Day 3: Stormwater Sampling Methods and Automatic Sampler Setups

Mostly excerpted from: Burton, G.A. Jr., and R. Pitt. Stormwater Effects Handbook: A Tool Box for Watershed Managers, Scientists, and Engineers. CRC Press, Inc., Boca Raton, FL . 2002. 911 pages Freely available at: http://unix.eng.ua.edu/~rpitt/Publications/BooksandReports/Stormwater%2 0Effects%20Handbook%20by%20%20Burton%20and%20Pitt%20book/MainED FS_Book.html

Plus excerpts from various research projects

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Types of Stormwater Sampling for Different Objectives

- Source area sampling to identify and quantify sources of stormwater pollutants
- Performance testing of stormwater controls
- Outfall sampling to quantify land use discharges and benefits of distributed controls
- Receiving water sampling to supplement study on beneficial use impairments







WinSLAMM Model Strength – Based on Extensive Field Monitoring Data

- Source Areas Roofs, Streets, etc.
- > End of Pipe Many Land uses
- Stormwater Control Practices

Lawn Sheet Flow Sampler: Tipping Bucket for Flow and Cone Splitter for Water Sample



Controlled tests in small areas were used in conjunction with long-term rainfall/runoff monitoring at larger parking lot areas to develop actual hydrological relationships for paved areas, the most significant source of runoff for most urban areas during small to intermediate-sized rains.



This is an example of a rainfall-runoff plot from one of many controlled street washoff and runoff tests. About 1/3 of the rainfall is infiltrated through the street pavement for many of these events (up to 20 mm rains in this plot). No further infiltration was observed for larger events, resulting in classical pavement Rv values 0.0.8 to 0.95 for large rains of interest for drainage design.



Other Source Area Sampling Methods

Paved areas become less important flow sources when landscaped areas start to contribute flows during later periods of the event (in this case, after about 0.5 in or 10 mm of rain)

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Manual Sampling Procedures

Dipper Samplers

- The simplest manual sampler is a dipper sampler
- These samplers can only obtain samples from the surface of the water. If subsurface samples are needed, then samplers having closure mechanisms need to be used.
- A dipper allows sampling of surface waters away from the immediate shoreline and from outfalls or sewerage pipes more conveniently than by using other types of samplers.
- Dippers are commonly used to sample small discharges from outfalls, where the flow is allowed to directly pour into the sampler.
- The sample is poured directly into sample bottles, or into a larger container (preferably a churn sampler splitter) for compositing several dipped samples.

Light Industrial Area Runoff Sources 100 Streets, intermediate texture 80 8 **Relative Contributions** 60 Paved parking and storage areas 40 20 Flat roofs, directly connected 0 0.01 0.05 0.1 0.25 0.5 0.75 1 1.5 2 2.5 3 Rain Depth (inches)

Flow source changes are less dramatic for areas that are mostly paved and have large roof areas. Travel time to the outfall is the predominant factor affecting source contributions for this case.

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Manual Sampling Procedures Submerged Water Samplers with Remotely Operated Closures

- This design allows unhindered flow through the sample container before closure, enabling faster equilibrium with surrounding waters.
- Several of the vertical units can be used on a single line to obtain water samples from various depths simultaneously.
- A weighted messenger slides down the line that the samplers are attached to, striking a trigger mechanism that closes the end seals, releasing the next messenger for the next sampler on the line.

Manual Sampling Procedures Depth-Integrated Samplers for Suspended Sediment

- Suspended sediment is usually poorly distributed in both flowing and quiescent water bodies. The sediment is usually in greater concentrations near the bottom. Larger and denser particles are also predominantly located in lower depths.
- Depth-integrating sampling is commonly done in small upland streams. Sampling in smaller and more turbulent flows (such as in some sewerage or at outfalls during moderate to large storms) is not as severely affected by sediment stratification.

When collecting a depth-integrated sample, the sampler needs to stand to the side and downstream of the sampling area to minimize disturbance. The rod is lowered vertically through the water column at a constant rate at about 0.4 times the stream velocity. The sampler is lowered at this constant rate from the surface of the stream to the stream bottom, and then reversed and brought back to the surface at the same rate.

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Manual Sampling Procedures

Source Area Sheetflow Samplers

- Manual sheetflow samplers are usually used when collecting grab samples from many different sampling locations.
- A small team can visit many sampling sites during a single rain to obtain multiple grab samples for statistical comparisons.
- The main drawback is that the samples are not composited during the rain and only represent the conditions during the short sampling period.

Manual Sampling Procedures

Manual Pump Samplers

Pump water sampling systems commonly used for well sampling can be used to deliver a water sample to a convenient location, especially useful when sampling wide and swift streams from a bridge, if weighted.

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Monitoring to Evaluate Performance of Stormwater Controls

Basic Monitoring Strategy to Verify Stormwater Controls

- Scale-up of monitoring from field, to pilot, to full-scale stormwater control devices
- Need flexibility of small units with flow control and convenient sampling ports to test many variables under large variety of conditions
- Need to verify with full-scale units to check performance under real-world conditions

Milwaukee, WI, Ruby Garage Public Works Maintenance Yard MCTT Tests (0.25 acre site)

Different Pilot-Scale Stormwater Treatment Setups

May have small biases with automatic vs. manual sampling, but automatic sampling allows unattended operation under a variety of conditions and captures complete event. Manual sampling can better represent complete range of particulate matter in sample.

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Outfall Monitoring to Characterize Land Use Discharges and to Measure Benefits of Distributed Stormwater Controls

Advantages and Disadvantages of Manual and Automatic Sampling

Түре	Advantages	DISADVANTAGES	
Manual	Low capital cost	Probability of increased variability due to sample handling	
	Point-in-time characterization	Not a composite unless long duration visit	
	Compensate for various situations	Inconsistency in collection	
	Note unusual conditions	High cost of labor	
	No maintenance	Repetitious and monotonous task for personnel	
	Can collect extra samples in short time when necessary		
Automatic	Consistent samples	Considerable maintenance for batteries and cleaning; susceptible to plugging	
	Probability of decreased variability caused by sample handling	by solids	
		Restricted in size to the general	
	Minimal labor requirement for sampling	specifications	
		Inflexibility	
	Has capability to collect multiple		
	bottle samples for visual estimate of variability and	Sample contamination potential	
	analysis of individual bottles	Subject to damage by vandals	

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Monitoring Equipment Descriptions

- Automated Precipitation Measurement (Recording rain gauge)
- Manual Precipitation Measurement (Non-recording rain gauge) as a standard
- Automated Flow Measurement (primary devices including pipes, gutter, flumes and weirs, and secondary devices including bubbler level sensor and area-velocity sensors).
- Manual Flow Measurement (direct velocity reading using velocity meter or similar device combined with level measurement using field rulers) to calibrate automatic flow measurement equipment.
- Automated Water Quality Sample Collection (composite sampling equipment).
- Field Water Quality Measurement (pH, temperature, ORP, dissolved oxygen, turbidity, and conductivity meters).

sampler used to monitor snowmelt in Toronto, Ontario, manhole

ISCO sampler used in instrument shelter with flow monitoring and telemetry equipment in Madison, WI

Intermittent stream monitoring in Austin, TX

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Refrigerated automatic sampler located at detention pond outfall in Madison, WI

Composite sample bottle from Toronto snowmelt sampler.

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Losses of Particles in Automatic Sampler Intake Lines									
	30 cm/sec	flow rate	100 cm/sec flow rate						
	Critical settling rate (cm/sec)	Size range (μm, for ρ = 1.5 to 2.65 g/cm ³)	Critical settling rate (cm/sec)	Size range (μm, for ρ = 1.5 to 2.65 g/cm ³)					
100% loss	30	2,000 - 5,000	100	8,000 - 25,000					
50% loss	15	800 - 1,500	50	3,000 - 10,000					
25% loss	7.5	300 - 800	25	1,500 - 3,000					
10% loss	3.7	200 - 300	10	350 - 900					
1% loss	0.37	50 - 150	1	100 - 200					

Typical 3/8 inch sample line is about 9,500 μ m in diameter (about the same for holes in inlet strainer) which restricts the absolute maximum size particle. Goal of 10% maximum loss associated with about 350 μ m particles, or less, for super-speed sampler. To Data Loger

base for ISCO

automatic sampler.

Non-Recording Rain Gauge and Tipping Bucket Rain Gauge

and inlet strainer and tubing

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It is difficult to program an automatic sampler to collect flow-weighed samples over a wide range of flow conditions.

> 0:20 Time 3:00 use timecompositing instead of flow-weighted sampling and then manually composite the sample using the available flow data

0:30

use a large sample base in order to accommodate a wide range of runoff events

Simple methods to obtain representative sample: create cascading and well-mixed flow at sampling location (wellmixed flow with bedload and no stratification). Examples shown for gutter and pipe flow installations.

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The use of continuous water quality sondes can supplement other sampling programs by providing high resolution data for a variety of constituents (turbidity, temperature, DO, ORP, and conductivity).

Sonde data analysis screen showing ten days of highresolution (every 15 minute) water quality measurements

End of pipe monitoring to check mass balance using source area flow and pollutant contribution calculations/modeling

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Issues Concerning Stormwater that May Need to be Addressed

- Rainfall patterns must be considered for area being studied, and accurate flow measurements are necessary as performance is commonly related to hydraulic conditions. Most flow instruments must be calibrated at the site.
- The variability of stormwater quality must be considered when designing a sampling program.
- Incorrectly reported data can have a very large effect on many statistical analyses
- Variability of stormwater quality does not always vary as anticipated ("first-flush" relatively rare, unless mostly paved areas and small drainage areas; little relationship with rain depth of event, but stronger relationship with peak rain intensity energy)
- Sources of flows and pollutants vary with land use and development characteristics

Continuous Simulation can be used to Determine Needed Treatment Flow Rates: - 90% of the annual flow for SE US conditions is about 170 gpm/acre pavement (max about 450).

- treatment of 90% of annual runoff volume would require treatment rate of about 100 gpm/acre of pavement. More than three times the treatment flow rate needed for NW US.

Typical Stormwater Constituent Probability Distribution Many stormwater constituent concentrations are log-normally distributed between about the 5th and 95th percentiles of the observations (this example is for several thousand residential stormwater copper observations from the National Stormwater Quality Database, NSQD)

Many US NPDES stormwater monitoring programs only monitor the first three hours of the runoff event, possibly missing much of the event and possibly missing the peak flows where the highest concentrations are most likely to occur

Programming Stormwater Samplers

 Need to program automatic samplers to collect samples under a wide-range of flow conditions.

Automatic samplers can generally operate in two sampling modes, based on either time or flow increments. The sample bases can generally hold up to 24 bottles, each 1 L in volume. A single sample bottle of up to about 20 L is generally available for compositing the sample into one container. These bottle choices and the cycle time requirements of automatic samplers restrict the range of rain conditions that can be represented in a single sampler program for flow-weighted sampling.

It is important to include samples from small rains (from about 0.01 to 0.2 inch) in a stormwater sampling program because they are very frequent and commonly exceed numeric water quality criteria. Moderate sized rains (from about 0.2 to 3 inches) are very important because they represent the majority of flow (and pollutant mass) discharges. The largest rains (greater than about 3 inches) are important from a drainage design perspective to minimize flooding and safety problems.

It is very difficult to collect a wide range of rain depths in an automatic sampler using flow-weighted sampling. Conflicts occur between needing to have enough sub-samples during the smallest event desired (including obtaining enough sample volume for the chemical analyses) and the resulting sampling frequency during peak flows for the largest sampling event desired.

Programming an Automatic Sampler

Automatic samplers go through three phases to collect a sample. First, the sample line is back-flushed to minimize sample cross-over and to clear debris from the sample intake. Next, the sample is collected. Finally, the sample is back-flushed again before going into a sleep mode to await the next sampling instruction. It can require several minutes to cycle through this process. A volume of 1850 mL of water fills a 10 mm (3/8 inch) diameter sample line that is 7.5 meters (25 feet) long. If a sample volume of 350 mL is to be collected for each sample instruction:

back-flush line:	1850 mL
fill tube:	1850 mL
collect sample:	350 mL
back-flush line:	1850 mL

This totals about 6 L of water to be pumped. Typical automatic samplers have a pumping rate of about 3.5 L per minute for low head conditions (about 1 meter). It would therefore require about 1.7 minutes to pump this quantity of water. With pump reversing and slower pumping speeds at typical pumping heads, this could easily extend to 2 minutes, or more. If the sampler collects 3 liters of sample instead of 350 mL, then another minute can be 38 added to this sampling time for one cycle.

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Problem: desired minimum rain to be sampled: 0.15 inch in depth, 4 hour runoff duration, having a 0.20 Rv (volumetric runoff coefficient); largest rain desired to be sampled: 2.5 inch in depth, 12 hour runoff duration, having a 0.50 Rv; the watershed is 250 acres in size and 3 samples, at least, are needed during the smallest rain.

The calculated total runoff for these conditions is therefore:

minimum rain: 0.10 (0.15 in) (250 ac) (ft/12 in) (43,560 ft²/ac) = 13,600 ft³.

maximum rain: 0.50 (2.5 in) (250 ac) (ft/12 in) (43,560 ft²/ac) = 1,130,000 ft³.

The average runoff flow rates expected are roughly estimated to be:

minimum rain: (13,600 ft³/4 hr) (hr/3600 sec) = 0.95 ft³/sec.

maximum rain: (1,130,000 ft³/12 hr) (hr/3600 sec) = 26 ft³/sec.

Based on monitoring of many runoff events, the peak flows are estimated to be about 3.8 times these average flow rates:

minimum rain: 3.6 ft³/sec.

maximum rain: 100 ft³/sec.

As the smallest storm is to be sampled three times during the runoff period, the volume of flow per sub-sample is simply:

13,600 ft³/3 @ 4,500 ft³.

Therefore, the total number of samples collected during the maximum rain would be:

1,130,000 ft³/4,500 ft³ @ 250 samples.

If the minimum sample volume required was 1 L, then each sub-sample could be as small as 350 mL. This would result in about 1 L of sample during the minimum storm, but would result in about 90 L during the maximum storm (obviously much larger than the typical 10 to 20 L container). During the estimated high flow conditions of the largest storm, a sub-sample would be collected every:

4,500 ft³ per sample/100 ft³/sec @ 45 seconds

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Double monitor setups for sampling over a wide range of flow conditions

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If the sampler required 2 minutes to collect 350 mL, the sampler would not complete its cycle before it was signaled to collect another subsample. This would result in the sampler pump running continuously during this peak time. Since the peak flow period is not expected to have a long duration, this continuous pumping may not be a serious problem, especially considering that about 250 samples are being collected. The biggest problem with this setup is the large volume of sample collected during the large event.

Automatic sampler with large base for monitoring wide range of flows, with large chest freezer USGS discrete sampler in background, at Bellevue, WA

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Alternatives to using a large sample base in order to accommodate a wide range of flows include:

- use time-compositing instead of flow-weighted sampling (if discrete sampling, the individual time-initiated samples can be manually composited after the event, but this requires substantial labor time),
- use two samplers located at the same location, one optimized for small flows, the other optimized for larger, or
- visit the sampling station during the storm and re-program the sampler, switch out the bottles, or manual sample.

Programming of Automatic Samplers

- System counters (e.g., precipitation, runoff volume, sample count, etc.) are reset to zero.
- The mode is switched from non-storm monitoring mode to storm monitoring mode, which typically will increase data collection frequency (to 1-minute logging intervals) and allow the system to begin sample collection once thresholds are met.
- Thresholds are set for sampling locations to allow stations to enter sample collection mode. Thresholds can include the minimum precipitation amount, flow depth, or flow volume required to initiate the sample collection routine.
- For flow-paced sampling, the flow volume per sample (i.e., the flow volume that passes between each composite aliquot collected) is set based on the expected amount of runoff generated from the rainfall event.
- The system must have "start sampling" and "stop sampling" options that can be selected when appropriate (e.g., at the beginning of a storm, during bottle changes, at the end of a storm).
- When samples have been collected, the sampling event is terminated and software is switched back to the non-storm monitoring mode.
- Data are downloaded from the datalogger to a personal computer immediately following the storm event.

Example Stormwater Monitoring (San Diego evaluation of biofilter)

Sample Number Requirements

Coefficient of Variation, <i>CV</i> , of	Statistical Confidence Level,	Power of Detecting Specified Percent	Sample Si Specified Pe	ze to Detect rcent Removal
Percent Removal	1-α	Removal, 1- β	Removal, 1- <i>β</i> 25%	
0.4	90%	80%	9	3
0.6	90%	80%	18	4
0.8	90%	80%	28	6

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Sampling Information Needs

- Model sites for expected runoff conditions (runoff volume vs. rain depth; concentrations expected; expected performance)
- Bottles and preservatives
- Sampler programming (volume per sample pulse as a function of sample volume needs)
- Maintenance issues (clogging, bypassing, chemical capacity)
- Design suggestions (sizes of treatment units, etc.)

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Site Name	Location	Type of BMP	Monitoring Sample Location Description	Type of Samples
Bior-I	N. of Intersection of 43 rd Street and Logan Avenue	Bioretention Basin	Modified Reverse Curb Outlet	Stormwater
Bior-E	N. of Intersection of 43 rd Street and Logan Avenue	Bioretention Basin	Perforated Drain Pipe Entering Type F Catch Basin	Stormwater
Bior-B	N. of Intersection of 43 rd Street and Logan Avenue	Bioretention Basin	Outlet Pipe from Type F Catch Basin	N/A – Flowrate only
Filt-I	NW Corner of 43 rd Street and Newton Ave. – gutter flow line	Filtration Unit	Gutter Upstream of 1st Filtration Unit Curb Inlet Opening	Stormwater
Filt-E	E. 43 rd Street just S. of Intersection with Logan Ave. Catch Basin drain from Filtration Units	Filtration Unit	Perforated Drain Pipe Entering Catch Basin Downstream of Filtration Unit	Stormwater
Filt-B	E. 43 rd Street just S. of Intersection with Logan Ave. Catch Basin Flow (Bypass from Filtration Units)	Filtration Unit	Catch Basin Downstream of Filtration Unit at Curb Inlet Opening	N/A – Flowrate only

Comparison of Watershed Areas and Land Uses

Watorshod	HSA		Land Use									
watersneu	No.	Ag	Auto	Comm.	Ind.	Inst.	Parks	LDR	HDR	Roads	Trans.	Water
City of San Diego		4,618	341	6164	10,952	15,027	83,935	38,558	13,384	7,405	4,091	5,829
(all watersheds)	-	2.4%	0.2%	3.2%	5.8%	7.9%	44.1%	20.3%	7.0%	7.0%	2.1%	3.1%
Chollas (within	000.00	14.43	30.97	695.39	518.93	1,177.08	2,397.83	4,967.80	2,643.57	967.62	234.93	32.42
City boundary)	908.22	0.1%	0.2%	5.1%	3.8%	8.6%	17.5%	36.3%	19.3%	7.1%	1.7%	0.3%
Triangle Lat	000.00						0.33			0.38		
Triangle Lot	908.22		-		-	-	46.47%			53.53%	-	-
Monitored								0.99	0.21	.092		
Filtration Unit	908.22	•		-	-	-		46.70%	9.90%	43.40%	-	1
(Dasin'i I)												
Filtration Unit	908.22		-	-	-	-		-		0.25	-	-
(Basin F2)										100%		
Unmonitored				0.44				0.42	0.27	2.26		
Filtration Unit	908.22	-	-	12.98%	-	-	-	12.40%	7.96%	66.66%	-	-
(Dasin P3)												

Drainage Map – Filtration Unit Stormwater Controls – 43rd Street and Logan Avenue

Basin	Land Use	Area (acres)	с	Composite C	Rainfall Intensity (in)	Water Quality Event Runoff (cfs)
F1	Single Family Residential	0.99	0.55			
	Multi-Family	0.21	0.55			
	Street	0.92	0.70			
	Total	2.12	0.90	0.72	0.20	0.56
F2	Street	0.25				
	Total	0.25	0.90	0.90	0.20	0.05
F3	Single Family Residential	0.42	0.55			
	Multi-Family	0.27	0.70			
	Commercial	0.27	0.85			
	Street	2.26	0.90			
	Vacant	0.17	.050			
	Total	3.39		0.82	0.20	0.56
В	Street (B1)	0.38	0.00			
	Park, vegetated (B2)	0.24	0.38		0.20	0.44
	Park, bioretention basin (B3)	0.11	0.24		0.20	0.11
	Total	0.73	0.11	0.78		

Basin Land Use and Composite Runoff Coefficient for Filtration Units

Site Inspections

- Photo documentation of site conditions and accumulation of gross solids.
- Recording visual estimates of the total volume of gross solids and percent composition by volume of trash, sediment, and organic debris (i.e., leaf litter and other vegetative material) in the stormwater control, curb and gutter both upstream and downstream of the stormwater controls, and in the catch basin immediately downstream of the stormwater control.
- Visual assessment of stormwater control for clogging.
- Visual inspection for proper drainage of the stormwater control (no standing water) in the monitoring wells.
- Inspection for presence of vectors.
- Noting condition of treatment media.
- Documenting observations related to stormwater control
- integrity/structural deterioration.
- Notifying Division Project Manager of any maintenance issues that require immediate attention.

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Analytic	Targe	t Detection	Analytical Technique	Method	
Analyte	Limit Units		Analytical Technique	Number	
Conventionals					
Hardness as CaCO ₃	2.0	mgiL	titrimetric/colorimetric; ICP, calculation	EPA 130.2; 130.1, 200.7; SM 2340B, 2340C	
Turbidity	0.05	NTU	Nephelometric	EPA 180.0; SM 130B, 2130B	
Total Suspended Solids (TSS)	1.0	mg/L	dried filter weight	EPA 160.2, SM 2540D	
Total Dissolved Solids (TDS)	1	mg/L	Gravimetric	EPA 160.1/ SM 25400	
Suspended Sediment Concentration (SSC)	1	mg/L	Gravimetric	ASTM D3977; SM 2450 F	
Particle Size Distribution	varies	mgikg	Beckman-Coulter Counter, Laser Particle Counter	ASTM 4464; Bob Pitt's Method	
Conductivity	0.1	µmhosicm	conductivity meter	EPA 120.1; SM 2510B	
pH	0.1	std. units	Electrometric	EPA 150.1; SM 4500H+B	
Redox Potential	1	mV	Electrode	ASTM D-1498; SM 2580	
Biochemical Oxygen Demand (BOD)	1	mg/L	Electrode	SM 5210B	
Chemical Oxygen Demand (COD)	5	mg/L	Colorimetric	SM 5220C, 5220D	
Total Organic Carbon (TOC)	0.5	mg/L	Combustion	SM 5310D	
Dissolved Organic Carbon (DOC)	0.5	mg/L	Combustion	SM 4500-O G, 5310B	
Nutrients					
Nitrate as Nitrogen (NO3-N)	0.1	mg/L	IC	EPA 300.0	
Nitrite as Nitrogen (NO2-N)	0.1	mg/L	IC	EPA 300.0; SM 4500NO2B	
Ammonia Nitrogen (NH3-N)	0.1	mg/L	Electrode; Titrimetric	SM 4500-NH3 B	
Total Kjeldahl Nitrogen (TKN)	0.1	mg/L	Colorimetric; Titrimetric; Potentiometric	EPA 351.2, 315.3	
Total Nitrogen (TN)	0.1	mg/L	Calculation	SM4500-NORG B	
Total Phosphorus	0.03	mgʻL	Colorimetric	EPA 365.2; SM 4500PB	
Dissolved Ortho-Phosphorus	0.1	mal	IC	EPA 300, 365.2	

			Chain-o	f-Custo	bdy I	Form					
Laboratory Date Rec'd	r: Lab #		Frem: Crowillan Name Address Telebane Number Fax Number								
Project Nat P.O.#:	me:				Pro Reg	ject #: uired Com	pletion D	Date:			
Sample ID #	Site ID #	Lab ID #	Matrix/Analysis	Containers	Pres.	Samı Date/T	ple Time	Condition Upon Receipt			
					-						
Data Report applicable, l	ts MUST Date of A	include the nalysis, Ani	following: Sample/Site alytical Results and Sig	ID, Analytical M nature of QA Rev	ethod, Dete	ection Limit,	Date of	Extraction if			
Special Inst	ructions/C	omments:									
Relinquishe	d By: Dat	e/Time		Transporter	Received	By: Date	e/Time				
Relinquishe	d By: Dat	e/Time		Transporter	Received	By: Date	e/Time				
Relinquishe	d By: Dat	e/Time		Transporter	Received	By: Date	e/Time				

Analuta	Targe	t Detection	Analytical Technique	Method
Analyte	Limit	Units	Analytical rechnique	Number
Major lons	·			
Sulfide, Total	0.5	mg/L	Colorimetric	SM 4500 S2-D
Chloride	1.0	mg/L	IC	EPA 300.0
Sulfate	0.5	mg/L	IC	EPA 300.0
Sodium	0.5	mg/L	ICP	EPA 200.7
Calcium	1.0	mg/L	ICP	EPA 200.7
Magnesium	0.1	mg/L	ICP	EPA 200.7
Potassium	0.5	mg/L	ICP	EPA 200.7
Silicon	0.05	mg/L	ICP	EPA 200.7
Boron	0.02	mg/L	ICP	EPA 200.7
Fluoride	0.1	mg/L	Titrimetric	SM 4500 F C
Metals (Total Recoverable and Dissolve	d)			
Aluminum	0.05	mg/L	ICP-MS; ICP	EPA 200.7, 200.8
Antimony	0.001	mg/L	ICP-MS	EPA 200.8
Arsenic	1.0	μg/L	GF-AA; ICP-MS	EPA 206.3; 1632a 200.8
Barium	0.001	mg/L	ICP-MS	EPA 200.8
Beryllium	0.001	mg/L	ICP-MS	EPA 200.8
Cadmium	0.2	µg/L	GF-AA; ICP-MS	EPA 213.2; 200.8
Chromium	1.0	μg/L	GF-AA; ICP-MS	218.2; 200.8b
Cobalt	0.001	mg/L	ICP-MS	EPA 200.8
Copper	1.0	µg/L	GF-AA; ICP-MS	220.2; 200.8b
Iron	0.05	mg/L	ICP-MS	EPA 200.8
Lead	1.0	μg/L	GF-AA; ICP-MS	239.2; 200.8b
Mercury	0.002	mg/L	CV-AA	EPA 245.1
Molybdenum	0.001	mg/L	ICP-MS	EPA 200.8
Nickel	2.0	ua/L	GF-AA; ICP-MS	249.2; 200.8b
Selenium	0.001	mg/L	ICP-MS	EPA 200.8
0 hore	0.001	ma/l	ICP-MS	EPA 200.8
Silver				

Analyte	Target	t Detection	Analytical Toologian	Method	
Analyte	Limit	Units	Analytical Technique	Number	
Zinc	5.0	μg/L	GF-AA; ICP-MS	289.2; 200.8b	
Biologicals					
Total Coliform	1	MPN/100mL	Incubation	SM 9221B	
Fecal Coliform	1	MPN/100mL	Incubation	SM 9221E	
Enterococcus	1	MPN/100mL	Incubation	SM 9230B	
		Organics		1	
Oil and Grease	1	mg/L	Gravimetric	EPA 1664	
TPH (Diesel)	13.6	μg/L	GC-MS	EPA 8015DRO	
TPH (Gasoline)	12.4	μg/L	GC-MS	EPA 8015GRO	
TPH (Motor oil)	39.4	μg/L	GC-MS	EPA 8015DRO	
Chlordane	0.5	μg/L	GC-ECD	EPA 608	
DDT	0.05	μg/L	GC-ECD	EPA 608	
Diazinon	0.005	μg/L	GC-NPD	EPA 8141	
PAHs	10, 25, 50	μg/L	GC-NPD; GC-MS	EPA 610/8100, 8270	
Organochlorine Pesticides and PCBs	0.2	μg/L	GC-ECD	EPA 8081/8082/608	
Arochlor and PCB Congeners	0.5 / 0.2	μg/L	GC-MS	EPA 8270 SIM	
Organophosphorus Pesticides	0.01, 0.02, 0.04, 0.005	mg/L	GC-NPD	EPA 614/ 8141	
Synthetic Pyrethroid Pesticides	0.002	μg/L	GC-MS SIM	EPA 8270	
Notes: a EPA Method 1632 is an additional availab	ole "clean techniq	ue" GH-AA method th	at can be used for this constituent.	EPA method approval is in	

progress.

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EPA Method 1638 is an additional available "clean techniqu	e" GH-AA method that can be used for this	constituent. EPA method approval is i
progress.		

Analyte	Holding Time	Minimum Sample Volume ^a	Container Type	Preservation
Conventionals				
Hardness as CaCO ₃	6 months	100 mL	Glass or Plastic	4°C , HN03 or H2SO4 to pH < 2
Turbidity	48 hr	100 mL	Glass or Plastic	4°C
Total Suspended Solids (TSS)	7 days	100 mL	Glass or Plastic	4°C
Total Dissolved Solids (TDS)	7 days	500mL	Glass or Plastic	4°C
Suspended Sediment Concentration (SSC)	7 days	500mL	Glass or Plastic	4°C
Particle Size Distribution	24 hrs	1L	Glass	4°C
Conductivity	28 days	50 mL	Glass or Plastic	4°C; filter if hold time > 24 hrs
pH	Immediately	50 mL	Glass or Plastic	4°C
Redox potential	24 hrs	50 mL	Plastic	4°C
Biochemical Oxygen Demand (BOD)	48 hrs	300 mL	Plastic	4°C
Chemical Oxygen Demand (COD)	28 days	50 mL	Glass	4°C and H₂SO₄
Total Organic Carbon (TOC)	28 days	150 mL	Glass	4°C and H ₂ SO ₄
Dissolved Organic Carbon (DOC)	28 days	150 mL	Glass	Field filter, 4°C and H ₂ SO ₄
Nutrients				
Nitrate as Nitrogen (NO3-N)	48 hr	200 mL	Glass or Plastic	4°C
Nitrite as Nitrogen (NO2-N)	48 hr	200 mL	Glass or Plastic	4°C
Ammonia Nitrogen (NH3-N)	28 days	500 mL	Amber Glass	4°C and H ₂ SO ₄
Total Kjeldahl Nitrogen (TKN)	28 days	500 mL	Glass or Plastic	4°C and H₂SO4 to pH<2
Total Nitrogen (TN)	28 days	500 mL	Amber Glass	4°C and H ₂ SO ₄
Total Phosphorus	28 days	100 mL	Glass or Plastic	4°C and H ₂ SO ₄ to pH<2

Recommended Quality Control Sample Frequency

QA/QC Sample Type	Minimum Sampling Frequency	Constituent Class
Field Duplicate	Once every ten samples collected at a given sampling station.	All
Laboratory Duplicate	Once every ten samples collected at a given sampling station.	All
Equipment Blank	Equipment blanks should be collected prior to each sampling season for each piece of equipment to be used for sample collection (tubing, strainers).	Metals and other common contaminants. ¹
Bottle Blank	Composite and sample bottles should be blanked every batch ² at a 2% frequency; or manufacturer or laboratory- certified to concentrations below the reporting limits used for the sampling program.	Metals and other common contaminants. ¹
Field Blank	Once every ten samples collected at a given sampling station.	Metals and other common contaminants. 1
Matrix Spike/Matrix Spike Duplicate	Once every ten samples collected at a given sampling station.	Metals and other common contaminants. ¹

Analyte	Holding Time	Minimum Sample Volume ^a	Container Type	Preservation
Dissolved Ortho-Phosphorus	48 hrs	50 mL	Plastic	4°C
Major lons				
Sulfide, Total	7 days	50 mL	Plastic	ZnAc ₂ and NaOH and 4°C
Chloride	28 days	50 mL	Plastic	4°C
Sulfate	28 days	50 mL	Plastic	4°C
Sodium	6 months	100 mL	Plastic	HNO3
Calcium	6 months	100 mL	Plastic	HNO3
Magnesium	6 months	100 mL	Plastic	HNO3
Potassium	6 months	100 mL	Plastic	HNO3
Silicon	6 months	100 mL	Plastic	HNO ₃
Boron	6 months	100 mL	Plastic	HNO ₃
Fluoride	28 days	100 mL	Plastic	4°C
Metals ^{b,c} (Total Recoverable and Dissolved) Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium, Cobalt, Copper, Iron, Lead, Molybdenum, Nickel, Selenium, Silver, Thallium, Zinc	6 months (filter for dissolved fraction and preserve within 48 hrs, 6 months to analysis)	100 mL	Teflon, Plastic or Borosilicate Glass	4°C and HNO₃ to pH < 2°
Mercury	28 days	500 mL	Plastic or Glass	4°C and HNO ₃
Biologicals				
Total Coliform	8 hrs	100 mL	Sterile Plastic or Glass	<10°C
Fecal Coliform	8 hrs	100 mL	Sterile Plastic or Glass	<10°C

Analyte	Holding Time	Minimum Sample Volume ^a	Container Type	Preservation
Enterococcus	8 hrs	100 mL	Sterile Plastic or Glass	<10°C
Organics		,		
Oil and Grease	7 days	1 L	Amber Glass	4°C and H ₂ SO ₄
TPH (Diesel)	7 days / 40 days post extraction	500 mL	Amber Glass	4°C
TPH (Gasoline)	7 days	2 x 40 ml	Glass VOA vials	4°C and HC1
TPH (Motor oil)	7 days / 40 days post extraction	500 ml	Amber Glass	4°C
Chlordane	7 days / 40 days post extraction	1 L	Amber Glass	4°C
DDT	7 days / 40 days post extraction	1 L	Amber Glass	4°C
Diazinon	7 days / 40 days post extraction	1 L	Amber Glass	4°C
PAHs	7 days / 40 days post extraction	1 L	Amber Glass	4°C
Organochorine Pesticides and PCBs	7 days / 40 days post extraction	1 L	Amber Glass	4°C
Arochlor and PCB Cogeners	7 days / 40 days post extraction	1 L	Amber Glass	4°C
Organophosphorus Pesticides	7 days / 40 days post extraction	1 L	Amber Glass	4°C
Synthetic Pyrethroid Pesticides	7 days / 40 days post extraction	1 L	Amber Glass	4°C

Notes:

nuous: a Parameters with like preservatives can be combined into a single container if the same laboratory is performing the analyses. For example, TDS, TSS, thirdidit, conductivity, and HI can be put in a single 1 L plastic container. b Metals are collected in a single container. c Filter dissolved samples before preservation.

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Conclusions

- Many options for collecting stormwater samples for analyses
- Automatic flow-weighted composite sampling considered the "gold standard"
- However, manual sampling may be best for some conditions

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• Many steps are necessary to ensure problem-free sampling