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Chapter 5

Quality assurance/ quality control in stormwater sampling

David McCarthy & Daren Harmel

Sampling stormwater presents unique challenges because stormwater flow is relatively short-lived with drastic variability. Furthermore, storm events often occur with little advance warning, outside conventional work hours and under adverse weather conditions. Therefore, most stormwater sampling projects utilize automated water quality samplers so that personnel are not forced to travel to multiple sites during events and manually collect samples under potentially hazardous conditions. This chapter discusses project objectives and resource considerations along with discharge measurement, sample collection, number of samples required, and the resulting uncertainty in reported constituent concentrations and loads. This will assist technical staff and project managers in designing, implementing and operating stormwater sampling projects, while efficiently utilizing project resources and minimizing data uncertainty.

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While **Chapter 4** provides an overview of surface water sampling, this chapter focuses on stormwater sampling. In this chapter, stormwater is defined as stream flow or surface runoff produced by precipitation excess, often referred to as 'wet weather' events, in the context of stormwater sampling. Due to the breadth of this topic, this chapter addresses only common land uses, including agricultural, urban (non industrial), range/pasture and forest. In addition, only selected constituent types are addressed (nitrogen [N], phosphorus [P], sediment and *Escherichia coli*). However, the principles, techniques and tools outlined are generally applicable to a range of other constituents and/or land uses.

Stormwater sampling is required to quantify constituent transport in runoff events and to differentiate between various processes, such as in-stream or channel, point-source and/or nonpoint-source. Indeed, many countries have regulations, policies or guidelines that require the sampling of stormwater. As an example, point sources of pollution (e.g., urban stormwater, industrial discharges and construction activities) are regulated in the USA under the National Pollutant Discharge Elimination System permit program, which falls under the Clean Water Act [1–4]. Another example is the European Water Framework Directive [5], which aims to protect and improve aquatic ecosystems by reducing emissions of various pollutants, including those from point and diffuse urban pollution sources. Many other nonregulatory drivers for stormwater sampling include:

- Conducting quantitative or qualitative risk assessments; for example, ecological protection [6], human health [7] and water reuse [8]
- Identifying pollution hotspots [9]
- Estimating constituent loads from agricultural areas [10]
- Assessing best management practice performance [11]
- Understanding constituent dynamics for research purposes and/or for the development and testing of water quality models [12]

Sampling stormwater is difficult because storm flows are relatively short-lived and are highly variable, which is inherently dependent on the local climatic conditions and land-use types. Urban land uses, which are typically dominated by impervious surfaces, often produce stormwater after a very small amount of rainfall and, hence, respond very quickly. On the other hand, catchments in rural, agricultural and forested areas have a higher proportion of permeable surfaces. Along with typically larger catchment sizes, they require significantly higher rainfall to initiate stormflow. Climatic conditions also govern the intensity (flow rate) and frequency of stormflows, with tropical climates often producing intense rainfall events and stormwater flows only during certain months.

Stormwater constituent concentrations vary spatially (within and between catchments), temporally and by constituent type. Again, climatic conditions and land use often have a significant impact on the magnitude and variability of stormwater constituent concentrations [12–14]. For example, McCarthy *et al.* showed that the average concentrations of *E. coli* (a marker of fecal contamination) in urban stormwater were quite different for four catchments, with an industrial site having the lowest *E. coli* concentrations together with the lowest temporal variability [12]. The same study showed that suspended sediment and *E. coli* were similarly variable in four urban catchments. Harmel *et al.* also reported considerable variability in *E. coli* concentrations within rural catchments [15]. Other constituents are far less variable (e.g., N in urban stormwater) [16], and some constituents also display long-term variations. For example, it is commonly observed that *E. coli* concentrations in stormwater fluctuate seasonally [17], while the gradual development of a catchment from a forest to an urban land use will cause year-to-year fluctuations in many constituents [18].

Storm events often occur with little advance warning, outside conventional work hours, and under adverse weather conditions [19]. As a result, most stormwater sampling projects utilize automated water quality samplers so that personnel are not forced to travel to multiple sites during events and manually collect samples under potentially hazardous conditions. Major advantages of automated samplers are their ability to use a consistent sampling procedure at multiple sites and to take multiple samples throughout entire storm events [20]. Automated samplers are also able to sample within the quick hydrologic response time of small catchments. Although the US Geological Survey and various state agencies in Australia (e.g., Melbourne Water and the EPA Victoria) do maintain the necessary expertise and personnel for manual field sampling, smaller councils and government agencies typically do not have adequate resources to properly fund an on-call field staff to perform manual storm sampling. This chapter focuses on automated stormwater sampling on common land uses and for selected constituents; however, the principles, techniques and tools outlined are generally applicable to other constituents and/or land uses.

Methods other than automated sampling are available, such as passive sampling technologies or real-time continuous water quality probes (both of which were discussed in **Chapter 4**), but readers are referred to other publications for information about these sampling methods [21–24].

Consideration of project objectives

Prior to designing stormwater sampling projects, the objectives must be clearly understood and communicated with stakeholders and technical staff because these objectives will influence project design and implementation. For example, if the objective is to understand the mechanisms or model the dynamics of constituent flux, then the number of stormwater events to be sampled would be higher than for compliance monitoring to estimate mean annual loads. However, it is noted that while Fletcher and Deletic showed that simple grab sampling methods could produce reasonable estimates of mean annual loads [25], others demonstrate that even when using rigorous automated sampling strategies, uncertainties in measured cumulative loads for study periods of 8–12 months can range from ±5 to 32% [26].

Objectives also govern the constituent type investigated. If the aim is ecosystem protection, then sediment or nutrients might be considered. For human health protection (or recreational water quality), pathogens or their indicators (e.g., *E. coli*) might be preferred. Furthermore, depending on the local context, the constituents of interest for the same overall objective will also vary. For example, in Melbourne (Australia) mitigating high concentrations of both N and P are critical for the protection of downstream coastal water bodies [27], while P concentrations are considered more important in some parts of the USA [28].

The success of stormwater sampling projects is typically determined by the trade-off between the availability of sampling resources and accurate characterization of stormwater quality. Achieving an appropriate balance requires careful decision-making on the type, amount and quality of data collected, along with the realization that stormwater sampling is difficult, time consuming and expensive [20,29]. The subsequent sections of this chapter discusses the components that ultimately determine the resource requirements and data quality (uncertainty) associated with stormwater sampling to assist with efficient resource allocation and collection of data with minimal uncertainty. **Figure 5.1** can assist with proper consideration of project objectives relative to available resources and sampling strategy components.

Sources of uncertainty in stormwater sampling

In the following discussion of the sources of uncertainty in stormwater sampling, research results are presented when available to quantify the uncertainty contributed by various sources and to support recommended practices. However, it is often difficult to quantify the resulting reductions due to a lack of rigorous scientific study on the uncertainty associated with various steps or procedures. In these instances, recommendations and discussions are based on field experience and logic.

Discharge measurement

Streamflow (discharge) data are vital in most stormwater quality sampling projects. In addition, discharge data along with associated constituent concentrations are needed to determine mass transport (load values) and to differentiate between transport mechanisms. This chapter focuses on stormwater quality sampling, thus readers interested in assessment methods and uncertainties associated with discharge measurement should use other sources [12,30–41].

Site establishment, equipment & personnel resources

To sample stormwater, field-scale sites are best established at the field boundary, preferably within the natural drainage way [42]. However, construction of small earthen berms/barriers may be necessary to direct runoff to a single outlet. To sample streams or stormwater drains such that integrated effects of upstream conditions are quantified, the location and influence of constituent sources such as wastewater treatment plants, construction sites and stream modification should be considered. If the influence of a point source is important to quantify, then minimum mixing length calculations should be conducted to determine an appropriate sampling position [43,44]. Due to the difficulty of establishing sites and stage–discharge relationships in morphologically active natural channels, sites should be located at existing flow gauges or hydraulic control structures with an available historical flow record and established stage–discharge relationship where possible [20]. If flow gauging or measurement equipment needs to be installed, the location of a sampling site should be sufficiently downstream and upstream of any channel changes (usually 10x channel width in both directions of a cross-sectional area change, gradient change, or sharp turn [corner] in a pipe). For urban stormwater monitoring, it is important to select easily accessible locations: free from traffic and above a manhole or side entry pit for equipment installation. Confined space entries are often required, which can restrict the location of monitoring stations for urban drains.

At all sampling sites, shelters should be built to house and protect sampling equipment from natural and anthropogenic threats. They should be located above the

> Where possible, sites should be located at existing flow gauges or hydraulic control structures with an available historical flow record and established stage–discharge relationship due to the difficulty of establishing sites and stage–discharge relationships in morphologically active natural channels.
>
> Since automated samplers are far from trouble-free, commitment to proactive maintenance and prompt repair will limit measurement uncertainty resulting from data loss and equipment malfunction.

Figure 5.1. Designing and implementing automated stormwater sampling.

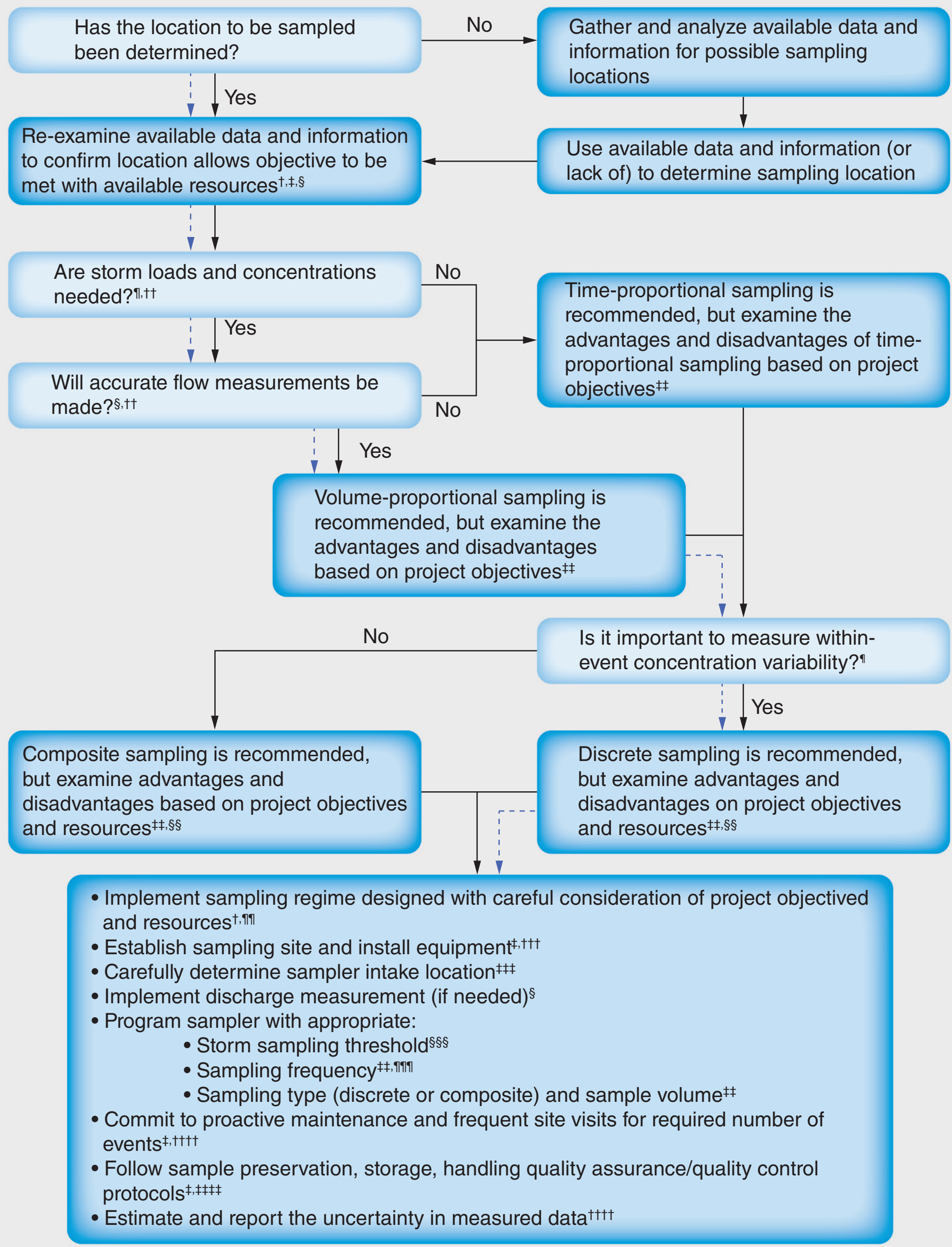


Figure 5.1. Designing and implementing automated stormwater sampling (cont.). Please see the previous page.
†See section entitled: 'Consideration of project objectives'.
‡See section entitled: 'Site establishment, equipment & personnel resources'.
§See **Table 5.1**.
¶See section entitled: 'Sources of uncertainty in stormwater sampling'.
#See section entitled: 'Discharge measurement'.
††See section entitled: 'Timing & frequency of sample collection during an event'.
‡‡See section entitled: 'Discrete versus composite sampling'.
§§See introduction.
¶¶See section entitled: 'Sampling tube type, installation & pumping techniques'.
##See section entitled: 'Locations of sample collection (intake)'.
†††See section entited: 'Storm sampling threshold'
‡‡‡See **Table 5.2**.
§§§See section entitled: 'Combining sources of uncertainty'.
¶¶¶See section entitled: 'Sample preservation & storage'.
Dashed lines indicate the decision path used for the case study presented in section entitled: 'Case study: stormater sampling'.
Adapted from [82].

highest expected flow elevation, and should be accessible during high flows **(Figure 5.2)** [19,40]. The shelter location should be as close to the water as possible to reduce pumping distances. Livestock, rodents and insects can damage equipment and contaminate samples, so they should be controlled in and around equipment shelters, electric lines, communication cables and sample tubes.

Purchase of automated stormwater sampling equipment requires a substantial initial investment **(Table 5.1 & Figure 5.2)**. In addition to the sampler, backup equipment to substitute for malfunctioning components is recommended along with a precalibrated weir or flume to reduce discharge measurement uncertainty. Since automated samplers are far from trouble-free, commitment to proactive maintenance and prompt repair will limit measurement uncertainty resulting from data loss and equipment malfunction [19,20,42]. Maintenance visits to each sampling site, whether remote or readily accessible, should be made weekly or biweekly to:

- Inspect power source, stage recorder, pump, sample tube, sample intake and desiccant strength
- Calibrate stage recorder to ensure flow measurement accuracy
- Retrieve collected data to limit the amount of data lost in potential power failures or other malfunctions

Committed, on-call field staff are essential for successful stormwater quality sampling. Field personnel should be well-trained on quality assurance/quality

Figure 5.2. Storm sampling sites and equipment.

(A–C) Equipment shelters for automatic sampling equipment. **(A & C)** Rural examples, showing solar panel, logging hut, equipment shelter and an automatic sampler. **(B)** Urban example, showing equipment shelter, which contains logging equipment, automatic samplers and batteries for power. The artwork avoids unnecessary graffiti/tagging. **(D)** Flow control device (with depth probes) and monitoring shelter (containing logging equipment and automatic sampler) in rural/agricultural settings.

control methodology, equipment operation, basic hydrology and safety considerations [19]. In addition to routine maintenance visits, personnel must visit sampling sites as soon as possible after rainfall events (as determined by quality assurance/quality control guidelines) to collect data, retrieve samples, inspect flow measurement and equipment function, and make necessary repairs.

Sample collection with automated samplers

Locations of sample collection (intake)

As mentioned in **Chapter 4**, to reduce uncertainty related to the location of sample collection, the intake should be located in well-mixed flow, either

Table 5.1 Equipment requirements and estimated costs for a typical stormwater sampling site.

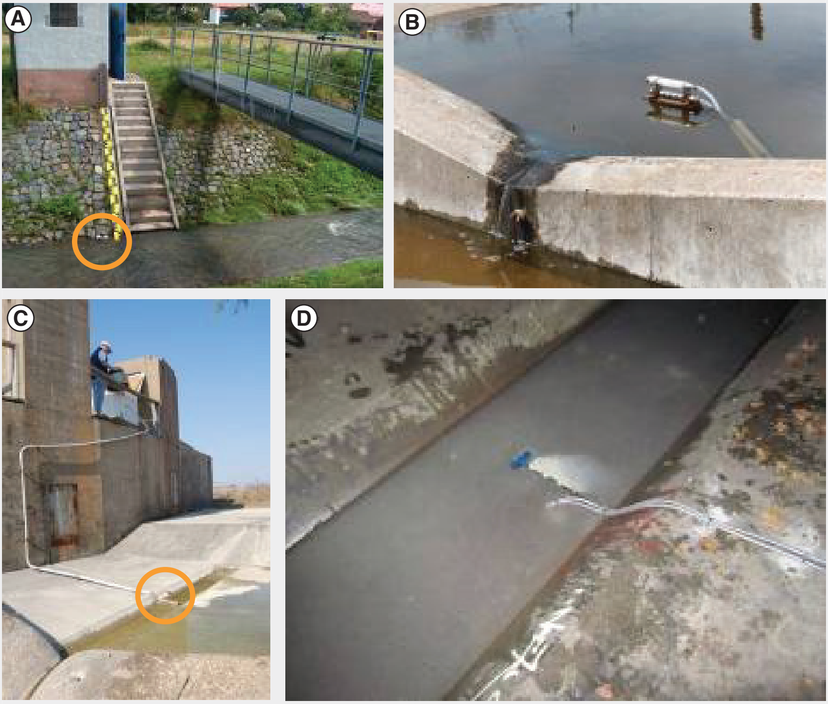
Equipment	Cost (2013 US$)	Function
Precalibrated flow control structure	3500	Accurately measure discharge
Depth (stage) sensor	3000	Measure flow depth
Area-velocity sensor (alternative to depth [stage] sensor)	4000–9000	Measure depth and velocity, commonly used in urban stormwater drains/pipes, and reduces requirements for control structure unless accurate low flows are required
Rain gauge: standard tipping bucket type	1500	Measure precipitation
Automated sampler with bottles and tubing	5000	Collect and house stormwater samples
Refrigerated automated sampler (alternative to automated sampler with bottles and tubing)	6000–9000	Collect and house stormwater samples that require refrigeration during storage (e.g., microorganisms)
Power source (solar panel, controller and battery)	1500	Power equipment
Equipment shelter	1000–2000	House and protect equipment
Communications	2200	Notify staff of sampling events and errors
Miscellaneous (e.g., connectors, cables and tubing)	1000	Required for installation and operations

in the center of the channel in a run/riffle, not a pool, or immediately upstream of the crest elevation of a hydraulic control structure **(Figure 5.3)**. To prevent pump malfunction, ensure that the sampler intake is located such that it is completely submerged at the storm sampling threshold (discussed subsequently).

In spite of proper location, the typical single intake design of automated samplers can prevent them from capturing vertical and horizontal concentration variability and thus introduces uncertainty into measured constituent concentrations. The only known evaluations of a single intake are McGuire *et al.* [45], Ging [46], Harmel *et al.* [47] and Selbig *et al.* [48]. Ging compared concentrations produced by integrated and automated sampling on eight streams in

Aa Storm sampling threshold: generally a minimum stage or discharge at which sampling is initiated. When flow exceeds this threshold, sampling begins and typically continues as long as the flow remains above this threshold or until flow ceases; therefore, the sampling threshold directly affects the number of samples that are taken and the proportion of the event that is sampled.

Figure 5.3. Example sample collection (intake) locations.



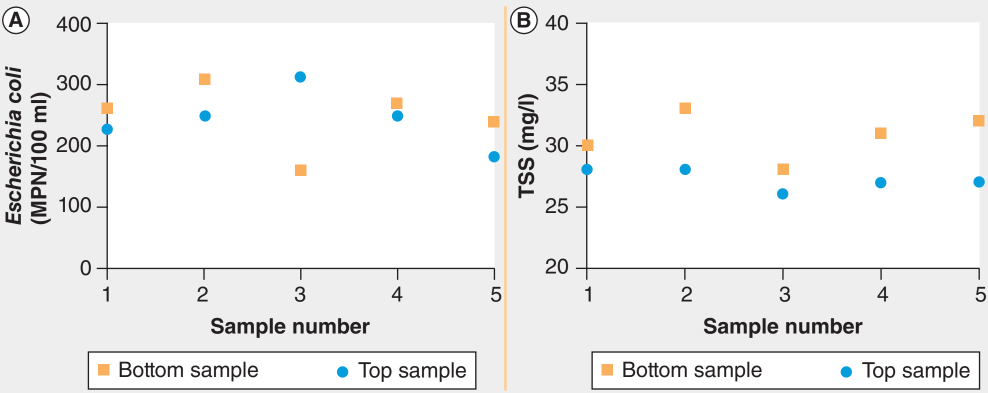
(A) Sampling tubing and intake position (circle) at gauging station; note the location of the sampling tube is just above the dry weather flow position. **(B)** Sampling tubing and protected intake upstream of a flow control structure; note the position of the intake is just upstream of the crest elevation. **(C)** Sampling tubing and intake position (circle) in a large flow control structure. **(D)** Sampling tubing (and flow meter) in an urban stormwater drain; note that in this instance they are facing downstream, to protect them against build-up/impact from bed sediments.

Texas (USA) [46]. For 26 constituents analyzed, only dissolved calcium, total P and dissolved and suspended organic carbon showed statistically significant differences in median values from integrated and single-intake automated sample collection. Harmel *et al.* compared stormwater constituent concentrations (including NO_3^--N, NH_4^+-N, PO_4^{3-}-P, sediment, total N, and total P) measured with automated samplers and manual grab sampling from three streams in Texas [47]. Mean concentrations were significantly different for some constituents in individual storms but not for others. Selbig *et al.* showed that using a single sample intake at the bottom of an urban stormwater pipe overestimated actual sediment concentration by 96%, whereas sampling at three and four points spaced vertically throughout the water column reduced overestimation to 49 and 7%, respectively [48].

At field-scale sites and in small streams or storm drains, a single sample intake is often assumed to be adequate for sampling well-mixed and/or shallow flows. Indeed, McCarthy *et al.* showed the concentrations of *E. coli* and total N in the bottom and top of the flow in a 600 mm pipe during stormwater events were statistically indifferent **(Figure 5.4)** [49,50], suggesting that one sampling intake at the bottom of the drain would be sufficient for constituents associated with fine particulates in urban stormwater [16,51]. However, for constituents commonly associated with larger particulates (e.g., total suspended solids and total P [16]), 90% of urban stormwater samples collected from the bottom had equal or slightly higher concentrations than those collected from the top of the water column **(Figure 5.4)** [50]. As such, caution is still needed even in these constrained, well-mixed urban stormwater drains.

While previous publications urged caution in the use of single-intake autosamplers for collection of suspended sediment and sediment-associated constituents [41,42,46,52], only McGuire *et al.* [45] and Harmel *et al.* [47] have expressed similar caution for dissolved constituents. The US Geological Survey 'rule of thumb' for determining whether a stream is well-mixed suggests that if four parameter probe values (pH, temperature, specific conductance and dissolved oxygen) taken throughout a stream

Figure 5.4. Spatial distribution of constituents in urban stormwater flows.



(A) *Escherichia coli* and **(B)** TSS concentrations taken from the surface of the water column (top sample) and from the invert of the circular pipe (bottom sample). Top and bottom samples were taken simultaneously.
MPN: Most probable number; TSS: Total suspended solid.
(A) Reproduced from [49].

cross-section differ by <5%, then a single sampling point at the centroid of flow adequately represents the mean cross-sectional concentration for dissolved constituents. A similar approach could be conducted using a turbidity meter for particulate material. This should be repeated to cover a range of possible flow regimes.

If the cross-section constituent profile varies significantly, alternative procedures may be necessary to reduce uncertainty associated with the location of the sample collection (intake). The best option involves development of a relationship between concentrations at the sampler intake and mean concentrations as determined by integrated sampling (e.g., equal-width increment or equal-discharge increment [53]) at a range of discharges [46]. With such a relationship, concentrations at the intake can be adjusted to represent mean concentrations for the total cross-section [Slade R, Pers. Comm.]. This option is, however, labor intensive, time-consuming and requires periodic revision. Another alternative is to vertically orientate sampler intakes, which better captures vertical gradients at sites with adequate flow depth to completely submerge the intake; however, shallow flow makes this method infeasible at many ephemeral sites because the intake must be fully submerged to allow sample collection. Another option is to use a vertical or horizontal intake that has multiple entry points extending throughout the water column [54]. However, no such intakes are commercially available and care must be taken to ensure that the proportions from each intake are kept constant. Floating intakes (especially important for tidal stormwater monitoring sites [45]), or depth-integrated sampling arms [54,48], have been developed and could be adopted. Installing multiple tubes and connecting them to multiple autosamplers is also possible, but costly.

Sampling tube type, installation & pumping techniques

All sampling components in contact with the sample, including the sample tubing, should be made of inert material that does not impact the sample. All autosamplers rely on suction-based pumping methods, which require the use of stiff or reinforced tubing material to avoid collapse. The most important aspect in installing sample tubing is to ensure a continuous negative gradient, so as to facilitate drainage of residual water after sample collection and minimize the build-up of sediment and other constituents [55]. Residual contaminants may interact with each other, or even with the sampling tube, causing contamination of subsequent samples. For example, the authors have found that if reinforced braided food grade tubing is used for sample collection, the residual water left in the tubing between uses will slowly uptake N from the sampling tube, thereby contaminating the next sample. As such, the use of Teflon® (DE, USA; or Teflon-coated) tubing could be a safe option, so as to avoid the adsorption of the compound to the tubing or leaching from the tubing into the water sample [56]. Purging the sample line also reduces residual contamination (discussed subsequently).

In all systems, but especially in urban stormwater drains, it is also important to ensure the sampling tube is securely attached to the channel/drain. The tubing should not block the flow in the drain, as unnecessary build-up of materials may occur and decrease the representativeness of subsequent samples. For example, build-up of sediment often occurs during dry periods, especially if the sampling tube is installed at the invert of the drain where it contacts the flow. Raising the intake slightly off the bottom of the drain will mitigate this, while not impacting the representativeness of subsequent samples (although this may increase the storm sampling threshold, discussed subsequently). Another solution to avoid excess intake of bed sediment built up during antecedent dry periods is to install the intake tube perpendicular to the flow direction or facing downstream, care should be taken when doing this in high-velocity waters as vortices may form and impede sample uptake. The sample tube should also be covered from direct exposure to sunlight to avoid early deterioration or algal build-up.

The pumping capacity of the automated sampler should be taken into account. In general, the rate of pumping should be maintained at or above a velocity that ensures that any solids in the water being sampled are kept in suspension during sample withdrawal. The required velocity depends on the type of solids in the water (e.g., sand dominated constituents require higher pumping velocities than clayey/silty constituents). Suction pumps, which pull samples up from the water to the sampler, are typically used and are available in two types: suction cup, which withdraws the sample by applying negative air pressure to a suction chamber connected to the sampling tube; and peristaltic, which passes the suction tube through a peristaltic pump. The former is preferred for samples to be processed for particle size distribution, as the mechanical process of the peristaltic pump may disturb the sample. Either way, peristaltic or suction cup pumps have a limited pumping capacity and can often only maintain adequate pumping rates for heads ≤10 m (30 ft) [57]. Where heads exceed 10 m, multiple pumps (in series or parallel) can be employed, or the efficiency of a peristaltic pump can be improved by removing the pump from the automated sampler and placing it at the water surface level, thereby allowing the pump to ‘push’ the sample to the autosampler instead (as the pumps are more efficient when tubes are filled with water). Another option for pumping large distances is to use a submersible centrifugal pump, but care should be taken here as the pumping process could significantly impact the particle size distribution and particle association of the constituents.

Appropriate pre- and post-collection tube rinsing must be conducted to clean the sample tube between samples and between events [55,57,58]. In general, two prerinsing cycles should be carried out by pulling stormwater through the sampling tube up to the closest point possible to the sample bottle then purging the tube and repeating. Under these conditions, Solo-Gabriele *et al.* found that carry-over between two subsequent samples from a riverine system was less than 0.5% for *E. coli* samples [58]. Where pumping distances are long, and the response of the water system being monitored is fast, the two rinsing cycles can cause significant delay in the sample being taken. Here, one rinse cycle could be employed, as the error in sample quality caused by carry-over may be outweighed by the error in missing the dynamics of the water system. One postcollection cycle should be conducted, such that residual water is purged from the sample tubing following sample collection.

The sampling tube should be maintained regularly. Depending on the constituents being monitored, monthly rinsing of the tubes with chemicals or disinfectants could be employed. Some authors suggest cleaning the sampling tubes between every event. For example, in sampling projects in the USA, sample tubes were removed regularly and replaced with cleaned and autoclaved tubes [17,59].

Storm sampling threshold

Appropriately setting a storm sampling threshold, generally a minimum stage or discharge at which to initiate sampling, is critical for reducing uncertainty in stormwater sampling. When flow exceeds this threshold, sampling begins and typically continues for as long as the flow remains above this threshold or until flow ceases; therefore, the sampling threshold directly affects the number of samples that are taken and the proportion of the event that is sampled.

Results from Harmel *et al.* suggest that substantial sampling uncertainty is introduced as storm sampling thresholds are increased; therefore, thresholds should be set to sample as much of the storm duration as possible [60]. It is difficult to provide a generic flow rate recommendation due to the variability in catchment sizes; however, in general, if rainfall runoff produces water deep enough to sample then sampling should commence. For stormwater sampling in flashy urban systems, it can be important to capture the so-called 'first flush' [61,62]. Thus, the storm sampling threshold should be set to capture even small increases in flow. This is relatively simple in ephemeral settings where sampling can be initiated when flow is first detected (although the flow depth must cover the sample intake). In perennial streams, however, the storm threshold will probably need to be adjusted seasonally, or supplemented with rainfall measurements (tipping bucket rainfall gauges or radar), changes in turbidity, electric conductivity or temperature to ensure that the level changes resulted from rainfall/runoff [63]. This option is especially useful in tidal sampling (i.e., for monitoring a submerged stormwater outlet discharging into a coastal environment).

Regardless of the storm sampling threshold, the programing option of collecting a sample each time flow rises and/or falls past the threshold should be avoided because flow fluctuation near the threshold can result in excessive (and unnecessary) samples.

Timing & frequency of sample collection during an event

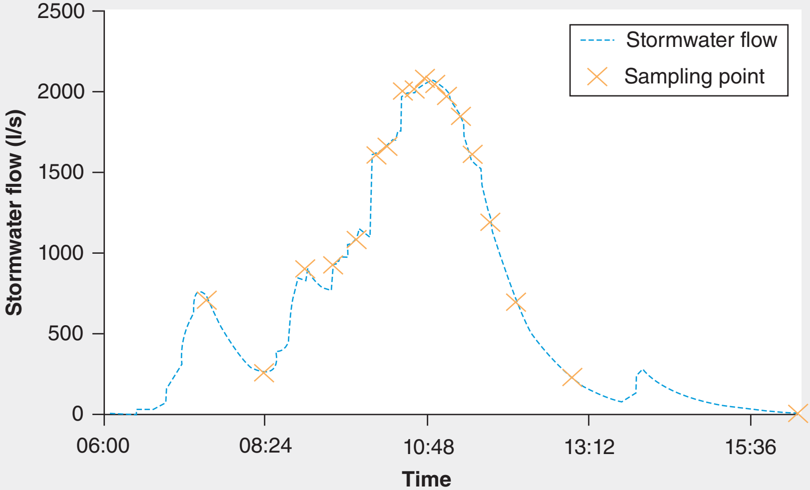
As identified in **Chapter 4**, the variations in stormwater flows and constituent concentrations inherently govern the design of the sampling regime. For example, a constituent that does not vary considerably during stormflows will require significantly fewer samples to characterize.

In stormwater monitoring, the timing of sample collection (or sampling interval) is typically determined based on time or volume intervals. With time-proportional sampling as defined by Ort *et al.*, samples are taken on time increments, such as every 30 min [64]. Time-proportional sampling is a simple and reliable procedure since accurate time intervals are easy to measure and clock failures are rare; however, if small time intervals are used, frequent sampling can produce numerous samples and quickly reach the sampler capacity, thus missing a majority of the runoff event. Time-proportional sampling does not eliminate the need for discharge measurement necessary for load determination, but it does mean that the flow measuring and autosampling devices do not need to be directly linked. In most situations, it is desired that they are at the same location, but sometimes it is necessary for the systems to be separated for logistics or accuracy (e.g., if the flow measurement is in a large weir, then the sampler needs to be upstream of this to achieve appropriate flow conditions as highlighted in the section entitled: 'Locations of sample collection [intake]').

With volume-proportional sampling as defined by Ort *et al.* , samples are collected on volume increments, such as every 2000 m^3 or 2.5 mm volumetric depth **(Figure 5.5)** [64], referring to discharge intervals in volumetric depth units such as millimeters, which represents mean runoff depth over the entire catchment, as opposed to volume units such as meters cubed, normalizes discharge over various catchment sizes. This notation allows a consistent transfer of methods and results to catchments of differing sizes. Volume-proportional

> Referring to discharge intervals in volumetric depth units such as millimeters, which represents mean runoff depth over the entire catchment as opposed to volume units such as metres cubed, normalizes discharge over various catchment sizes. This notation allows a consistent transfer of methods and results to catchments of differing sizes.

Figure 5.5. Example hydrograph and constant volume-proportional sampling for an urban stormwater event.



In this example, 1 l samples were taken after every 1200 m³ of stormwater flow.

sampling requires continuous discharge measurement to determine sampling intervals. It readily produces the event mean concentration (EMC), a common method for reporting constituent concentrations defined as the arithmetic mean of individual sample concentrations collected on equal discharge (volume-weighted) intervals. The EMC multiplied by the total volume represents the constituent load for a particular event.

Statistical sampling theory indicates that the smaller the sampling interval (the more samples taken), the better actual population characteristics are estimated [65]. Several studies demonstrate this theory regarding storm sampling [66–72], thus, small sampling intervals should be used to reduce the uncertainty in water quality measurements. However, intervals must also be set to sample throughout runoff events of various durations to capture the various transport phenomena such as lateral subsurface return flow. King and Harmel [71] and Harmel *et al* [41] provide guidance on selecting time and volume intervals for automated sampling on small catchments **(Table 5.2)**, and King *et al.* [73] developed a procedure to determine sampling intervals based on catchment and constituent characteristics. Although King *et al.* concluded that volumetric depth intervals up to 6 mm may be appropriate in certain conditions, smaller

Aa Event mean concentration: a common method for reporting constituent concentrations defined as the arithmetic mean of individual sample concentrations collected on equal discharge (flow or volume-weighted) intervals.

Table 5.2. Sampling frequencies and composite samples per bottle for time interval and volumetric depth interval sampling.

Parameter	Composite samples per bottle			
	Discrete	*2*	*4*	*6*
Time interval (min)				
10	S	S	S	
15	S	S		
30	S			B
60			B	
120		B		
180	B			
240				
Volumetric depth interval (mm)				
0.5	S	S	S	B
1.0	S	S	B	B
2.5	S	B	B	B
5.0	B	B	B	B
7.5				
10.0				
12.5				

†Criterion 1: completely capture 90% of runoff events within a 24-bottle limitation based on the number of samples and maximum runoff duration (or runoff volume) from King and Harmel [71]. This approximate criterion represents complete sampling for storm durations less than 2160 min (for time-proportional sampling) and runoff depths less than 96 mm (for volume-proportional sampling).
‡Criterion 2: the strategy will on average measure loads within 20% of the true load based on results of King and Harmel [71] with similar errors presented by Miller *et al.* [68].
Suggested sampling frequencies indicated by 'B' (based on meeting criteria 1† and 2‡ and research on catchments less than 6300 ha). On smaller, more arid, and/or more flashy (often urban) catchments, these intervals should be reduced (to values indicated by 'S') to adequately sample less frequent, shorter duration, and/or lower volume runoff events.

intervals (1–2.54 mm) are more widely applicable [73]. These smaller volumetric depth intervals allow smaller storm events to be sampled and moderate-to-large storm events to be sampled more intensively with little to no increase in uncertainty, especially if composite sampling is utilized (discussed subsequently).

There is some evidence that suggests that constituent concentrations during the

Aa Composite sampling: collecting more than one sample aliquot in each sample bottle followed by mixing, which increases sampler capacity, making it a valuable, cost-saving alternative; however, composite sampling does reduce information on the within-event distribution of constituent concentrations.

initial portion of storm events are more variable (and sometimes a first-flush exists [61,62]). Although volume-proportional sampling does not normally collect a sample at the initiation of runoff, automatic samplers can be programed to do so, thus allowing capture of the so-called 'first flush'. Another alternative is to sample more frequently during the initial portion of storm (e.g., every 0.5 mm to more adequately capture initial conditions and every 1.5–2.5 mm for the remainder of the event). McCarthy *et al.* showed that the estimated error between such a sampling regime and an estimated 'true' value of the event mean concentration for turbidity in a stormwater system was less than 10% across four sites [49]. Time-proportional sampling to capture first flush is risky as the duration of the event is so variable; indeed, Bach *et al.* suggests that there is a first-flush volume rather than a first-flush duration, meaning that volume-proportional sampling is most adequate to capture it [62].

Some suggest a minimum number of samples to be collected within an event. For example, Leecaster *et al.* suggest that a minimum of 12 samples be collected to accurately characterize the constituent concentrations [69]. However, according to statistical theory, the number of samples required for adequate event characterization should vary depending on the event length (or volume), thus a strict minimum should not necessarily exist unless robustly based upon site- and procedure-specific uncertainty analysis.

Discrete versus composite sampling

Automated samplers typically have the option of collecting discrete samples (one sample per bottle) or composite samples (more than one subsample aliquot per bottle). Discrete sampling strategies provide the best representation of temporal variability of constituent concentrations throughout storm events, which facilitates understanding of system dynamics. However, discrete sampling can produce substantial uncertainty even with small sampling intervals. This increased uncertainty is most pronounced in large-volume and/or long-duration runoff events, when sampler capacity is exceeded prior to the end of storm runoff.

Composite automated sampling increases sampler capacity by collecting more than one sample aliquot in each sample bottle, which makes it a valuable, cost-saving alternative. For example, composite sampling with two or four aliquots per bottle reduces sample numbers to 50 and 25% of those collected by discrete strategies **(Table 5.2)**. Several recent studies have concluded that composite sampling introduces less error

> Single-bottle, composite volume-interval sampling is a powerful option that reduces analysis costs while intensively sampling entire event durations.

than increasing minimum flow thresholds or increasing sampling intervals, especially for volume-proportional sampling [60,68,71,72].

Composite strategies are valuable for projects designed to quantify average concentrations or total loads. The composite sample is usually produced using volume-proportional sampling [20], which allows determination of the EMC for the constituent(s) of interest. Furthermore, larger volume composite samples allow for the analysis of a higher number of constituents and/or constituents with large volume requirements (e.g., pathogen assays). Single-bottle, composite volume-interval sampling is a powerful option that reduces analysis costs while intensively sampling entire event durations [20,67,71]. With this strategy, 80–160 volume-interval samples of 100–200 ml can be composited into a single sample (assuming a 16 l bottle capacity) to produce the EMC. Composite sampling does, however, reduce information on the distribution of within-event constituent behavior, which limits the study of various transport mechanisms.

For composite sampling, subsample aliquot volumes should be at least 100–200 ml due to the difficulty to accurately pump small volumes [20]. On the other hand, pumping large sample volumes can take 2–7 min per sample (depending on the pumping rate, head and tubing length), especially when pre- and post-collection line purging is used, which can result in missed samples. Therefore, unnecessarily large sample aliquots should be avoided because they do not allow the frequent sampling necessary in dynamic stormwater systems (e.g., urban stormwater drains).

An alternative to collecting composite samples in the field involves manually compositing discretely collected samples in the laboratory [49]. For discrete volume-proportional samples, equal-volume subsamples can be withdrawn and later combined to create composite samples. For discrete time-proportional samples, volumes proportional to the flow during each time interval can be withdrawn from each discrete sample and combined to create composite samples. Although these manual techniques produce valid volume-weighted concentration estimates, they require considerable postprocessing time and effort. Manually compositing in the laboratory does, however, produce considerable flexibility. For example, each discrete sample can be analyzed for one constituent, while the composite sample can be analyzed for others. Similarly, manual compositing can minimize errors associated with sampler failure during an event (i.e., missing one sample in a volume-proportional, composite strategy

The preservation and storage of samples collected by automated samplers is more important than for other types of environmental sampling because samples are stored in the field for some duration between sample collection and retrieval, which increases the potential for substantial constituent alterations.

will increase uncertainty as the volume sampled is no longer accurate; while manual compositing can compensate for missed samples).

Sample preservation & storage

The preservation and storage of samples collected by automated samplers are important determinants of uncertainty in automated stormwater sampling. It is more important than for other types of sampling because samples are stored in the field for some duration between sample collection and retrieval, which increases the potential for substantial constituent alterations. Numerous factors, such as the container characteristics, storage environment, chemical preservatives and filtration methodology, all influence these potential alterations. Physical, chemical and biological processes can alter nutrient and microorganism concentrations during the interval between sample collection and analysis [49,50,74,75]. In general, sediment is affected much less than nutrients and microorganisms; however, care must be taken when samples are being analyzed for particle size distributions, as natural flocculation or disaggregation may occur during storage or transport.

In terms of stormwater sampling, the storage environment probably exerts the strongest influence on constituent concentrations. In all cases, the exclusion of light is recommended to inhibit photosynthesis, and thus reduce algal growth and nutrient uptake. If microorganism concentrations are of interest, light exclusion is required to prevent accelerated die-off of fecal microorganisms [76]. The effects of storage temperature and storage time have received considerable attention in recent years. For polluted sites with high nutrient concentrations (i.e., ammoniacal N >0.1 mg/l; oxidized N, total Kjeldahl N, total P >1.0 mg/l), little proportional change in nutrients was typically observed for up to 6 days of storage without temperature control [77]. By contrast, up to 90% of ammonia N, 50% of oxidized N, 84% of total Kjeldahl N and 67% of total P may be lost from samples with low nutrient concentrations after 6 days of storage without temperature control [77]. McCarthy *et al.* found that *E. coli* concentrations in urban stormwater samples left in the field (without refrigeration) decreased with time [49]. However, the same study showed that the concentrations found after 24 h were not statistically significantly different than those analyzed immediately.

Freezing of samples, impractical in the field, is generally reserved for long-term laboratory storage, and is not recommended for raw samples to be analyzed for microorganisms. Sample refrigeration of samples stored in automatic samplers is often the preferred method of preservation. Low temperatures (~4.0°C) reduce microbial activity, thereby reducing microbially mediated nutrient transformations or microbial die-off and interactions. The effectiveness of refrigeration appears to vary, with some previous studies demonstrating effective preservation of samples for nutrient analysis for up to 8 days at 4.0°C and others reporting significant changes in nutrient concentrations within 4–48 h [74]. Kotlash and Chessman reported effective preservation by refrigeration for up to 2 days for a broad range of sites and nutrient concentrations under varying weather conditions [77]. Although McCarthy *et al.* found that using refrigerated autosamplers (compared with using unrefrigerated samplers) slightly reduced the die-off of *E. coli* in samples stored for 24 h, they also found that there was no difference in the two methods (with and without refrigeration) if the samples were stored for less than 8 h [50].

Sample analysis

Although sample analysis is certainly a source of uncertainty in stormwater sampling, this topic is discussed elsewhere [41,49,50,75,78].

How many events should be monitored?

The previous section focuses on how to collect samples during an event and provides guidance on how many samples are required to adequately characterize a single event. However, as stormwater constituent concentrations are inherently variable between stormwater events, it is important that more than one event is monitored [12]. Some researchers have attempted to quantify the number of events required to adequately characterize a site; however, these studies have only used a finite number of measured data to infer the number of events required, and hence only present estimates of the 'real' or 'true' number of events required to characterize a site. Bertrand-Krajewski and Bardin [79], Francey *et al.* [80], and McCarthy *et al.* [49] all used boot-strapping procedures to determine how many events are required to adequately estimate the site mean concentration (SMC) of a particular constituent (the annual constituent load from a system is equal to SMC × annual flow volume). Francey *et al.* found that more than 50 events were required for total suspended solids but only 25 for total N [80]. Indeed, much like the question of 'how many samples should be taken during an event?', the number of events to be monitored to adequately characterize the SMC is dependent on the constituent variability between events. Other project objectives may govern the number of events to be monitored, including whether seasonality or long-term changes of the constituent are of interest.

Combining sources of uncertainty

As highlighted above, many sources of uncertainty (e.g., flow measurements, sample collection, sampling frequency, sample preservation and storage, sample analysis, and number of events monitored) contribute to uncertainty in the final reported concentration or load of interest. As such, there is often a requirement to combine these sources of uncertainties to estimate the error in the final value, or rather to understand which sources of uncertainty are most significant.

To address this issue, Harmel *et al.* developed an uncertainty estimation framework and the first cumulative uncertainty estimates for measured water quality data [41]. From that framework, Harmel *et al.* developed the Data Uncertainty Estimation Tool for Hydrology and Water Quality (DUET-H/WQ) [26]. DUET-H/WQ assists the user in assigning appropriate data-specific uncertainty estimates by providing published uncertainty information for data collection procedures. DUET-H/WQ then calculates the uncertainty for individual discharge values and for concentration and load values (for sediment, dissolved and particulate N and P). Results of DUET-H/WQ application to several real-world data sets indicate that substantial uncertainty can be contributed to by each of the uncertainty sources identified above [26]. For event loads, the mean uncertainty was typically least for discharge (±13%), higher for sediment (±20%) and dissolved N and P (±23%) loads, and higher yet for total N and P (±27%).

McCarthy *et al.* expanded this into a framework for including all sources of uncertainties when estimating concentrations and loads from urban stormwater systems [49]. They used the Law of Propagation of Uncertainties [81] to evaluate the contributions of sampling (i.e., location of sampling intake), storage and analytical uncertainties in the estimation of *E. coli* concentrations in discrete stormwater samples taken using automated samplers. They showed that storage and analytical uncertainties were most significant. They further propagated these uncertainties to determine that the uncertainties in the estimated *E. coli* EMCs were between 15 and 27%, and showed that the uncertainties in event *E. coli* loads (20–45%) were higher due to the uncertainties involved with discharge measurements. They finally combined these with the error in sampling only a limited number of events, to determine that the overall SMC uncertainty of *E. coli* from four urban stormwater sites ranged between 35 and 55%.

Case study: stormwater sampling

Site description

Longbeach Pond (a hypothetical case study) frequently experiences algal blooms caused by excessive nutrients from wastewater treatment plant effluent, groundwater (contaminated by local septic systems), agricultural runoff and urban stormwater. This case study presents a stormwater monitoring regime to determine the wet weather SMCs and site loads for NO_3-N, NH_4-N and PO_4-P during a 3-year period, as per local council mandates. The area of this predominately residential catchment is 30 ha, and 75% of its surfaces are impervious and connected (e.g., roads and roofs). Long-term data suggest that 90% of the precipitation falls in events less than 30 mm. Rainfall excess is drained from the catchment into Longbeach Pond via a 575 mm diameter stormwater pipe.

Discharge measurement

As the council requires loads to be determined, an accurate method of measuring discharge is required. A submerged area-velocity probe was installed just below the dry weather flow water level to avoid bed sediment build-up (~3 cm from the invert) and at a position 5.75 m downstream of the nearest pipe turn and more than 5.75 m upstream of the outfall. The probe's velocity and depth sensors were calibrated in a certified laboratory prior to installation. Once installed, the depth and velocity sensors were checked *in situ* on a monthly basis. The flow meter cable was securely fixed to the side of the pipe and connected to the flow meter in the sampling shelter. The flow meter was set to record depth, velocity and calculate discrete discharge every 6 min. These data were downloaded each week and checked for inconsistencies.

Sampling site establishment

The sampling site was established close to the outfall of the stormwater pipe, and an equipment shelter was installed in a secure area free from traffic, with easy access and above the high watermark.

Location of sample collection (intake) & sample tubing

A Teflon 10 mm diameter suction tube was installed 3 cm from the invert of the stormwater pipe. The tube was installed with a continuous positive (uphill) gradient to the sampling hut, where it was firmly connected to an automated sampler with 24 1 l sample bottles. The automated sampler was programed to rinse the sample tubing twice prior to collection of each sample. The sampling tube was removed and replaced every 6 months.

Storm sampling threshold, timing & frequency of sample collection, & discrete sampling

The storm threshold was set at 4 cm (i.e., the water depth that exceeds the dry weather flow depth by 1 cm or 30%). Once the threshold was exceeded, the automated sampler collected volume-proportional samples on 1-mm volumetric depth intervals. The 1-mm sampling interval was derived to capture runoff from 90% of the average annual rainfall; therefore, the sampler was programed to collect samples throughout the hydrograph of a 30-mm rainfall event, which in this catchment would generate roughly 22 mm of runoff (75% connected imperviousness). This allows the sampler to completely sample a 24-mm runoff event using its 24 sample bottles.

The automated sampler was programed to take discrete 500 ml samples. This sample volume provides sufficient volume for analysis of NO_3-N, NH_4-N, and PO_4-P but not excessive volume that would produce excessive sample pumping and rinse/purge times. Although discrete samples were taken by the automated sampler, one single composite sample representing the EMC was manually made. This was done using the flow data and the date/time stamp of each collected sample to reconfirm the proper subsample aliquot volume withdrawn from each sample.

Sample storage & preservation

Samples were retrieved from the site within 12 h of collection. The bottles were then placed inside a cooler box with ice and kept at 4°C until delivery to the analytical laboratory for refrigerated storage and subsequent analysis within a week of collection.

Number of events to monitor/monitoring period

A total of 25 sampling events were targeted, as per the section entitled: ‘How many events should be monitored’. Long-term data suggests that rainfall is relatively consistent during the year and that rains occur approximately twice per week. Assuming a monitoring period of 1 year (52 weeks), this provides sufficient time for event sampling, with some buffer to allow for equipment failure. This also agrees with the objective from the council for annual discharges in that the seasonal fluctuations will be captured during this monitoring period.

Calculation of SMCs

The load for each event was determined by multiplying the EMC by the measured flow volume. The SMCs of NO_3-N, NH_4-N and PO_4-P were then determined by dividing the sum of measured event loads by the sum of the measured event volumes. These SMCs were used with the mean annual flow volumes to determine annual site loads.

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Summary.

- Most stormwater sampling projects utilize automated water quality samplers so that personnel are not forced to travel to multiple sites during events and manually collect samples under potentially hazardous conditions.
- Achieving an appropriate balance between the availability of sampling resources and accurate characterization of stormwater quality requires careful decision-making on the type, amount and quality of data collected, along with the realization that stormwater sampling is difficult, time consuming and expensive.
- Appropriately setting a storm sampling threshold, generally a minimum stage or discharge, at which to initiate sampling, is critical for reducing uncertainty related to stormwater sampling.
- Time-proportional sampling is a simple and reliable procedure since accurate time intervals are easy to measure and clock failures are rare; however, if small time intervals are used, frequent sampling can produce numerous samples and quickly reach the sampler capacity, thus missing a majority of the runoff event.
- Volume-proportional sampling readily produces the event mean concentration, a common method for reporting constituent concentrations, defined as the arithmetic mean of individual sample concentrations collected on equal discharge (volume-weighted) intervals.
- Discrete sampling strategies provide the best representation of temporal variability of constituent concentrations throughout storm events, which facilitates understanding of system dynamics.
- Composite automated sampling increases sampler capacity by collecting more than one sample aliquot in each sample bottle, which makes it a valuable, cost-saving method for estimating event mean concentrations or event loads.
- Many sources of uncertainty (e.g., flow measurements, sample collection, sampling frequency, sample preservation and storage, sample analysis, and number of events monitored) contribute to uncertainty in the final reported concentration or load of interest.

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