouling by oil and grease, adhesive organics, and bacterial and algal films. Therefore, these instruments should always be cleaned and calibrated before use. Because water quality probes are designed to operate while submerged in water, exposure of the electrochemically active probe surface to air should be minimized.

4.3.3.3 Remote Communication with Automatic Equipment

The ability to remotely access the memory and programming functions of automated samplers is a highly desirable feature for large stormwater sampling networks. Although this feature increases the capital cost for a system, it can greatly reduce the expertise and training necessary for field crews because many of the technical aspects of equipment set-up and shut-down can be conducted by a system supervisor remotely.

Currently, modem communication is an available option to most commercially-produced automated samplers. However, there are several common drawbacks that may be encountered with the communication systems currently offered by manufacturers:

- Full access to all sampler programming features may be limited. This means that trained field crews may still be necessary to ensure sampler programming is correct.

- For multiple instrument systems (i.e., separate flow meter and automated sampler), communication and complete operation of both components through one modem system is generally not available.

Remote communication for both samplers and flow meters is a rapidly advancing technology. Stormwater monitoring applications should continue to benefit from advances made in wastewater and drinking water monitoring applications. Some of the newer cellular modems and software now allow for Supervisory Control and Data Acquisition (SCADA) of automatic

samplers, allowing for improved remote programming, monitoring of sampler status and review of data as it is collected.

4.3.4 Manual Sampling

Manual monitoring involves sample collection and flow measurement by personnel using hand-operated equipment such as a bailer or bottle. For a monitoring program that is modest in scope (i.e., relatively few sampling sites and storm events), manual methods for obtaining grab and composite samples may be preferable to those employing automated equipment. For programs that require monitoring large streams, manual methods may be needed to collect cross-section composites. The principal advantages to manual sampling are its relatively low capital cost and high degree of flexibility. In addition to the capital outlay required for the purchase of automated samplers, other costs, such as installation, training personnel to use the samplers correctly, and field maintenance and operations (e.g., replacing batteries, interrogating data loggers, retrieving and cleaning sample jars) can be substantial.

Manual sampling is usually preferred under the following circumstances:

- When available resources for equipment purchase/installation (e.g., funds, personnel, time) are very constrained and/or there is not the political will to invest in a program.
- When the target pollutants do not lend themselves to automated sampling or analysis (e.g., oil and grease, volatile organic compounds, bacteria).
- When the physical setting of the BMP does not allow the use of automated systems.

However, manual monitoring may not be feasible if:

- Monitoring personnel are not available after normal working hours.
- Monitoring personnel have strict job descriptions that do not include sampling.
- The organization's insurance policy doesn't cover stormwater monitoring activities.
- Managers and monitoring personnel are not able to deal with sick days, vacations, and competing priorities.

Manual sampling is generally less practical than automated monitoring for large-scale programs (e.g., monitoring programs involving large numbers of sites or sampling events over multiple years). It is difficult to collect true flow-weighted composites using manual methods. Under these circumstances, labor costs and logistical problems can far outstrip those associated with automated equipment. For the same reason, manual sampling is seldom practiced if specific program objectives require that samples be composited over the entire duration of a storm, which is recommended for BMP monitoring.

Manual equipment can be used in collecting grab samples, composite samples, or both, as described below.

4.3.4.1 Manual Grab Sampling Equipment

Manual sampling techniques and equipment have been reviewed in detail by Stenstrom and Strecker (1993). If site conditions allow, a grab sample can be collected by holding the laboratory sample bottle directly under the lip of an outfall or by submerging the bottle in the flow. A pole or rope may be used as an extension device if field personnel cannot safely or conveniently approach the sampling point. Alternatively, a clean, high-density polyethylene bucket may be used as a bailer and sample bottles may be filled from the bucket. Care should be taken not to stir sediments at the bottom of the channel.

As described earlier, the concentrations of suspended constituents tend to stratify within the flow stream depending on their specific gravity and the degree to which flow is mixed by turbulence. Use of a discrete-depth sampler for multiple samples should be considered when constituents lighter or heavier than water are targeted, or if the flow is too deep and/or not well mixed enough to be sampled in its entirety (Martin et al. 1992). However, stormwater BMPs often drain relatively small catchments and contain fairly shallow flows. Collection of depth-integrated samples at these sites is not usually performed.

Given the extremely low detection limits that laboratory analytical instruments can achieve, leaching of water quality constituents from the surface of a bailing device or sample bottle can affect water quality results. Sample bottles of the appropriate composition for each parameter are usually available from the analytical laboratory. Depending upon the pollutant to be analyzed, bailers and discrete-depth samplers should be made of stainless steel, Teflon®-coated plastic, or high-density polyethylene. When in doubt, a laboratory analyst should recommend an appropriate material type for the collection device. (Method blanks are an important quality control tool that can help determine whether leaching of materials from sampling equipment is an issue.)

4.3.4.2 Manual Composite Sampling Equipment

If grab samples will be composited based on flow rate (i.e., grab samples collected during high flow contribute more to the composited sample than those collected during low flow), some receptacle for storing the individual grab samples prior to compositing will be required. The use of polyethylene jugs, or polyethylene cubes with screw-on caps manufactured for shipping chemicals, is recommended. These can be shaken to remix the sample prior to pouring out the required volume. The volume required from each receptacle can be measured in a graduated cylinder and poured into a bucket for compositing. Both the cylinder and the bucket should be made from a Teflon™-coated plastic or high-density polyethylene and should be cleaned prior to use. Be aware that every transfer of sample from one container to another risks losing sample volume and pollutants; thereore, care should be taken during sample transfers. Sample splitting is complex and prone to error. References to ensure good sampling procedures are provided in Exhbit 4-9.

Exhibit 4-9. Supplemental References Regarding Sample Spliting

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4.4 Sediment Sampling

Many constituents either settle out of the water column or prefer not to be in the water column (due to hydrophobicity) and become incorporated in the sediment. Sediment can store significant amounts of certain constituents, such as benzene, toluene, ethylbenzene, and xylenes (BTEX), PCBs, metals, and microbes. During high flows, these sediments are stirred up and can release potentially high concentrations of accumulated constituents. Many BMPs are designed to remove the sediment from runoff, theoretically removing the associated constituents as well.

Sediment sampling can determine concentrations of constituents not necessarily found through water column monitoring. Sediments can be sampled upstream and downstream of BMPs, as well as internal to the BMP, to assess removal and effluent efficiencies as well as internal accumulation of sediment and associated constituents.

When sampling sediment from the creek bed or internal to the BMP (e.g., sampling the filter media or detention pond bottom sediments), sediments should be collected minimizing disturbance or resuspension of the sediment bed so that the original settled material is captured in the sample apparatus. Depth of sediment sample should also be noted as constituent concentrations can vary with depth.

Bedload sampling can be conducted to sample sand, silt, gravel or rock debris carried by channel on or immediately above its bed. Bedload materials have particle sizes or a density that do not allow movement far above or for long distances out of contact with the streambed. Bedload samplers can either be hand-held or cable-suspended. Standard sampler bags come with a 250 micron mesh size (ASTM specs) made out of nylon for abrasion resistance. Bags can also be provided with 125, 500, and 1000 micron openings, if needed. Several different types of bedload samplers are available. See ASCE (2007), USGS (2005), the Federal Interagency Sedimentation Project (http://fisp.wes.army.mil/), and vendor websites for more information on features of these samplers.

4.5 Soil (Infiltration Media) Sampling

As infiltration-oriented stormwater management practices are increasingly advocated, collection of soil and infiltration media samples become increasingly important. This type of sampling is helpful in assessing depth and extent of pollutant accumulation in soil layers and relationship of pollutants in groundwater or the vadose zone to accumulated pollutants in the infiltration media (Clark, Pitt, and Field 2009). Additionally, documentation of soil chemical properties is important in identification of factors influencing BMP performance. For example, microbial groundwater contamination from infiltrated urban runoff is influenced by soil chemical properties that promote adsorption and retention of microbial organisms (Clark et al. 2006; Clark, Pitt, and Field 2009). Other soil characteristics influence infiltration rates and nutrient loading to groundwater. For example, compost-amended soils may improve infiltration rates, but may also contribute to nutrient loading to groundwater if not carefully selected (Pitt et al. 1999; Clark, Pitt, and Field 2009.). Sample collection from infiltration media is important to help further the understanding of the lifespan and maintenance requirements of infiltration devices.

Site soil evaluations should include several components, including infiltration measurements, soil density, texture, and moisture determinations. Soil chemical measurements should include a variety of parameters, including soil texture (i.e., percent of sand, silt, and clay), organic matter, cation exchange capacity and general nutrients (Pitt 2009). Organic carbon content and phosphorus index ("P Index") are also useful. Chapter 8 provides additional infiltration-related monitoring information.

4.6 Groundwater Sampling

A discussion of groundwater sampling is beyond the scope of the current monitoring manual; however, it is increasingly important for LID and infiltration-oriented BMPs. The references listed in Exhibit 4-10 are good resources for guidance with regard to groundwater sampling.

Exhibit 4-10. Supplemental Groundwater Monitoring Resources

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Brown, C. J., Scorca, M. P., Stockar, G. G., Stumm, F., and H.F. Ku. 1997. *Urbanization and recharge in the vicinity of East Meadow Brook, Nassau County, New York*. U.S. Geological Survey WRI 96-4289. http://pubs.er.usgs.gov/usgspubs/wri/wri964289

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4.7 QA/QC for Water Quality Sampling

4.7.1 Sampling Methods

Proper sampling methods are essential in conducting a BMP monitoring program in order to ensure resulting data are meaningful and representative of the water and other media being processed by the BMP. Sampling methodologies and techniques that maintain and confirm the integrity of the sample are discussed below.

4.7.2 Grab Sample Collection Techniques

During moderate flow events, grab samples can be collected at some stations simply by approaching the water to be sampled and directly filling up the bottles, being careful not to lose any preservative already contained in the bottle. It is important also to be aware of surface conditions of the sampled water body, avoiding layers of algae and debris and areas of dense vegetation if possible. The bottle cap should be handled carefully, making sure not to introduce any extraneous dirt, water, debris, or vegetation while filling the bottle; bottle caps should not be placed on the ground facing downward. Sample labels should be placed on bottles, not bottle caps.

Low flow events may not provide sufficient flows to allow filling of bottles directly. In this case, sample collectors may be used to collect the low flow runoff and transfer the water into the sample bottles. These sample collectors are typically cup- to bucket-sized containers with a wide mouth and no neck, allowing the collector to be placed close to the bottom surface of the flow path and then filled with the small depth of flow. Sample collectors must be compatible in material with the sample bottles and the constituents to be analyzed. Sample collectors made of stainless steel, Teflon® or glass could be considered after investigating the compatibility of these materials with each constituent to be analyzed. After each sample bottle has been filled, and before the next monitoring site is to be sampled, the sample collector should be rinsed thoroughly with deionized water to prevent cross-contamination between sites. At least four rinses with deionized water are necessary, followed by filling the sample collector several times with new monitoring site runoff before finally using the collector to fill the sample bottles.

During high flow events, runoff may be unsafe to approach directly to collect the sample. Modified sample collectors can be designed to allow remote sampling. Many stainless steel buckets or cookware (asparagus cookers) have handles to which ropes may be tied at a length that allows the sample collector to be lowered into the runoff and raised back up after filling with water. These sample collectors with rope are ideal to use if sampling a creek from a bridge or sampling an outfall from a creek bank. In addition, modified sample collectors will work well to sample runoff in a manhole, eliminating the need to enter the confined space during higher flows. The advantage of the rope-and-bucket device is that a significant length of rope can be attached to the sample bucket to allow for sampling from great heights, yet the rope can be coiled and stored compactly. If a sturdier sampling device is needed, sample collectors may be attached to a pole using tape or rope and lowered into the runoff. Again, cross-contamination between sample sites should be prevented by rinsing the sampling collector with deionized water and new sample water several times.

4.7.3 Contamination/Blanks

Control over sample contamination is critical when attempting to measure concentrations of compounds at the parts-per-billion level. Contamination can be introduced either during the bottle/equipment preparation steps or during the sample collection, transport, or analysis steps. Control over all of these steps can be achieved through the use of standardized equipment cleaning procedures, clean sampling procedures, and clean laboratory reagents. The level of contamination introduced during each of these steps is determined by analysis of different types of blank samples. Each of these different types of blanks is described below:

- Method Blanks are prepared by the laboratory by analysis of clean Type II reagent water. They are used to determine the level of contamination introduced by the reagents and laboratory processing.

- Source Solution Blanks are determined by analysis of the deionized or Type II reagent water used to prepare the other blanks. The source solution blank is used to account for contamination introduced by the deionized water when evaluating the other blanks.

- Bottle Blanks are prepared by filling a clean bottle with source solution water and measuring the solution concentration. Bottle blanks include contamination introduced by the source solution water and sample containers. By subtracting the source solution blank result, the amount of contamination introduced by the sample containers can be determined.

- Travel Blanks are prepared by filling a sample container in the laboratory with Type II reagent water and shipping the filled water along with the empty sample containers to the site. The travel blank is shipped back with the samples and analyzed like a sample. The bottle blank result can be subtracted from the travel blank to account for contamination introduced during transport from the laboratory to the field and back to the laboratory.

- Equipment Blanks are usually prepared in the laboratory after cleaning the sampling equipment. These blanks can be used to account for sample contamination introduced by the sampling equipment, if the bottle blank results are first subtracted.

- Field Blanks account for all of the above sources of contamination. Field blanks are prepared in the field after cleaning the equipment and sampling Type II reagent water with the equipment. They include sources of contamination introduced by reagent water, sampling equipment, containers, handling, preservation, and analysis. In general, field blanks should be performed prior to or during the sample collection. Because the field blank is an overall measure of all sources of contamination, it is used to determine if there are any blank problems. If problems are encountered with the field blank, then the other components of the sampling process should be evaluated by preparation of other blanks in order to identify and eliminate the specific problem.

EPA's recent guidance on the use of clean and ultra-clean sampling procedures for the collection of low-level metals samples (EPA 1993a,b) should be considered to ensure bottles and equipment are cleaned properly and samples are collected with as little contamination as

possible. While ultra-clean techniques throughout are likely not necessary for stormwater runoff samples, some of the laboratory procedures should be employed. For example, metals levels in highway runoff are typically much greater than introduced errors associated with in-field clean sampling techniques. These techniques are typically employed in receiving waters where their applicability is more relevant.

4.7.4 Reconnaissance and Preparations

Reconnaissance and preparation is an important component of any field sampling program. Proper reconnaissance will help field operations run smoothly and ensure field personnel are familiar with the sampling locations. During the planning stage, a site visit should be performed by the field personnel, prior to conducting sampling. The purpose of the site visit is to locate access points where a sample can be taken and confirm that the sampling strategy is appropriate. Because of the transient nature of meteorological events, it is possible sites may need to be sampled in the dark. For this reason, the actual persons involved in the field sampling should visit the site during reconnaissance as a complement to a training program for the monitoring effort.

The training program should include:

- A discussion of what the programs goals are and why their efforts are important.
- Familiarization with the site.
- Training on the use and operation of the equipment.
- Familiarization with field mobilization, sampling, and demobilization procedures.
- Health and safety requirements.
- QA/QC procedures.

4.7.4.1 Laboratory Coordination

Coordination with the laboratory is a critical step in the planning and sampling process. The laboratory should be made aware of specific project requirements such as number of samples, required laboratory performance objectives, approximate date and time of sampling (if known), required QA/QC samples, reporting requirements, and if and when containers or ice chests will be required. Laboratory personnel should be involved early in the process so they can provide feedback on methods and performance standards during the planning phase. For example, in cold climates where deicers are used, chlorides can significantly affect detect limits for nutrients; so communicate with the lab on this type of factor. Notifying the laboratory that stormwater sampling is planned is also important to allow the laboratory to plan for off-hours sample delivery and to set-up any analysis with short holding times.

4.7.4.2 Sample Containers/Preservation/Holding Times

EPA recommends that samples be collected and stored in specific types of sample container materials (e.g., plastic, glass, Teflon®). For analysis of certain parameters, addition of specific chemical preservatives is recommended to prolong the stability of the constituents during storage. Federal Register 40 CFR 136.3 outlines recommended sample containers, preservatives, and maximum recommended holding times for constituents. Exhibit 4-11 summarizes container types, holding times, and other requirements for various analytes. Sample holding times should be compared to the recommended maximum holding times listed in the Federal Register. Laboratory quality control sample data should be compared to target detection limits as well as precision and accuracy goals and qualified specified in Quality Assurance Project Plans (QAPPs).

If composite sampling procedures are to be used to collect one large sample that will be subsampled into smaller containers, the composite sample bottle should be compatible with all of the constituents to be subsampled. In general, the use of glass containers will allow subsampling for most parameters (with the exception of fluoride).

Sample volumes necessary for the requested analysis should be confirmed with the laboratory prior to sample collection. Extra sample volume should be collected for field and laboratory QA/QC samples. As a general guide, if one station is to be used for both field and laboratory QA/QC measurements, four times the normal volume of water should be collected.

Exhibit 4-11. Summary of Special Sampling or Handling Requirements*

(Source: Standard Methods for the Examination of Water & Wastewater, APHA 2005)

Determination	Container†	Minimum Sample Size *mL*	Sample Type‡	Preservation§	Maximum Storage Recommended/ Regulatory‖
Acidity	P, G(B)	100	g	Refrigerate	24 h/14 d
Alkalinity	P, G	200	g	Refrigerate	24 h/14 d
BOD	P, G	1000	g	Refrigerate	6 h/48 h
Carbon, organic, total	G	100	g, c	Analyze immediately; or refrigerate and add H_3PO_4 or H_2SO_4 to pH<2	7 d/28 d
COD	P, G	100	g, c	Analyze as soon as possible, or add H_2SO_4 to pH<2; refrigerate	7 d/28 d
Chloride	P, G	50	g, c	None required	28 d
Chlorophyll	P, G	500	g, c	30 d in dark	30 d/N.S.
Conductivity	P, G	500	g, c	Refrigerate	28 d/28 d
Hardness	P, G	100	g, c	Add HNO_3 to pH<2	6 months/6 months
Metals, general	P(A), G(A)	500	g	For dissolved metals filter immediately, add HNO_3 to pH<2	6 months/6 months
Chromium VI	P(A), G(A)	300	g	Refrigerate	24 h/24 h
Copper by colorimetry*					
Mercury	P(A), G(A)	500	g, c	Add HNO_3 to pH<2, 4°C, refrigerate	28 d/28 d
Nitrogen:					
Ammonia	P, G	500	g, c	Analyze as soon as possible or add H_2SO_4 to pH<2, refrigerate	7 d/28 d
Nitrate	P, G	100	g, c	Analyze as soon as possible or refrigerate	48 h/48 h (28 d for chlorinated sample
Nitrate + nitrite	P, G	200	g, c	Add H_2SO_4 to pH<2, refrigerate	none/28 d
Nitrite	P, G	100	g, c	Analyze as soon as possible or refrigerate	none/48 h
Organic, Kjeldahl*	P, G	500	g, c	Refrigerate; add H_2SO_4 to pH<2	7 d/28 d
Oil and grease	G, wide-mouth calibrated	1000	g, c	Add HCl to pH<2, refrigerate	28 d/28 d
Organic compounds:					
MBAS	P, G	250	g, c	Refrigerate	48 h
Pesticides*	G(S), TFE-lined cap	1000	g, c	Refrigerate; add 1000 mg ascorbic acid/L if residual chlorine present	7 d/7 d until extractic 40 d after extractic
Phenols	P, G	500	g, c	Refrigerate, add H_2SO_4 to pH<2	*/28 d
Purgeables* by purge and trap	G, TFE-lined cap	2×40	g	Refrigerate; add HCl to pH <2; add 1000 mg ascorbic acid/L if residual chlorine present	7 d/14 d
Oxygen, dissolved:	G, BOD bottle	300	g		
Electrode				Analyze immediately	0.5 h/stat
Winkler				Titration may be delayed after acidification	8 h/8 h
pH	P, G	50	g	Analyze immediately	2 h/stat
Phosphate	G(A)	100	g	For dissolved phosphate filter immediately; refrigerate	48 h/N.S.
Salinity	G, wax seal	240	g	Analyze immediately or use wax seal	6 months/N.S.

Solids	P, G	200	g, c	Refrigerate	7 d/2–7 d; see cited reference
Sulfate	P, G	100	g, c	Refrigerate	28 d/28 d
Sulfide	P, G	100	g, c	Refrigerate; add 4 drops 2*N* zinc acetate/100 mL; add NaOH to pH>9	28 d/7 d
Temperature	P, G	—	g	Analyze immediately	stat/stat
Turbidity	P, G	100	g, c	Analyze same day; store in dark up to 24 h, refrigerate	24 h/48 h

* See text for additional details. For determinations not listed, use glass or plastic containers; preferably refrigerate during storage and analyze as soon as possible.

† P = plastic (polyethylene or equivalent); G = glass; G(A) or P(A) = rinsed with 1 + 1 HNO_3; G(B) = glass, borosilicate; G(S) = glass, rinsed with organic solvents or baked.

‡ g = grab; c = composite.

§ Refrigerate = storage at 4°C, in the dark.

‖ Environmental Protection Agency, Rules and Regulations. 40 CFR Parts 100–149, July 1, 1992. See this citation for possible differences regarding container and preservation requirements. N.S. = not stated in cited reference; stat = no storage allowed; analyze immediately.

If sample is chlorinated, see text for pretreatment.

4.8 Field QA/QC Procedures

Listed below are the recommended quality control samples and field procedures.

- Field Blanks: Field blanks should be prepared at least once by each field sampling team to prevent or reduce contamination introduced by the sampling process. It is recommended that field blanks be routinely prepared and analyzed with each sampling event. In addition, it is desirable to prepare field blanks prior to the actual sampling event as a check on procedures. This will ensure field-contaminated samples are not analyzed. Additional field blanks should be prepared if sampling personnel, equipment, or procedures change.

- Field Duplicate Samples: Field duplicate samples should be collected at a frequency of 5 percent or a minimum of one per event, whichever is greater. Field duplicate samples are used to provide a measure of the representativeness of the sampling and analysis procedures. These types of duplicates are recommended, but often not collected due to expense.

- Field Sample Volumes: Sufficient sample volumes need to be collected to enable the required laboratory QA/QC analysis to be conducted. In general, one station should be targeted for extra sample volume collection and identified on the chain-of-custody as the laboratory QA/QC station. If possible, this station should be the one where the data quality is most critical.

- Chain of Custody: All sample custody and transfer procedures should be based on EPA-recommended procedures. These procedures emphasize careful documentation of sample collection, labeling, and transfer procedures. Pre-formatted chain-of-custody forms should be used to document the transfer of samples to the laboratory and the analysis to be conducted on each bottle.

4.9 Laboratory QA/QC Procedures

Listed below are key aspects of laboratory QA/QC procedures.

- Method Blanks: For each batch of samples, method blanks should be run by the laboratory to determine the level of contamination associated with laboratory reagents and glassware. Results of the method blank analysis should be reported with the sample results.

- Laboratory Duplicates: For each batch of samples, one site should be used as a laboratory duplicate. For the laboratory duplicate analysis, one sample will be split into two portions and analyzed twice. The purpose of the laboratory duplicate analysis is to assess the reproducibility of the analysis methods. Results of the laboratory duplicate analysis should be reported with the sample results. Be aware that sample splitting methods such as churn and cone splitters may result in higher error for TSS duplicates.'

- Matrix Spike and Spike Duplicates: Matrix spike and spike duplicates should be used to determine the accuracy and precision of the analysis methods in the sample matrix. Matrix spike and spike duplicate samples are prepared by adding a known amount of target compound to the sample. The spiked sample is analyzed to determine the percent recovery of the target compound in the sample matrix. Results of the spike and spike duplicate percent recovery are compared to determine the precision of the analysis. Results of the matrix spike and spike duplicate samples should be reported with the sample results.

- External Reference Standards: External reference standards are artificial standards prepared by an external agency. The concentrations of analytes in the standards are certified within a given range of concentrations. These are used as an external check on laboratory accuracy. One external reference standard appropriate to the sample matrix should be analyzed and reported at least quarterly by the laboratory. If possible, one reference standard should be analyzed with each batch of samples.

4.10 Conclusion

A successful and economically viable water quality sampling program requires careful forethought regarding the types of equipment for sample collection and types of constituents to be analyzed. To yield usable data, procedures for proper sample collection and analysis must be clearly defined upfront in a written monitoring plan and carefully followed in the field. A successful water quality monitoring program is also dependent on strong experimental design that will yield data sets enabling statistically significant conclusions to be drawn regarding BMP performance.

4.11 References

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