

Monitoring water quality in urban streams and stormwater

Guidance for New Zealand practitioners

NIWA
Taihoro Nukurangi

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Contents

Executive summary

Contaminant concentrations in urban streams and stormwater are highly variable in both space and time. This is particularly the case in wet weather when flows increase rapidly due to high volumes of runoff from impervious surfaces such as roofs, roads and carparks. The highly variable nature of urban waters means that traditional – typically monthly – grab or spot sampling will seldom capture the 'average' (or maximum and potentially toxic) concentrations of contaminants entering streams or coastal receiving environments during wet weather. Intensive, time-integrated sampling is required to obtain a more representative understanding of urban waters and enable meaningful comparisons of water quality data between sites and/or to guidelines. Water quality data that are more representative of wet weather conditions are particularly important for calculations of catchment contaminant loads given storm events contribute the greatest volumes of sediment, nutrients, metals and other contaminants to downstream receiving environments.

Automatic water samplers (autosamplers) are suitable for intensive, time-integrated sampling but cost, effort and expertise associated with deployment and operation can be a major barrier. In 2016/17 NIWA and the regional sector's Coastal Special Interest Group (C-SIG) identified a need for guidance on tools and techniques to cost-effectively monitor urban waters. A project was established for this purpose, funded by an MBIE Envirolink Tool grant (MBIE contract number C01X1701). This document, coupled with several short instructional sampling videos (https://www.niwa.co.nz/ sampling-urban-streams-stormwater), is the outcome of that project. It is a guidance document intended to assist practitioners that need information on water quality sampling in urban waterways, including scientists, monitoring officers and resource consent planners.

This document is divided into two parts. The first part of this document is the guidance, which includes an overview of urban water quality. The guidance provided in this report particularly focuses on the following methods for sampling urban streams and stormwater:

- Manual grab sampling;
- Grab samples using Nalgene bottles;
- DGT® samplers (diffusive gradients in thin-films passive sampling devices); and
- Automatic samplers.

We discuss the potential uses, advantages and disadvantages of these four different sampling methods for common water quality variables, sampling locations and resource requirements; then evaluate the suitability of each across four common water quality monitoring objectives, taking into account both accuracy and cost requirements:

- Objective 1: Compare water quality to guidelines, standards or limits based on mean or median concentration.
- Objective 2: Compare water quality to guidelines, standards or limits based on maximum concentration.
- Objective 3: Compare concentrations between multiple locations, within a single stream, catchment or in separate catchments.
- Objective 4: Measure Event Mean Concentrations (EMC) or loads at one or more locations within a catchment or in separate catchments.

The information and advice provided in this document is intended to help guide best-practice approaches to water quality *sampling* in urban waterways. The guidance is limited primarily to Nalgene bottles and DGT devices; it reflects current best available knowledge and experience and could be updated in the future with additional chapters for different sampling devices as these become available and have been tested in urban waters. The document does not cover site selection, water level and flow measurement, analytical methods; or provide instructions for collecting manual grab samples or operating automatic samplers.

The second part of this document summarises the two phases of trials undertaken for the Envirolink project which provided the basis for preparing the guidance.

In phase one of the project, sampling methods were selected that would assist in fulfilling common objectives for water quality monitoring in urban streams and stormwater. The focus was on testing existing available sampling devices that had not been widely used in New Zealand to date for urban stream or stormwater applications. Testing was restricted to key contaminants: suspended sediment, faecal indicator bacteria, nutrients, copper and zinc. The selected devices were:

- Stormwater sampler bottles that are deployed prior to storm events at pre-defined high water levels, self-seal after filling and enable the collection of samples in the absence of field personnel (we used both a commercially-produced bottle (Nalgene Storm Water Sampler bottles, hereafter Nalgene bottles) and a NIWA-designed bottle (modified from a siphon sampler); and
- Passive sampling devices that accumulate contaminants while deployed, providing a measure of average concentrations of contaminants across storm events (we used DGT® samplers (hereafter DGTs), Sorbisense Sorbicells™ and the ChemCatcher®).

The five sampling devices were trialled alongside existing autosamplers in both stormwater and urban stream settings in the Auckland region to assess their suitability, reproducibility and accuracy (by comparison to data from autosamplers). We found:

- The Nalgene bottles provided acceptable results for sampling of bacteria and dissolved variables but results were less reliable for suspended solids (SS), indicating suitability for SS screening only with this method.
- The DGTs had high precision and closely agreed with results from the autosampler for zinc. For streams, DGT copper concentrations were lower than the dissolved concentrations using autosamplers (copper has high affinity with dissolved organic matter which reduces the amount absorbed by DGTs).
- The Sorbicells, ChemCatchers and modified siphon bottles were either not suitable or needed further development and testing.

In phase two of the project, Nalgene bottles and DGTs (including DGTs for nitrate-N and phosphorus) were deployed by regional council staff in five separate trials in Hawke's Bay, Wellington, Canterbury, Southland and Bay of Plenty[1]. The deployments were primarily within urban streams, and followed receipt of draft guidance (written instructions and videos). The sampling results in most cases corroborated existing information on water quality for the locations sampled, but also provided additional information that would not have been possible to collect through manual grab sampling. Feedback from council staff was used to update and finalise the guidance presented in this document.

[1] Sampling was also intended to be carried out in Otago but did not eventuate. However, the results of recent DGT deployments in Bay of Plenty provided data from a fifth region.

1 Introduction

1.1 Background

Water quality in urban streams and stormwater systems is frequently poor, reflecting the activities present in urban catchments (Holland et al. 2018, Larned et al. 2018). Poor water quality can impact freshwater ecosystems, the ability to use waterways for recreation, and contribute to degradation of downstream receiving environments such as lakes, estuaries and nearshore coastal waters. As set out in the National Policy Statement for Freshwater Management 2014 (NPS-FM,New Zealand Government 2017), information on the sources, concentrations and loads of contaminants entering fresh waters and downstream receiving waters is critical to managing the values they support; in many urban locations across New Zealand this information is either not available or lacking.

Water quality in urban streams and stormwater systems is highly variable, across both space and time (Gadd 2016, Griffiths & Timperley 2005). This reflects a high proportion of impervious land cover and contaminant-generating land uses in the catchment, promoting rapid run-off to streams of a range of contaminants (Figure 1-1, (Mills & Williamson 2008)). Single discrete grab samples – which underpin most State of the Environment (SoE) monitoring and a significant number of resource consent monitoring requirements – cannot adequately capture the high variability in contaminant concentrations in stormwater and urban streams, either during or between storm events. Stormwater is particularly challenging to monitor as the flows are intermittent, catchments are typically small and runoff response to rainfall is rapid compared to 'natural' streams and rivers. Because field personnel usually travel to monitoring sites after rainfall has commenced, first-flushes and peaks in contaminant concentrations can easily be missed. Furthermore, rainfall events often occur outside of normal working hours when staff are not available, or it may be unsafe to collect samples.

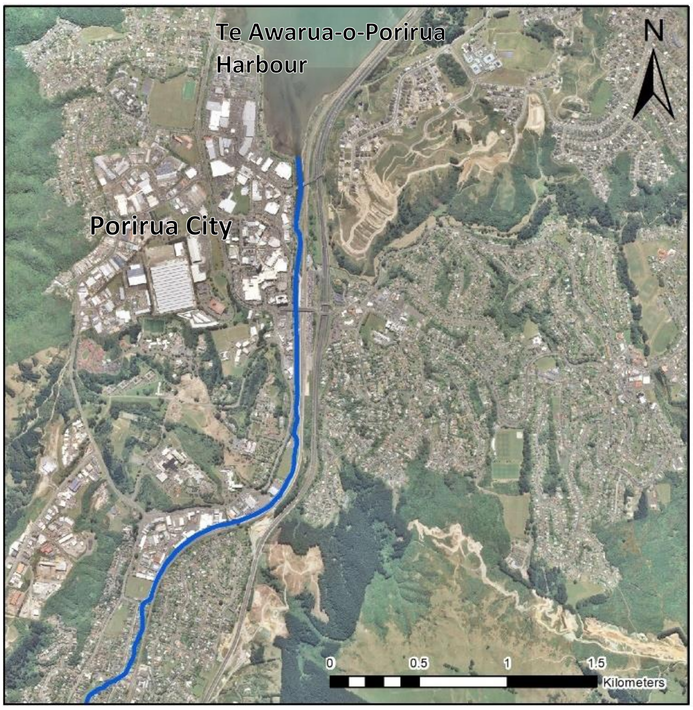

Figure 1-1: Aerial photo of Porirua City, north of Wellington, showing the Porirua Stream (blue line) flanked by a mix of urban land uses. The Onepoto arm of Te Awarua-o-Porirua Harbour is the ultimate receiving environment for Porirua Stream and a number of stormwater outfalls that discharge directly from the Porirua CBD and adjacent roads.

Automatic water samplers (autosamplers) are considered to be the most robust method for sampling storm events (Lee et al. 2007) as they can be triggered to collect samples based on an increase in flow, in the absence of field staff. However, the cost, effort and expertise associated with deployment and operation of autosamplers present major barriers to gathering the more reliable data that these can provide. In 2016/17 NIWA and the regional sector's Coastal Special Interest Group (C-SIG) identified a need for guidance on tools and techniques to cost-effectively monitor urban waters. The C-SIG recognised the need to better quantify contaminant inputs to estuaries, harbours and other depositional coastal environments arising from stormwater and streams in the upstream catchment.

This guidance is intended to assist both regional council environmental science and regulatory staff, and territorial authority (TA) stormwater managers and practitioners in improving current monitoring of water quality in urban waterways across New Zealand. Development of the guidance was funded by an MBIE Envirolink Tool grant (MBIE contract number C01X1701) championed by Dr Claire Conwell (Greater Wellington Regional Council, GWRC) of the C-SIG and supported by the Surface Water Integrated Management (SWIM) SIG. Additional co-funding was provided by NIWA and by Auckland Council.

1.2 Development of this guidance

A Stakeholder Engagement Group (SEG) was established during the scoping of the project comprising scientists from NIWA, GWRC, Auckland Council (AC), Hawke's Bay Regional Council (HBRC), Environment Canterbury (ECan), Otago Regional Council (ORC) and Environment Southland (ES). The primary functions of the SEG were to guide the development of the Envirolink proposal, facilitate field testing of selected sampling devices, and review the draft video and written guidance.

Independent technical advisors (Dr Mike Stewart, Streamlined Environmental Ltd; Dr Will Bennett, Griffith University, Australia; Dr Hubert de Jonge, Sorbisense, Denmark[2]) with expertise and experience in using different sampling devices assisted with the project trial by reviewing the deployment plan for phase 1. These advisors also answered technical queries that arose during the preparation of this guidance document.

The project comprised two phases, each phase lasting approximately 12 months.

1.2.1 Phase 1 (July 2017 – June 2018)

In this first phase NIWA trialled a suite of existing devices potentially suitable for sampling urban waters and prepared draft video guidance and written instructions to assist regional council and TA staff with trialling the devices in Phase 2. The devices included in the project had not been widely used in New Zealand within urban waters. These devices included:

- stormwater sampler bottles that self-seal after filling and enable the collection of samples at high water level (stage) in the absence of field personnel (we used both a commercially-produced bottle (Nalgene Storm Water Sampler bottles, hereafter Nalgene bottles) and a NIWA-designed bottle (modified from a siphon sampler); and
- passive sampling devices that accumulate contaminants while deployed, providing a measure of average concentrations across storm events (we used DGT® samplers

[2] When this project was proposed, the technical advisors named were Dr Mike Stewart and Dr Sylvia Sander, who both had expertise in using DGTs in NZ. These advisors were amended during the project as Dr Sander was on leave and advice was required for the other devices.

(diffusive gradients in thin-films passive sampling devices, hereafter DGTs), Sorbicells and ChemCatchers).

The scope of testing was restricted to key contaminants for urban environments identified with the SEG: suspended sediment, faecal indicator bacteria, nutrients, copper and zinc. Five devices were tested within at least one stormwater and one stream location, and sampling results compared to those determined from using autosamplers. From this initial testing, two devices were selected for further field testing in Phase 2.

1.2.2 Phase 2 (July 2018 – June 2019)

In Phase 2, further testing was undertaken by regional council staff to trial two devices – Nalgene bottles and DGTs – in different locations and for different purposes. The information obtained from this testing, including the experience of the field personnel in device deployment and retrieval, was used to refine the guidance presented in this document.

1.3 What does this guidance address?

This guidance focuses specifically on sampling of urban waters during *storm events* (also known as rain events). These events may be targeted for sampling to augment monthly SoE monitoring so that contaminant concentration data can more reliably inform toxicity assessments and catchment load assessments (e.g., as required for implementation of the NPS-FM), or as part of catchment studies (e.g., identification of contaminant 'hotspots'), resource consent applications or consent monitoring. Storm event sampling may form part of isolated investigations or on-going monitoring.

The focus of this guidance is on sampling for common water quality variables in urban stormwater networks and outlets, and drains and streams (including ephemeral and tidal reaches of streams): suspended sediment, faecal indicator bacteria, and both dissolved and total nutrients and metals. Some of the guidance may be relevant to sampling other contaminants, including hydrocarbons, pesticides or emerging contaminants, but additional specialist advice should be sought when sampling for these contaminants.

This guidance does not include sampling of sediments within urban streams or stormwater systems for the purposes of assessing sediment quality. This guidance is also not applicable to sampling water quality in large rivers or estuaries, harbours or coastal beaches. While some of the methods included here may also be suited to sampling during baseflow or for long-term monitoring programmes (e.g., SoE monitoring), grab sampling is likely to remain the key discrete sampling method for those purposes. Detailed guidance on collecting grab samples is available in the National Environmental Monitoring Standard "Water Quality Part 2 of 4: Sampling, Measuring, Processing and Archiving of Discrete River Water Quality Data" (NEMS 2019)[3].

Information in this manual is intended to guide best-practice approaches for water quality sampling using Nalgene bottles and DGT devices. Due to the site-specific nature of stormwater locations, the guidelines do not include provisions for sampling at all possible locations. However, the general principles for using these devices and the examples set out in these guidelines should provide a basis for sampling most urban waterways around New Zealand.

[3] NEMS (2019) http://nems.org.nz/documents/water-quality-part-2-rivers/

This guidance manual relates only to *sampling methods*. It does not cover other important factors in urban stream and stormwater monitoring such as:

- Selection of sampling sites;[4]
- Storm event characteristics for sampling (antecedent conditions etc)[5];
- Water level and flow measurement methods[6];
- Laboratory analysis of the samples (except sample preparation that is specific to the sampling devices)[7].

This guidance reflects current best available knowledge and experience, and guidance may always be improved as further knowledge and experience is gained in using the devices described. This guidance could be updated in the future with additional chapters for different sampling devices as these become available and have been tested in urban waters.

1.4 Assumptions and limitations

It is assumed that as a minimum, the reader of these documents has relevant experience in environmental sciences and has a basic understanding of water sampling techniques. Health and safety considerations are not included in this document and readers are referred to NEMS (2013) for general guidance on this.

1.5 Document outline

This guidance document comprises seven chapters separated into two parts.

Part 1 comprises three chapters that provide the guidance on sampling methods for urban streams and stormwater:

- Chapter 2 provides a brief background on the effects of urbanisation on waterways, and the challenges of stormwater and urban stream sampling. This is intended for readers who are relatively new to this field.
- Chapter 3 describes the four types of sampling methods that are addressed in this guidance; manual grab sampling, Nalgene Storm Water Sampler bottles (Nalgene bottles), DGTs and automatic samplers. The potential uses, advantages and disadvantages of these types of sampling methods are compared across common water quality variables, sampling locations and resource requirements.
- Chapter 4 provides guidance for determining which method would be suitable for your sampling situation, based on four core sampling objectives. Example sampling plans are provided for each objective.

[4] See NEMS (2019) for guidance on site selection that may be relevant to sampling urban streams. McCarthy & Harmel (2014) provide brief guidance relevant to sampling both urban streams and stormwater.
[5] See Gadd et al. (2014a) for general advice on this.
[6] See NEMS (NEMS 2016) for guidance on water level measurement and recording.
[7] See NEMS (2019) for guidance on many water quality variables relevant to urban waters.

Part 2 comprises two chapters describing the trials undertaken during this project that informed the development of the guidance:

- Chapter 5 presents the methods and findings of the first phase of the project trialling various sampling devices in urban waterways, primarily in the Whau catchment, Auckland.
- Chapter 6 presents the methods and findings of the second phase of the project trials undertaken by council staff in Napier/Hastings, Porirua, Christchurch and Invercargill. A further study undertaken in Tauranga, but not directly associated with this project, is also included as a further example of a sampling device application.

Chapter 7 provides a summary of this guidance document.

Appendices A and B provide specific instructions for the use of Nalgene bottles and DGTs, respectively. These are designed as stand-alone documents. A synopsis of the benefits and limitations of the sampling method can be found in each appendix, so that readers can evaluate each method for their specific situation. Each appendix contains instructions for applications of the methods in both urban stream and stormwater locations. Finally, each appendix has an attachment containing field sheets and additional technical information.

At the end of the document, the reader will find a glossary of key terms, a list of further reading and citations for all referenced material used in developing this document.

1.6 Guide to reading this document

This document is intended to assist anyone that requires some guidance on water quality sampling in urban waterways. It is intended to be used as a reference rather than be read from beginning to end. Most users will probably want to read chapters 3 and 4 to select a method, read the trial information for that device in chapters 5 and 6 and scan the appendices for detailed information and instructions for using the devices (Table 2-1).

Short videos demonstrating how to deploy Nalgene sampler bottlers and DGTs in streams and stormwater outfalls can be viewed at:

https://www.niwa.co.nz/sampling-urban-streams-stormwater

Table 1-1: Guide to reading this document.

Potential user	Relevant chapters	Benefit to the user
Environmental scientist planning a water quality programme	Read chapters 3 and 4; scan chapters 5 and 6	Understanding of possible devices that could assist with monitoring objectives Confidence in the data provided by devices
Environmental / field officer charged with using devices	Scan chapters 3 and 4, read appendices	Understanding the benefits of using devices Confidence to install and use devices with no further training
Consent officers processing consent applications	Read chapters 2 and 6	Awareness of alternative methods to grab sampling for consent conditions and understanding of the benefits
Consent holders and compliance monitoring officers	Scan chapters 3 and 4, read appendices	Understanding of devices that could assist with consent monitoring conditions Confidence to install and use devices without further training
Environmental consultants interested in trialling different methods	Read chapters 3 and 4; scan 5 and 6; scan appendices	Understanding of possible devices that could assist with monitoring Awareness of which devices can be used in which situations for future projects

PART 1: GUIDANCE ON URBAN STREAM AND STORMWATER SAMPLING METHODS

2 Urban stream and stormwater quality

This chapter provides contextual background to the project by overviewing the effects of urbanisation on waterways, and the challenges of stormwater and urban stream sampling.

2.1 Effects of urbanisation

During urban development pervious surfaces (grasslands, forests) are replaced with impervious surfaces (roads, buildings, paved areas). This disrupts the natural water balance by reducing infiltration of rain water into soil and groundwater thus increasing the volume of water that runs off into streams (Figure 2-1), resulting in an increase in the volume of storm flows and the magnitude of flood events (Figure 2-2). The impervious surfaces also increase the frequency of flood events (Elliott et al. 2004) and small-medium flow events (Roy et al. 2005) due to the reduced infiltration (Figure 2-3).

Stormwater networks in urban areas also affect stream hydrology (and water quality) as the piped networks rapidly transport the stormwater into streams with little or no attenuation of contaminants (Elliott et al. 2004, Suren & Elliott 2004). The result of these changes is the 'flashy' hydrology that is typical of urban streams, characterised by low baseflow, rapid increases in flow during small storm events and increased peak flows (Roy et al. 2005, Suren & Elliott 2004, Walsh 2004).

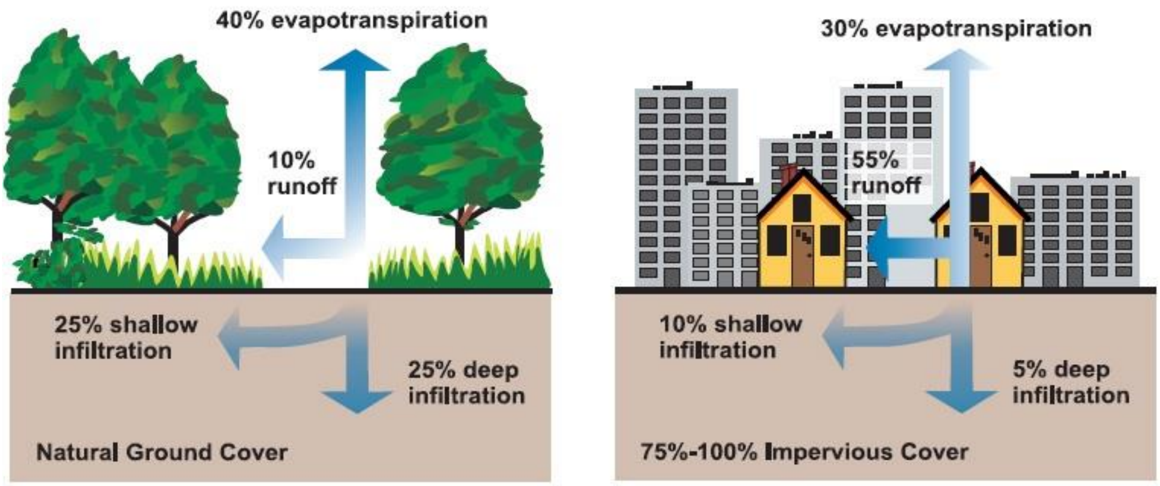

Figure 2-1: Comparison of water balance with natural ground cover (left) and with impervious cover. From USEPA (2003).

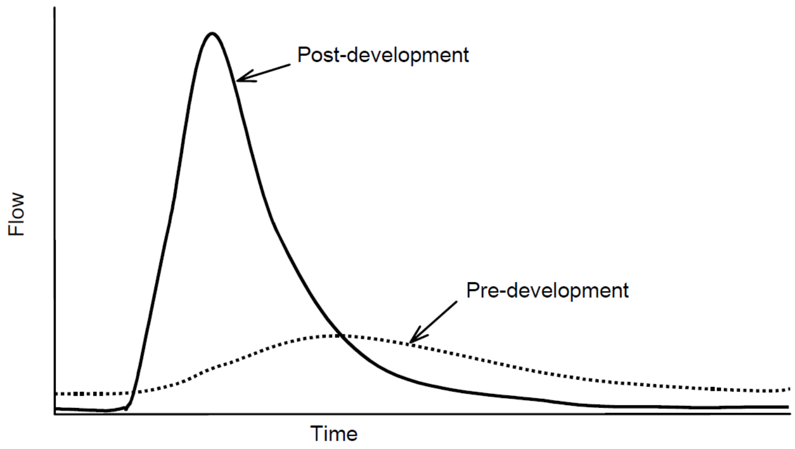

Figure 2-2: Schematic diagram of typical storm hydrograph before and after a high degree of urbanisation in the stream catchment, showing the higher sharper peak and reduced baseflow. From Elliott et al. (2004).

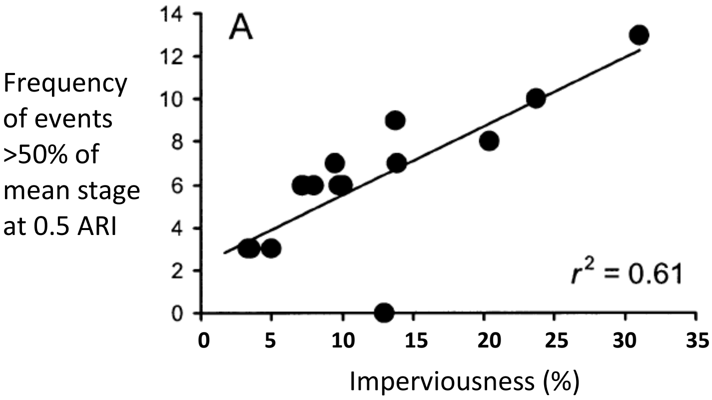

Figure 2-3: Increase in flood frequency with increased imperviousness in stream catchments. From Roy et al. (2005).

Impervious surfaces provide a hard surface on which contaminants accumulate (e.g., copper in vehicle brake dust accumulating on roads). A wide range of contaminants (Table 2-1) are produced in urban areas due to the variety of activities such as transport, industry (e.g., outdoor use and/or storage of chemicals and materials), and residential chemical use (pesticides, cleaning agents, painting). During storm events, water running over these impervious surfaces collects and transports the contaminants into drains and streams (Figure 2-4) resulting in higher contaminant concentrations in urban streams compared to streams in non-urban areas (Harding et al. 2016, Paul & Meyer 2001). In addition, some impervious surfaces themselves generate contaminants, for example zinc is released from zinc-based roofing materials (Kingett Mitchell Limited and Diffuse Sources Limited 2003) and copper is released from copper architectural material (Pennington & Webster-Brown 2008). Wastewater networks in urban areas can also affect stream water quality, due to discharges of untreated sewage during wastewater overflows (which can occur with both combined and separated sewer networks) or leakage from the piped network (Paul & Meyer 2001).

Table 2-1: Common contaminants in stormwater, their sources and effects.

Contaminant	Common sources	Effect
Suspended sediment	Bare earth, including earthworks	Sedimentation and reduced visual clarity in-stream and in downstream depositional environments (e.g., estuaries and harbours)
Nitrogen (N)	Fertilisers, vegetative matter, sewage, cleaning products	Some forms, principally nitrate-N and ammoniacal-N are toxic at high concentrations and can contribute to excess plant (algae and macrophyte) growth at lower concentrations
Phosphorus	Fertilisers, vegetative matter, sewage	Available forms can contribute to excess plant (algae and macrophyte) growth
Copper	Dust from wear of vehicle brake linings and copper building materials such as roofs, spouting and cladding	Acute and chronic toxicity to fish, invertebrates, plants and microorganisms
Zinc	Tyre wear, zinc-coated roofing materials	Acute and chronic toxicity to fish, invertebrates, plants and microorganisms
Bacteria and pathogens	Sewage, animal faeces (e.g., avian and pet)	Human health effects including gastrointestinal illnesses
Petroleum hydrocarbons including PAHs	Vehicle oil leaks and spills; industrial sites	Acute and chronic toxicity to fish, invertebrates, plants and microorganisms
Pesticides	Domestic and council use including road-side spraying	Acute and chronic toxicity to fish, invertebrates, plants and microorganisms

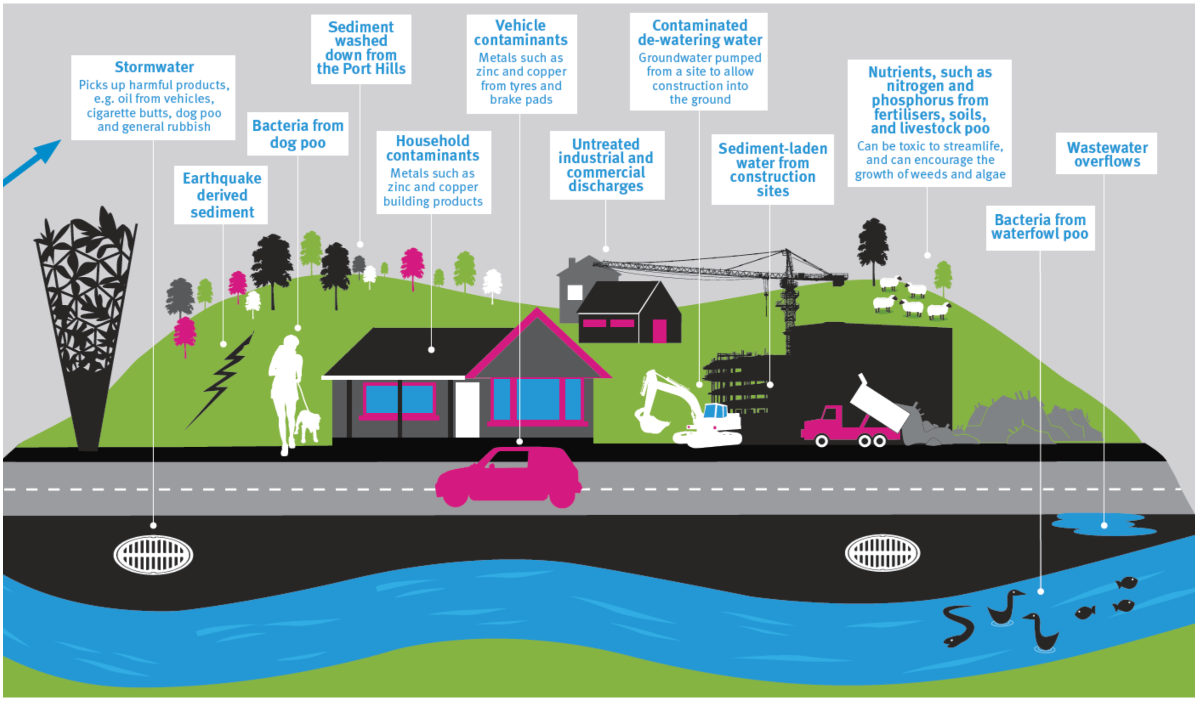

Figure 2-4: Sources of contaminants in urban stormwater and streams in Christchurch. Source: Christchurch City Council (Christchurch City Council undated).

Changes in stream hydrology and water quality are often coupled with geomorphological and riparian changes that occur during land development, such as straightening or realigning streams; channelising using concrete, wooden boxes or gabion baskets; concrete lining stream beds; and removing or reducing riparian vegetation (Suren & Elliott 2004). Further changes to geomorphology occur post-development, in response to changes in sediment supply and flows (Paul & Meyer 2001). In combination, these multiple pressures result in degradation of biological communities and reduced ecological functioning in urban streams, a condition that has been termed the 'urban stream syndrome' (Walsh et al. 2005). This condition is characterised by fewer sensitive invertebrates (Walsh 2006) and fish species (Roy et al. 2005, Wang et al. 2001). In New Zealand, urban streams are dominated by pollution-tolerant taxa (Harding et al. 2016, Suren 2000) as demonstrated by lower macroinvertebrate community index (MCI) (Collier et al. 2009, Larned et al. 2018) and Ephemeroptera-Plecoptera-Trichoptera (EPT) scores (Allibone et al. 2001, Collier et al. 2009). In some cases fewer fish species (Allibone et al. 2001, Kingett Mitchell & Associates 2000) have been noted in urban areas, though in some locations diversity remains high (Collier et al. 2009). The presence of barriers to fish passage and local habitat conditions are more important than the catchment land use in some cases (Mills & Williamson 2008).

In addition to effects on stream ecology, urbanisation and stormwater discharges can increase flooding of adjacent land and houses, increase rates of sedimentation in downstream receiving environments (Mills & Williamson 2008) and render waterbodies unsuitable for recreation (Mills & Williamson 2008).

2.2 Urban stream and stormwater quality

2.2.1 Introduction

Urban streams generally have poor water quality compared to streams within natural, forested or pastoral catchments (Larned et al. 2004, Larned et al. 2016, Larned et al. 2018), with higher concentrations of faecal indicator bacteria (e.g., *E. coli*), nutrients and metals (Figure 2-5). Furthermore, water temperature is frequently higher in urban streams, and dissolved oxygen concentrations can be lower (Holland et al. 2018, Margetts & Marshall 2018, Perrie et al. 2012).

Despite being generally poor, water quality in urban streams and stormwater shows a large degree of variation, both in space and in time (Gadd 2016, Griffiths & Timperley 2005). This creates difficulties in collecting representative samples. Awareness of the variations in water quality is important in deciding where, when and how to sample. Throughout this section, we use the term contaminant to refer to water quality variables of interest.

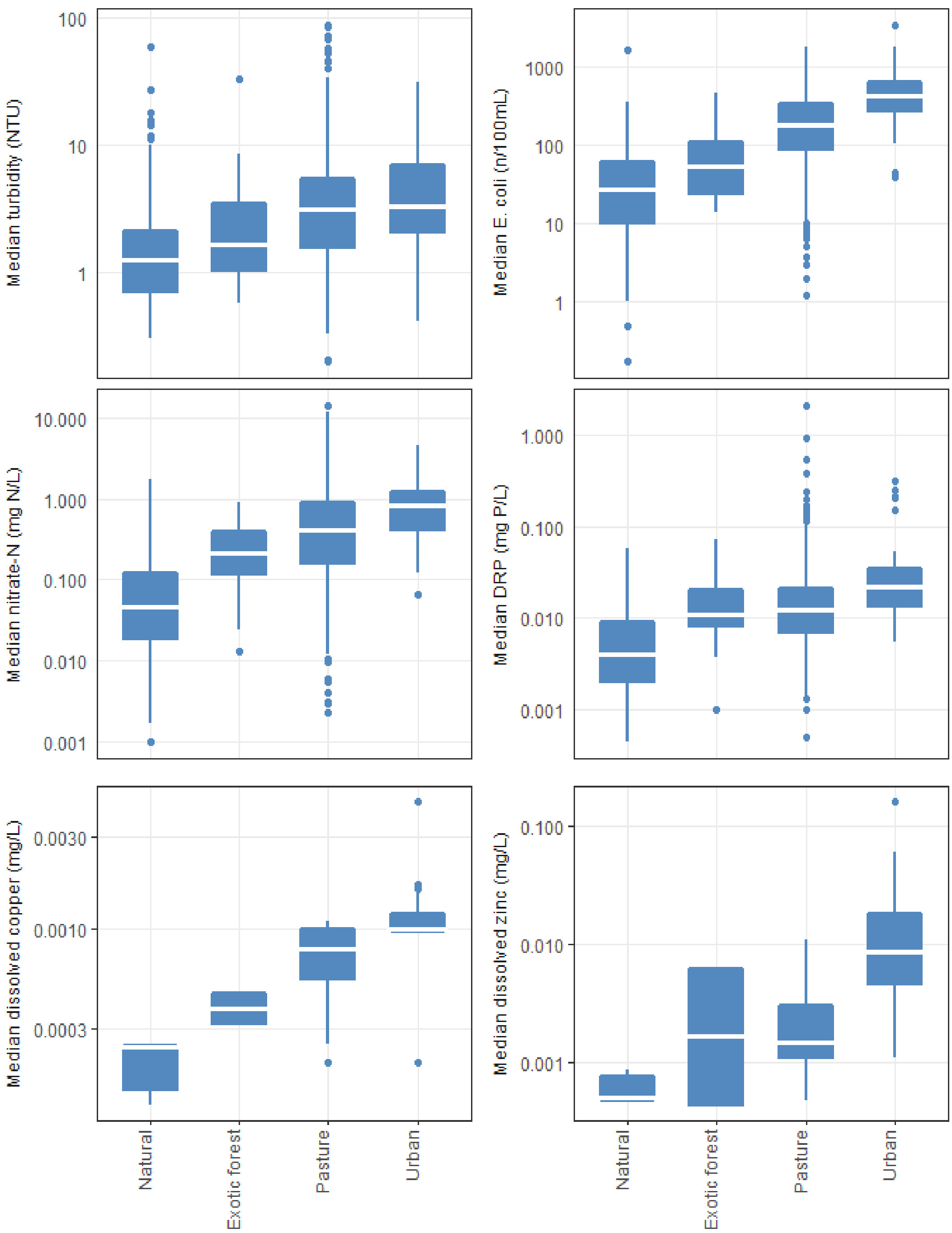

Figure 2-5: Median concentrations of a range of contaminants in streams in forested, natural, pastoral and urban stream catchments. Data from MfE data service[8], see Larned et al. (2018) and Gadd et al. (2016) for details of data sources and processing.

2.2.2 Spatial variability in urban water quality

Water quality varies considerably between different urban streams (Figure 2-6, Table 2-2), depending on aspects such as geology, source of flow (e.g., hill-fed vs spring-fed), rainfall, catchment land cover and use, stormwater treatment systems, and the presence and frequency of point source discharges. The variation in concentrations of some variables is even more pronounced for stormwater when comparing between different sites (Figure 2-7, Table 2-2).

[8] https://data.mfe.govt.nz/data/

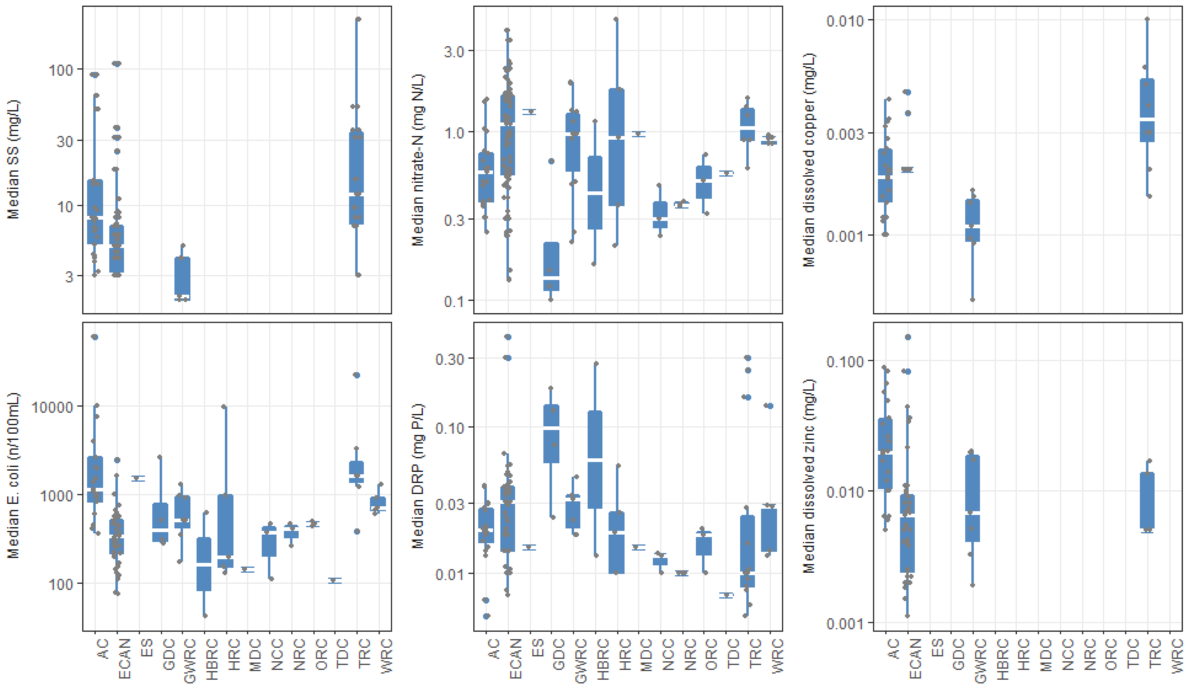

Figure 2-6: Concentrations of a range of contaminants in urban river and stream sites arranged by region. Data from URQIS[8] and council supplied SoE data and only includes sites with > 12 data points. Each point represents a site median, box plot indicates the 25th and 75th quartiles of site medians, white horizontal line in each box indicates the median of site medians, whiskers indicate the 1.5x inter-quartile range of site medians.

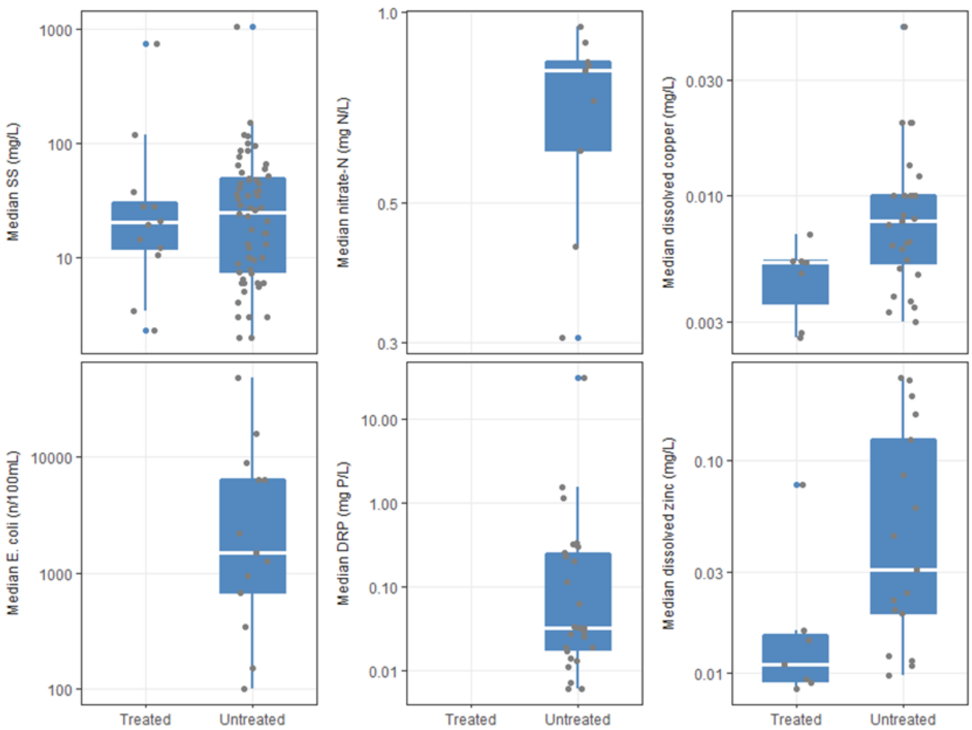

Figure 2-7: Distribution in median concentrations of a range of contaminants in stormwater from different sources. Data from URQIS [9] and only includes sites with > 12 data points. Each point represents a site median, box plot indicates the 25th and 75th quartiles of site medians, white horizontal line in each box indicates the median of site medians, whiskers indicate the 1.5x inter-quartile range of site medians.

[9] www.urqis.niwa.co.nz Gadd et al. (2014b)

Table 2-2: Typical contaminant concentrations in New Zealand urban streams and stormwater.

Contaminant	Typical values for NZ urban streams [1]		Typical values for NZ stormwater [2]	
	Mean and range of site median concentrations (mg/L, except *E. coli*, no./100mL)	Mean, 10th and 90th percentiles of site CV	Mean and range of site median concentrations (mg/L, except *E. coli*, no./100mL)	Mean, 10th and 90th percentiles of site CV
Suspended sediment	16 (20 – 230)	1.4 (0.6 - 2.5)	72 (2 - 1100)	1.4 (0.8 - 2.3)
Nitrate-N	1.0 (0.1 – 4.6)	0.7 (0.3 - 1.3)	0.71 (0.31 - 0.95)	1.7 (0.5 - 3.5)
Ammoniacal-N	0.13 (<0.01 – 2.6)	1.6 (0.6 - 3.2)	4.2 (0.01 - 63)	1.8 (0.8 - 2.7)
Total nitrogen	1.3 (0.16 – 4.7)	0.7 (0.3 - 1)	0.85 (0.66 - 1.1)	0.5 (0.2 - 0.8)
Dissolved reactive phosphorus	0.04 (0.005 – 0.42)	1.1 (0.4 - 2)	1.4 (0.01 - 32)	2.2 (0.8 - 3.5)
Total phosphorus	0.077 (0.018 – 0.61)	1.1 (0.5 - 1.8)	6.6 (0.02 - 26)	1.6 (1.3 - 2)
Total zinc	0.034 (0.002 – 0.23)	1.2 (0.6 - 2)	0.25 (0.01 - 1.4)	0.8 (0.5 - 1.4)
Dissolved zinc	0.017 (0.001 – 0.15)	1.1 (0.5 - 1.7)	0.06 (0.009 - 0.24)	0.6 (0.4 - 0.9)
Total copper	0.003 (0.001 – 0.017)	1.0 (0.5 - 2)	0.017 (0.003 - 0.06)	0.9 (0.5 - 1.3)
Dissolved copper	0.002 (0.0005 – 0.010)	0.5 (0 - 0.9)	0.009 (0.003 - 0.05)	0.7 (0.4 - 1)
E. coli	2250 (42 – 60,300)	2.7 (1.3 - 4.8)	6700 (46 – 49,000)	1.9 (1.1 - 2.6)

Notes: 1. Data from URQIS database and MfE data service; only sites with more than 12 data points included 2. Data extracted from URQIS database; only sites with more than 12 data points included. 3. 25th and 75th percentiles provided

Even at a single location, many contaminants exhibit within-channel variability – that is, variability across the stream and with depth. This is well-documented for large rivers but also occurs in small streams (Harmel et al. 2010). Variability may be highest downstream of point source discharges until these are completely mixed with the stream water. Because urban streams can have numerous stormwater outlets, there may not be complete mixing of one discharge before the next downstream discharge enters. Water samples are best collected in the centre of the channel, within a run or riffle section, rather than a pool (McCarthy & Harmel 2014, NEMS 2019). Samples collected near the stream bed or base of stormwater pipe can over-estimate sediment concentrations by nearly 100% (Selbig et al. 2012) and in some cases increases with depth have also been observed for dissolved constituents (Ging 1999, Harmel et al. 2010), indicating that sampling depth can have a significant effect on results.

2.2.3 Variability by flow

For many contaminants, large differences in concentration are measured between storm flows and baseflow (Figure 2-8). For example, in Whau Creek in west Auckland, total zinc concentrations were 0.014-0.020 mg/L during baseflow and frequently rose to over 0.05 mg/L during wet weather flows, at times between 0.1 and 0.3 mg/L (NIWA, unpublished data). Similarly, *E. coli*, total and dissolved zinc, total copper and forms of nutrients that include particulates (i.e., total nitrogen, Kjeldahl nitrogen, total phosphorus) are typically higher at higher flows (Figure 2-8). However, some contaminants vary less between storm events and baseflow, such as dissolved copper (in many cases) and dissolved nutrients (Figure 2-8).

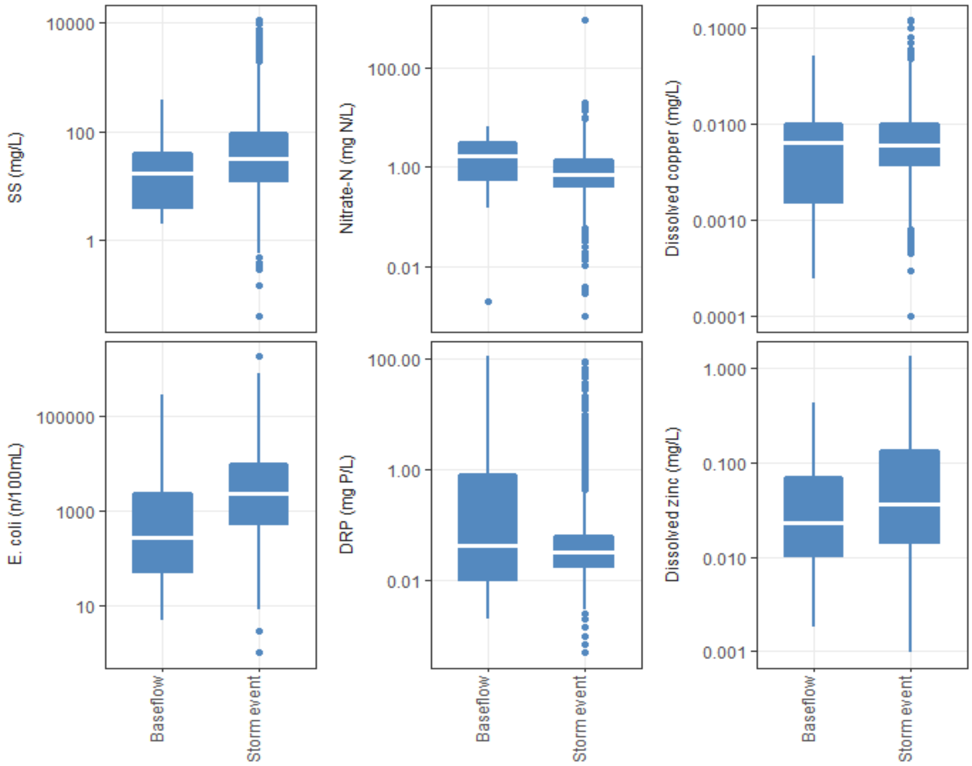

Figure 2-8: Distribution of contaminant concentrations in urban streams during baseflow and storm events. Note the logarithmic scale used on the y-axis. Data from URQIS (Gadd et al. 2014b).

Some contaminants demonstrate what is commonly called a 'first-flush' in stormwater, whereby a disproportionately high mass of contaminant is discharged during the initial part of the storm (Sansalone & Cristina 2004). Samples collected at the beginning of the event are more likely to have higher concentrations than samples collected subsequently, even for samples collected at the same flow rate. A first-flush is typically only observed where the supply of contaminant is limited (Shamseldin 2011), like metals are commonly presumed to be. First-flushes are usually more evident in stormwater discharges and less apparent in streams which are fed by combination of multiple stormwater discharges arriving at different times (Shamseldin 2011). Metals (both particulate and dissolved) and some faecal indicator bacteria can demonstrate a first-flush (Shamseldin 2011).

In contrast, sediment concentrations may not demonstrate first-flush as in some catchments there is essentially an unlimited supply of sediment, from soil erosion (Shamseldin 2011, Timperley & Reed 2005). In these cases, sediment is positively correlated with stream flow, in that higher concentrations occur with higher flows and samples collected during the flood peak (highest flow) will have higher concentrations than those collected before or after the peak, as shown in Figure 2-9. In more developed and highly impervious catchments, a first-flush may be present as accumulated sediment washes off impervious surfaces.

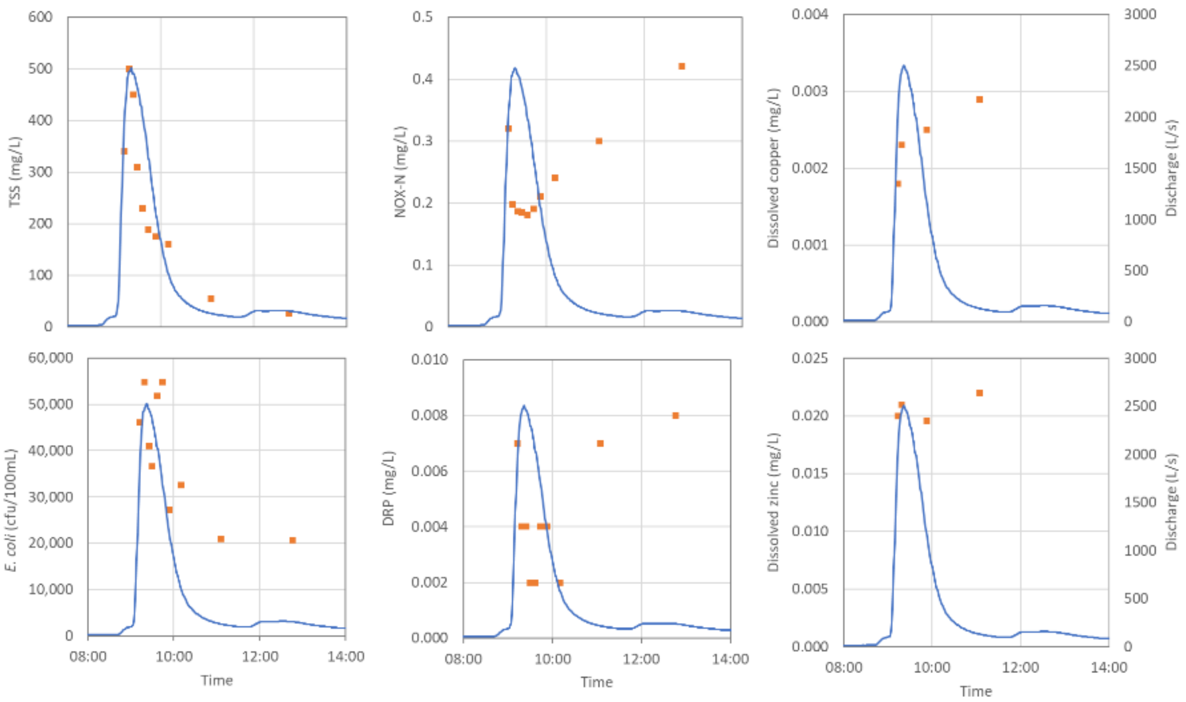

Figure 2-9: Selected contaminant concentrations compared to event hydrograph indicating range of different relationships. Data from NIWA unpublished data. This does not represent all events at all locations.

However, not all contaminants increase with increased flow or on the first-flush. Dissolved nutrient concentrations can be negatively correlated, with lower concentrations during the flood peak compared to before or after the peak (Figure 2-9). However, this may not occur in all locations or for all storm events as factors such as antecedent conditions and season can also influence contaminant generation and transport.

These differing relationships between concentrations and flow, depending on contaminant and in some cases, depending on location, mean that there may be no "best" time to take a water sample that represents the storm event concentration, whether it is the maximum concentration, or an event mean concentration (EMC) that is of interest. For many contaminants, it is likely that samples collected early in a storm event will have higher concentrations than samples collected later in the storm, and will over-estimate the EMC. For these reasons, most monitoring protocols recommend collecting multiple samples per event, especially for contaminants that are highly variable (see Table 2-2).

2.2.4 Variability between events

In addition to potential variation between events due to different flows, for many contaminants the period of time passed since a previous storm event (the antecedent dry period) can also affect contaminant concentrations (Kayhanian et al. 2003, Timperley & Reed 2005). This is especially true for contaminants that are source-limited and present in stormwater due to their build-up on impervious surfaces, followed by wash-off during rain events. This means that concentrations will be different between storms even when they have similar rainfall depth, intensity and duration (see Figure 2-10).

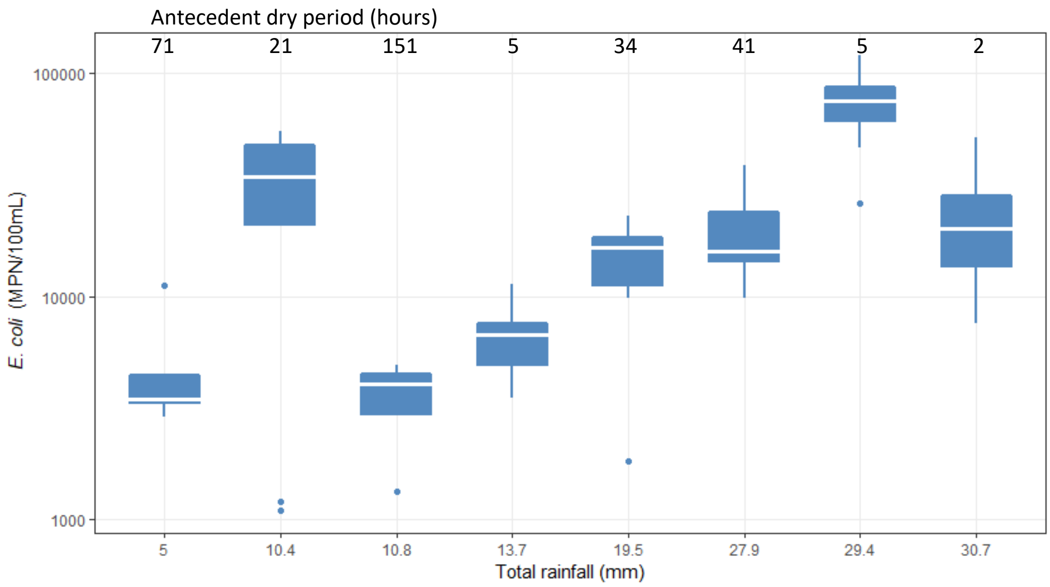

Figure 2-10: *E. coli* concentrations in nine different storm events in an urban stream. Unpublished data collected by NIWA from Whau Creek at Blockhouse Bay Road, Auckland.

Furthermore, some contaminants differ seasonally, for example, faecal indicator bacteria (FIB) are often found at higher numbers during summer months when warmer conditions enhance bacteria growth and survival (Hathaway et al. 2010, Muirhead & Meenken 2018, Paule-Mercado et al. 2016). However, for catchments affected by wastewater overflows, FIB may be found at higher numbers during *winter* months, when overflows are more frequent (e.g.,Milne & Wyatt 2006). Nitrate-N concentrations also differ seasonally in urban streams, with highest concentrations over winter and lowest concentrations in summer. The causes are complex, relating to differing nutrient inputs (e.g., increased leakage from sewerage systems in winter), differences in stream flow, and nutrient uptake by primary producers (e.g., decreased algal uptake during winter). Interactions between surface flow and groundwater can also contribute, for example in Christchurch streams, where in winter there are increased inputs of spring-fed groundwaters high in nitrate-N (PDP 2015).

It has been shown in overseas studies that contaminant concentrations are highest during the first few events following a long dry period (Lee et al. 2007) and this could occur in parts of New Zealand that also show seasonal rainfall, such as areas on the east coast of New Zealand. Monitoring programmes aiming to characterise long-term averages will be biased if sampling storms early in the season. On the other hand, these storm events could be targeted to assess maximum or worst-case conditions. This seasonal first-flush effect was not shown in locations with more even rainfall distributions (Lee et al. 2007), as occur in other parts of New Zealand (e.g., Auckland and Wellington).

These combined differences of differing rain event characteristics, antecedent periods and season necessitate sampling of multiple storm events to characterise either long-term average or maximum contaminant concentrations, with more events required for highly variable contaminants (see Table 2-2).

3 Storm event sampling methods

In this chapter we describe four different types of method for sampling storm events: manual grab sampling, stormwater sample bottles, DGTs and automatic samplers. The potential uses, advantages and disadvantages of these types of sampling methods are compared across common water quality variables (primarily referred to as contaminants in this chapter), sampling location and resource requirements.

3.1 Introduction to different sampling methods

As outlined in Chapter 2, contaminant concentrations differ between storm events, and within storm events, depending on the season, antecedent conditions, rainfall depth and intensity, event duration and time since onset of rainfall. This makes it extremely difficult to collect samples that accurately represent the storm event concentrations. Therefore, either multiple samples need to be collected, or sampling methods need to integrate over time to average out these effects. When multiple storm events are to be sampled (for example to understand average concentrations), it is advantageous to use sampling methods that provide high quality data yet minimise the effort required.

The ideal method for measuring urban stormwater and stream water quality is continuous *in situ* measurement, which provides a record of contaminant concentrations throughout both base flow and storm events, and avoids the risk of potential changes in contaminant concentrations between discrete sample collection and laboratory testing. Reliable continuous monitoring sensors have been available for a number of water quality variables for many years (e.g., temperature, dissolved oxygen, pH, conductivity, turbidity) and new sensors for nitrate-nitrogen and faecal indicator bacteria show promising results (Hudson & Baddock 2019); however, commercially available sensors for other variables of interest in urban waters (sediment and metals) are either not yet available or in their infancy.

This section briefly describes key methods that are currently available for sampling urban streams and stormwater. The methods considered in this guidance are:

- Manual grab sampling;
- Grab samples using Nalgene bottles;
- DGTs (a passive sampling device); and
- Automatic samplers.

Alternative passive sampling devices are also available and two of these (Chemcatchers and Sorbicell devices) were trialled in Phase 1 of this project along with a further sampling bottle system. These devices are not included in this guidance as either 1) there were clear disadvantages to the method; 2) there was greater cost associated with the device and no clear advantage; or 3) further development of the device was required for storm event sampling purposes. Information on the methods and results of testing is included in Chapter 5.

3.1.1 Manual grab samples

Water samples can be collected manually (grab samples) simply by filling a bottle with water from within a stream or from a stormwater discharge (Figure 3-1 and see NEMS (2019) protocol for details on grab sampling in rivers). Grab samples represent a snapshot of the water quality at the time of collection. It is for this reason, that SoE monitoring programmes base assessments of current state (typically representing baseflow conditions) and temporal trend on a large number of (typically monthly) samples; typically 1-3 years for state and 5+ years for trends.

A single grab sample is generally of limited use in storm sampling, particularly for comparing to guidelines or limits, or for comparing between sites, where it is important that all samples being compared represent the same conditions at each site (e.g., all samples represent the first-flush or storm peak). However, with sufficient resource, multiple grab samples can collected over various parts of the flow hydrograph, which may be sufficient information to calculate an EMC, provided that flow measurements are also collected at the same time (Roesner et al. 2007). Additionally, grab samples can be used to estimate long-term average concentrations if enough events are sampled, however this may require sampling over 30 storm events (Fletcher & Deletic 2007, McCarthy et al. 2018).

Figure 3-1: Collection of a manual grab water sample by hand (left) and using a telescopic pole (at base flow). [Photos: Juliet Milne].

3.1.2 Nalgene® Storm Water Sampler bottles

Nalgene® Storm Water Sampler bottles (Nalgene bottles, Figure 3-2) are commercially produced bottles that collect a grab sample of water, similar to a manual grab[10], but without the requirement for personnel on site. This avoids the need to rush out to a site in advance of forecast rain or during an event, or use of multiple personnel when sampling at multiple sites. The bottles are deployed above the water level prior to a storm event and fill once water either flows over them (e.g., if installed in a stormwater catchpit), or reaches the intake level when deployed in stream or drain. They close off by means of a float valve (also known as a ball cock), preventing any further water from mixing with the sample. The water sample retained can be shipped to a laboratory for analysis of any kind of contaminant. For organic contaminants, the plastic bottles can be replaced with glass bottles.

Nalgene bottles are designed for, and best suited to, collecting a sample from the first-flush in a stormwater location because they can be deployed well before a rain event, and at multiple locations. The bottles can also be used for collecting samples at high flows in streams and can be deployed at pre-defined heights to capture a defined part of a storm event. They can also be deployed as a series of bottles at increasing heights to collect samples across the rising limb of a storm event, which captures more of the temporal variability in concentrations. A further advantage of using Nalgene bottles over manual grab sampling is that you can install a replacement bottle when picking up a filled one, leaving the bottle in place for the next storm event, saving time and resources.

[10] Note that with a manual grab samples are usually collected below the water surface and can be integrated over depth. When deployed in a stream, Nalgene bottles will fill from the water surface and therefore represent a slightly different parcel of water from a grab sample. This effect is unlikely to be significant at higher flows when there is high turbulence (and mixing) of the stream water.

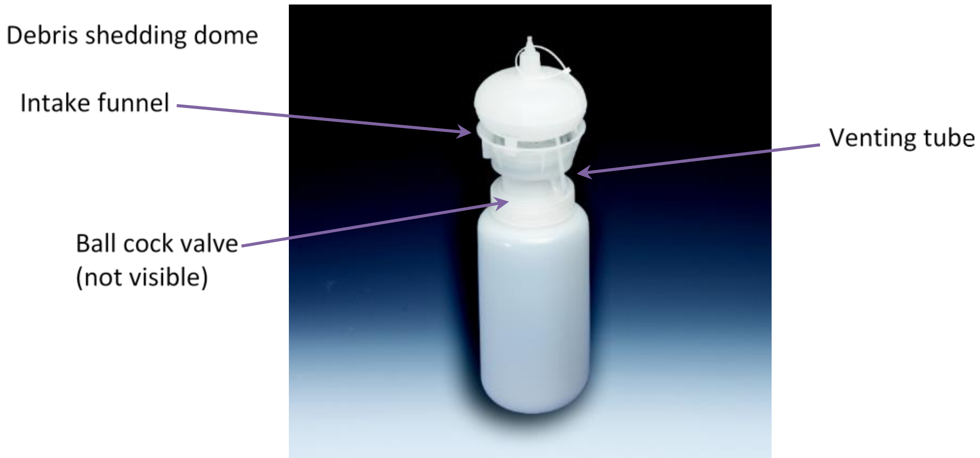

Figure 3-2: Nalgene® Storm Water Sampler bottles. Image from Thermoscientific.

3.1.3 DGTs

DGT (diffusive gradients in thin films) are small, simple passive sampling devices (Figure 3-3) that provide an integrated concentration over a sampling period. When deployed in the water column, the DGTs continuously absorb and concentrate dissolved substances in a controlled way. They provide a time-weighted average (TWA) concentration, an integration of the entire period the device was installed. DGTs cannot provide any information on peak concentrations or the range in concentrations throughout a storm. They do not require any power supply to work and are small enough (~40 mm in diameter) to be deployed in many locations but must not be allowed to dry out, either before or during use.

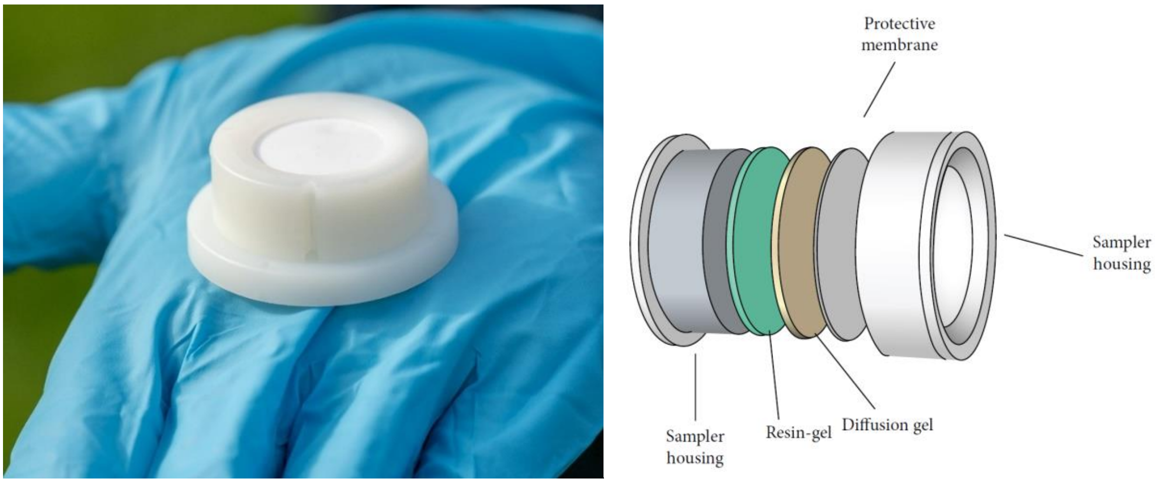

Figure 3-3: DGT devices for water sampling (left) and schematic of key components of DGTs (right). [Photo: Stuart Mackay. Schematic: Knutsson et al. (2014)]

The DGTs have three layers (Figure 3-3, right):

- A membrane filter to keep out solid particles;
- A diffusive gel layer which controls the diffusion of solutes (dissolved contaminants) and can be of different thicknesses; and
- A binding layer or gel, which selectively binds the contaminants of interest. This layer has a different composition depending on the contaminants (e.g., Chelex for metals and SIR-100-HP resin for nitrate-N).

DGTs are available for dissolved metals (cationic and oxyanions), some dissolved nitrogen and phosphorus species, and selected polar organic compounds. DGTs measure the "labile" metals in a water body, that is, the metals that can easily diffuse through the gel to be absorbed by a DGT. This excludes metals that are strongly bound to organic colloids, like humic acids. Because of this, DGT metal measurements are similar to the bioavailable fraction, and lower than dissolved metal concentrations. In contrast, measurements for nitrate and phosphorus using DGT are analogous to measurements of dissolved nitrate and dissolved reactive phosphorus (DRP) in water (Huang et al. 2016). Samplers for polar organic compounds are still in development (Guibal et al. 2019) and literature regarding their sampling methods and sensitivity should be consulted before using them for monitoring purposes.

The DGT devices need to be deployed in the field for one or more days to accumulate most contaminants in urban streams. They can be deployed for up to several weeks if desired for the sampling objectives (e.g., long-term averages) or, if necessary, to accumulate sufficient concentrations of the contaminant of interest (e.g., organic contaminants, or metals in pristine streams). They then need to be retrieved and shipped to a laboratory where they are disassembled under clean conditions, the contaminants are extracted from the binding layer, and the accumulated mass of contaminant is measured by routine methods. This mass, after subtraction of metals measured in blanks, along with water temperature and the length of time deployed, is used to calculate the time-weighted average concentration in the waterbody.

3.1.4 Autosamplers

Automatic samplers (autosamplers) are battery-operated[11] instruments that collect water samples into either a series of bottles or a single large bottle (Figure 3-4). For event monitoring, samplers are usually installed with a water level or flow instrument which enables the sampler to be 'triggered' (started) when the water level reaches a pre-determined level. Subsequent samples are collected at intervals of fixed time or water volume. Sample collection ends when all bottles are filled or the storm event ceases. Autosamplers can also be triggered manually by staff, either on-site or remotely using telemetry.

Autosamplers typically fill up to 24 sample bottles however, multiple sub-samples can be collected into each bottle to increase the total number of sub-samples collected. The greater the number of sub-samples, the better the representation of the storm event and a more reliable EMC or load (Ma et al. 2009). Further information on using autosamplers for stormwater applications can be found in McCarthy & Harmel (2014) and Gadd et al. (2014a).

[11] Autosamplers can be connected to mains power but this is rarely possible in field situations.

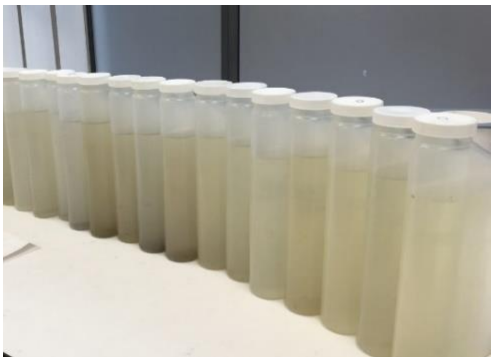

Figure 3-4: ISCO autosampler (left) for collection of multiple water samples (right). [Photos: Christian Hyde]

3.2 Sampling modes

The four sampling methods discussed in Section 3.1 collect samples in differing ways during storm events as illustrated in Figure 3-5.

A. DGTs integrate across an entire event, including the time prior to and following an event if deployed at a site with baseflow.

B. Manual grab samples can be collected at any point during a storm event.

C. Nalgene bottles collect samples on the rising limb only and are dependent on the deployment height and the timing of the rise in water level to that height.

D. Autosamplers are commonly configured in one of two ways for storm event sampling (see ISO 1991):

1. Time-proportional sampling: samples of equal volume are taken at equal time increments.
2. Volume-proportional sampling: samples of equal volume are taken at variable time intervals after a constant volume has passed that sampling point. A composite of samples collected this way provides a flow-weighted average or an EMC. This can also be calculated from the mean of concentrations in samples analysed discretely.

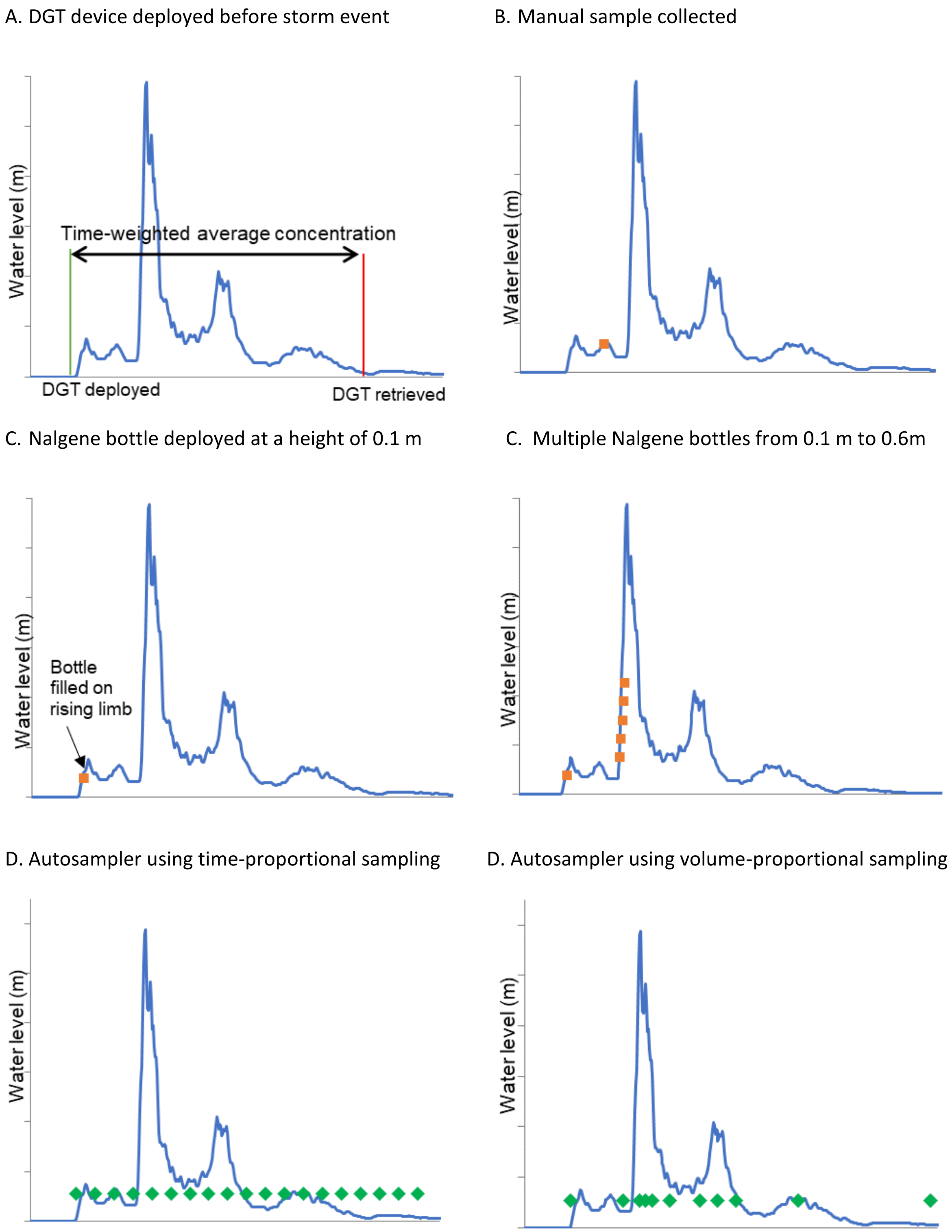

Figure 3-5: Example stream hydrographs indicating example timing of sampling for DGTs, manual grab samples, Nalgene bottles and autosamplers.

3.3 Water quality variables

Table 3-1 lists the water quality variables most commonly measured in urban streams and stormwater, along with two sampling considerations: variability in concentration during storm events and sample storage requirements. In this section, we use the term contaminant to refer to water quality variables of interest. The variability during events of the different contaminants influences the number of samples that should be collected to accurately represent storm event concentrations: more samples need to be collected for highly variable contaminants.

The stability over time of each contaminant also influences the sampling method or device, as some contaminants require analysis within short timeframes. Storage times are of most concern when sampling faecal indicator bacteria (FIB), as bacteria can grow quickly, multiplying at an exponential rate. Guidelines for analysis of FIB usually recommend analysis within 24 hours (APHA 2012) or 36 hours (NEMS 2019). Meeting this guidance is rarely an issue with manual grab sampling, and for autosamplers growth after collection can be reduced by using refrigerated samplers or filling bases with ice. When using Nalgene bottles, collected samples remain *in situ* without cooling until retrieval which increases potential for FIB growth, particularly for stream applications where it is not possible to safely retrieve the bottle until the flow has receded. However, this growth may be minimal, as testing (although limited) showed *E. coli* remain at similar levels in the Nalgene bottles retrieved up to 43 hours after sample collection (see section 5.2.1). This suggests these bottles are suitable for FIB applications, particularly for investigation and screening purposes, but possibly not for compliance with standards. For stormwater applications, it may be possible to place bottles in a location where they can be easily collected before the flow has completely receded, minimising elapsed time from sample collection and minimising FIB growth.

Not all sampling methods are suited to each contaminant (Table 3-1). Manual grab sampling is the only method that is suited to almost all variables, except for contaminants that are highly intermittent and/or at low concentration, such as pesticides, or industrial chemicals associated with spills or inappropriate disposal.

Nalgene bottles can be used for a similar range of contaminants to grab samples and the plastic sample bottle can be replaced by a glass sample bottle where appropriate. However in some cases, as described above, the filled bottles may remain in situ for several hours before being collected (and unlike autosamplers, the bottles cannot be kept cool with ice during that time). For this reason, Nalgene bottles may be of limited use for variables that are expected to change rapidly after collection (Table 3-1). Nalgene bottles can be acid-washed for trace metal analyses but the bottles are not autoclavable for sterilisation.

DGTs can only be used for the contaminants for which they have been designed and tested. Although this list is growing, DGTs are only suitable for dissolved contaminants. Some DGTs are suitable for use in saline environments but others are suitable for freshwater only.

Table 3-1: Contaminants of potential interest in urban waters, factors to consider when selecting a sampling method, and sampling method suitability. Tick indicates method is suitable; cross indicates unsuitable. Letters indicate suitability in some conditions, see table footnotes. CV = coefficient of variation.

	Factors to consider for sampling methods		Sampling method suitability			
Contaminant	**Variability during events**	**Storage requirements [1]**	**Manual grabs**	**Nalgene bottle**	**DGT**	**Auto-sampler**
Suspended sediment	Usually positively correlated with flow, can be variable (CVs frequently 1-2, see Table 2-2),	Best refrigerated and analysed within 48 hours to reduce flocculation or degradation of particles	✓	A	×	✓
Faecal indicator bacteria	Usually positively correlated with flow, highly variable (CVs often >2) especially in streams	Recommend samples chilled immediately and delivered to the laboratory for analysis <24 hours of collection; may be relaxed for some monitoring objectives	✓	✓	×	✓
Total metals	Zinc can display first-flush, can be moderately variable (CVs 0.8-2)	None – samples are stable and can be preserved with acid to pH <2 and stored up to 6 months	✓	✓	E	✓
Dissolved metals	Zinc can display first-flush, copper typically doesn't. Low variability (CVs usually <1)	Water samples should be filtered as soon as possible after collection, ideally within 36 hours. Filtered samples can be preserved with acid to pH <2 and stored up to 6 months	✓	✓	✓	✓
Nitrate-N	Concentrations in streams may decrease during storm flow or may not vary substantially. Moderately variable in stormwater (CV frequently 1-2), less in streams (CV < 1.3)	Best filtered as soon as possible (within 36 hours of collection) then stable for 6 months if frozen, or 48 hours if refrigerated	✓	✓	F	✓
Ammoniacal-N	Concentrations typically low at baseflow but can increase during storm events, particularly in presence of wastewater overflows (CV >1)	Unstable. Best filtered as soon as possible (within 36 hours of collection) then stable for 28 days if preserved with acid, or 48 hours if refrigerated	✓	H	V, F	H
DRP	Can be highly variable for some stormwater discharges (mean CV 2); low-to-moderate variability in streams (CVs <2)	Best filtered as soon as possible (within 36 hours of collection) then stable for 6 months if frozen, or 48 hours if refrigerated	✓	✓	✓	✓
Total N and Total P	Usually positively correlated with flow. TN typically has low variability (CVs < 1), TP moderate variability (CVs 1-2)	Best refrigerated and analysed within 48 hours or stable for 28 days if preserved with acid	✓	✓	×	✓
Petroleum hydrocarbons	May be only intermittently present at measurable concentrations	Should be collected in glass bottles. PAHs are stable, TPH degrades rapidly	G	G	×	G
Pesticides and other organics	May be only intermittently present at measurable concentrations	Should be collected in glass bottles. Many compounds are stable	L	L	D	L

Notes: 1 Information collated from NEMS (2019), AS/NZ 5667.1 and guidance from Hill Laboratories. A: Suspended solids concentrations measured in Nalgene bottles can be much higher than measured with an autosampler (see Section 5.2.3). E: In a typical urban stream, total zinc could be estimated from 1.6x the DGT concentration. This estimate would not be accurate for stormwater, as the ratio of total to dissolved differs between sources. H: Ammoniacal-N is unstable when unpreserved and samples should be analysed promptly after collection. V: DGTs may not be suitable as ammoniacal-N is highly variable in urban waters and high concentrations that occur over very short periods will not be noticeable in time-weighted average concentrations. G: Glass bottles required for these variables. F: Only suitable for freshwater locations. L: Limited suitability for variables that are present intermittently at low concentration. D: Some variables can be measured in DGTs, see dgtresearch.com for details.

3.4 Sampling location

Possible sampling locations in urban areas include piped stormwater networks, open drains, urban streams, lakes, estuaries and near-shore coastal waters (Table 3-2). There are also some distinctive features that may be only found in certain areas, such as pumped stormwater discharges.

Manual grab samples can be collected from essentially any location, though some may require additional equipment such as a sampling pole or even a boat. However other sampling methods are more restrictive (Table 3-2).

Nalgene bottles require a change in water level to fill and are therefore not suited to lakes (when the water level is unlikely to change substantially with rainfall) or to tidal locations (when the water level changes substantially in the absence of rainfall). In smaller pipes, or shallow streams, the bottles may be too tall for collection of water samples except at the highest of flows (intake funnel at 250 mm above base of bottle). In some locations it may be possible to partially bury the bottle to decrease the height to the intake funnel.

As DGTs must always be kept wet, some specialised equipment is required to deploy these in locations that are dry (or have only very low flows) during baseflow such as stormwater networks or ephemeral streams. Not all DGT devices can be used in saline environments, limiting the types of contaminants that can be measured in tidal stream reaches or estuaries. Furthermore, for accurate calculation of the in-water concentrations, DGTs are best deployed in locations where there is a decent flow past the device – such as in the run or riffle section of a stream. In locations where the stream flow is very slow, such as a pool or a tidal reach with backflow, concentrations calculated from DGTs may be less accurate (increased uncertainty of ~20%) and would under-estimate the in-stream metal concentrations [12].

Autosamplers are suitable for many types of locations though equipment may need to be tailor-made for each setting and in some locations a high degree of ingenuity is required. Tidal locations, such as near stream mouths, can be difficult to sample with an autosampler as water level can change due to tide rather than in response to rainfall; time-based sampling may be easier to use in these situations.

Although many of the devices are suitable for different locations, for most monitoring programmes sites should be visited before the sampling method of choice is selected. Characteristics of the site, such as water depth, velocity, tidal fluctuations, and the nature of the stream bed should be assessed during this visit. In particular, for the Nalgene bottles hydrological information is extremely important for determining the deployment height and such data may need to be collected sampling can commence.

[12] Accuracy can be improved by deploying DGTs with differing diffusive gel thickness to provide information on the diffusive boundary layer thickness which is then used in an more accurate calculation of in-stream concentrations.

Table 3-2: Device suitability within different urban sampling locations. Tick indicates device is suitable; cross indicates unsuitable. Letters indicate suitability in some conditions, see table footnotes.

Type		Details / definition	Sampling considerations	Device suitability: Manual grabs	Nalgene	DGT	Auto-sampler
Stormwater outlet		End of a stormwater network pipe, where it discharges into a stream, estuarine or marine receiving environment	Outlet pipe may be inundated from downstream during high stream flows or high tide Outlet may be dry most of the time or may have some baseflow	✓	✓	T	✓
Stormwater piped network		Inside the stormwater network, for example, within a manhole	Pipe may be dry most of the time or may have some baseflow	✓	H	T	✓
Open stormwater channels		Open channel or drain that conveys stormwater	Channel may be dry most of the time or may have some baseflow	✓	H	T	✓
Pumped stormwater discharges		Present in locations with flat topography, often close to estuarine or coastal environments. Stormwater retained behind weir and discharged via a pump station, usually on outgoing tide	Usually a pool upstream of pump, may be dry, or tidal downstream of pump. May be saline downstream of pump	✓	✓	S	✓
Urban streams		Natural waterway, though potentially highly modified	Likely to experience large range in water level May have concreted bottom or sides May be wadeable or may be too deep to wade There may be a tidal influence on water level at downstream locations	✓	✓	✓	✓

Type		Details / definition	Sampling considerations	Device suitability Manual grabs	 Nalgene	 DGT	 Auto-sampler
Ephemeral urban streams		A reach of stream that is dry in most conditions and has flow only during storm events	Rainfall conditions (depth, duration, antecedent conditions) required to generate a flow in the reach	✓	H	T	✓
Urban lake		A natural or man-made lake	Water level unlikely to rise significantly during storm events. Water quality may change slowly. Unlikely to be wadeable.	✓	×	L	A
Estuarine and coastal locations		Tidal streams, harbours and coastal areas adjacent to urban land	Water level change with tide is typically more than change due to rainfall.	✓	×	S, L	A

Notes: **H** = The height of the bottle may be an issue for sampling in these locations. The bottle intake funnel is ~250 mm above the base of the bottle, so the water depth in the pipe or stream must rise to at least 250 mm to collect a sample, precluding collection of first-flush samples. For an ephemeral stream it may be possible to partially bury the bottle to reduce the intake height. **T** = Must be installed in a trough to keep DGTs wet during dry period between deployment and storm event. Trough may not be suitable for cadmium and copper due to potential contamination of DGTs. **S** = Saline sites suitable for metals, metalloids and phosphorus but not nitrate-N or organic contaminants. **L** = Low velocities affect accumulation of contaminants by DGT devices. Concentrations calculated from mass accumulated in DGT may under-estimate true concentrations. Can use multiple DGTs with different diffusive layer thicknesses to assist here. Expert assistance may be required for this. **A** = an autosampler could be placed on a buoy or at end of pier with intake pipe extending into lake or coastal waters. It is unlikely that sampling could be triggered by water level and may need to be triggered manually and on a time-weighted basis, which may or may not be suitable for programme objectives.

3.5 Storm events

The combined effect of differing rain event characteristics, antecedent periods and season necessitates sampling of multiple storm events to get an idea of either the long-term average, or maximum concentrations. The required number of storm events to sample depends on the climate and rainfall distribution, the sampling method used, the variability of the contaminant of interest at that site and the level of precision (or confidence in results) required for the project objectives.

Higher confidence in results is gained when more storm events are monitored, relative to the number of storm events that occur in an average year. For example, 10% uncertainty can be achieved by sampling 50% of the storms in a year, or 20% uncertainty by sampling 20% of the storm events when using the same monitoring methods (Leecaster et al. 2002). Monitoring 20-50% of the storm events is unrealistic in locations like Auckland where there are very frequent rainfall events (110-150 rain days per year) but may be more realistic on the Kapiti Coast or in Canterbury, with lower total rainfall and fewer storm events.

Several researchers and practitioners have suggested that monitoring of 5-8 storms provides data with <20% uncertainty when collecting multiple (>12) samples per event (Leecaster et al. 2002, Maniquiz-Redillas et al. 2013, May & Sivakumar 2013); whereas for Auckland 15-20 storm events were suggested to achieve uncertainties of 5-20% (Fassman 2010). When only single samples are collected in a storm event, a greater number of events must be sampled. For example, when collecting only a single sample per event McCarthy et al. (2018) recommended sampling between 17 and 39 events (depending on the variability of the TSS concentrations in the catchment) to characterise long-term averages of TSS with low uncertainty.

The number of events also depends on the contaminant of interest. Contaminants with lower variability (as demonstrated by the CV, coefficient of variation) require fewer samples to adequately characterise a storm event or long-term average (Lee et al. 2007). Fewer events were required to characterise long-term average concentrations of *E. coli* and TN at 9-15 and 6-17 events respectively (McCarthy et al. 2018), due to their lower variability in the sampled catchments.

We are not aware of any estimates for the number of storms events required for total or dissolved metals. However this could be estimated from the coefficient of variation (CV) of the contaminant concentrations, based on a linear correlation found between CV and required number of events (McCarthy et al. 2018) with the following equation:

$$No. events = 18.3 \times CV - 7.9$$

where *No. events* is the number of events needed to achieve 90% confidence interval width of <1.0 (assuming a single random sample is collected per event) and *CV* is the coefficient of variation of the contaminant.

For dissolved zinc, with a CV of 0.6 in urban stormwater (Table 2-2), the required number of events to achieve a 90% confidence interval of width < 1.0 is at least 3 and for total zinc, with a CV of 0.8, 7 events would be required. For SS, which has a much greater CV (1.4), at least 17 events would be needed; and for *E. coli* (CV 1.9) 27 events would be required to characterise concentrations with high confidence. Note that these estimates are based on collecting single samples per event, so fewer events would be required where more samples are collected.

3.6 Resources

All monitoring programmes have a cost, including for both sampling and analysis stages (The Nalgene bottles have initial costs at approximately $50 per bottle, however if appropriately washed, the bottles can be reused for most contaminants of interest, to reduce on-going costs. DGTs have minimal capital cost but the devices are disposable (approximately $25 each, depending on type and exchange rate) and ideally duplicates or triplicates should be deployed at each site (for reasons explained in section 5.3.1). For both systems, it is preferable to also install some form of water level measurement as well, and a temperature logger is required for the DGTs.

Table 3-3). The capital and consumable costs for manual grab sampling are minimal, though if a large number of samples are to be collected or a large number of events sampled, the resource costs (i.e., labour) could be considerable. In contrast, autosamplers have high capital and installation costs, but in some cases can have lower on-going costs depending on the configuration and needs of the project (e.g., when there is a need to collect multiple samples throughout a storm).

The Nalgene bottles have initial costs at approximately $50 per bottle, however if appropriately washed, the bottles can be reused for most contaminants of interest, to reduce on-going costs. DGTs

have minimal capital cost but the devices are disposable (approximately $25 each, depending on type and exchange rate) and ideally duplicates or triplicates should be deployed at each site (for reasons explained in section 5.3.1). For both systems, it is preferable to also install some form of water level measurement as well, and a temperature logger is required for the DGTs.

Table 3-3: Comparison of device costs for sampling in urban waterways. - indicates negligible or no cost, $ relates to costs ~$100, $$ ~ $1,000, $$$ ~$10,000.

	Device			
	Manual grabs	Nalgene	DGT	Autosampler
Capital costs	-	$	-	$$$
Installation costs including consumables for installation	-	$	$	$$$
Time costs per event	$	$-$$ [a]	$$	$-$$ [a]
Consumable costs per event	$	$-$$ [b]	$	$-$$ [a]
Analytical costs per event	$	$	$$	$

Notes: [a] Depends on whether you need to go twice to the sites to deploy then retrieve samples; or whether subsequent deployments are undertaken at the same time as retrieval. [b] This is the cost for cleaning of bottles between events, depending on the number of bottles and the cleaning required (e.g., acid-washing 24 autosampler bottles for sampling of dissolved metals would have higher cost than washing two Nalgene bottles for sampling of suspended sediment).

For most sampling programmes using Nalgene bottles, DGTs or autosamplers, the site will need to be visited prior to a storm event to deploy (or set-up) the sampling system and after the event to collect the samples. In some cases, depending on the project purposes, replacement Nalgene bottles could be deployed at retrieval; and autosampler bottles can be replaced to reduce costs. This approach is not practical for the DGTs as they begin to absorb contaminants as soon as deployed.

Analytical costs will vary depending on the contaminant of interest, from as little as $10 per sample to over $200 for a suite of organic contaminants. Analyses of DGTs have additional costs compared to water samples due to the specialised sample preparation steps of opening the samplers and extracting the gels within a clean environment. Depending on the monitoring objective, analysis of replicate samples and blanks also need to be budgeted for.

For almost all project objectives, multiple storm events will need to be monitored. The overall costs of the sampling therefore depend on the balance between initial costs and on-going costs on an event-basis. Although some sampling methods, particularly manual grab sampling appear to be substantially cheaper, this cost needs to be weighed up against how well the data collected represent mean or maximum contaminant concentrations for contaminants that vary considerably, as detailed in sections 2.2.2 to 2.2.4.

3.7 Additional considerations

Some additional considerations for each sampling method are included in Table 3-4.

Table 3-4: Storm event sampling methods compared for additional important factors.

Factor	Manual grab sampling	Nalgene bottles	DGTs	Automatic sampling
Health and safety	May be hazardous to be on-site at some locations or during some events (e.g., at night)	Requires water entry to deploy and retrieve samplers. Ideally deployed where bottles can be removed soon after event	Requires water entry to deploy and retrieve samplers.	No hazards in sampling during events
Likelihood for vandalism	None	Potentially subject to vandalism depending on location as installed above water	Low likelihood of vandalism as usually installed underwater	High – secure housing required to prevent vandalism
Sampling at multiple locations	Difficult to obtain samples at multiple sites at the same time without large team of personnel	Suitable as can be deployed prior to event	Suitable as can be deployed prior to event	High instrument & installation costs, less feasible for multiple locations
Ability to capture first-flush	High probability of missing first-flush as staff may not be on-site quickly enough	Good, if bottle installed at appropriate height	Captured but integrated into time-weighted average	Samples can be collected very close to commencement of runoff flow
Ability to collect representative samples	Difficulty in obtaining representative samples throughout event. Can collect multiple samples throughout event if needed	Ability to take multiple samples at different water levels throughout a flow event but only on rising limb	Provides an average across event, highly representative of event	Ability to take multiple samples throughout a flow event, samples can be collected in multiple bottles for discrete analysis or composited
Laboratory analyses	Water samples can be analysed by most laboratories	Water samples can be analysed by most laboratories	DGTs require specialised extraction and digestion methods; currently only 2 laboratories with analysis capability	Water samples can be analysed by most laboratories
Suitability for difficult contaminants (i.e., unstable or those that adhere to bottle)	Fine as appropriate bottles can be used for each, samples sent straight away	Glass bottles can be used but samples remain unpreserved in situ until collected	Suitable for specified contaminants only, though the range is increasing. May need multiple DGTs at each site, specific for each different contaminant	Glass bottles can be used but samples generally remain unpreserved in situ until collected
Suitability for extreme events	Manual sampling may be unsafe and/or extremely difficult at high flows	Potential to be washed away; in streams flow must recede prior to retrieval	Potential to be washed away; in streams flow must recede prior to retrieval	Good but may be difficult to predict appropriate sampling scheme and therefore require replacement sample bottles during extreme events. Care needed to ensure sampler located above flood level
Suitability for baseflow sampling	Yes	No	Yes	Yes

4 Selecting the sampling methods

In this chapter we provide guidance for determining which sampling method would be suitable for four common monitoring objectives.

4.1 Introduction

There is no single best sampling method suitable for all circumstances for monitoring of urban stream and stormwaters. The most appropriate method depends on the project objectives, the type of data required to meet that objective, the water quality variables of interest and the specific locations for sampling and even then, a range of methods are likely to be available. The methods providing the most accurate data for characterising water quality are also typically the most resource intensive. Because storm event sampling is time-consuming and costly, there is a trade-off for all projects between the required level of confidence in the data obtained and the resources available. Figure 4-1 outlines the general process for determining the suitable sampling method for urban water projects, and indicates (in green) which of the steps are described in this document.

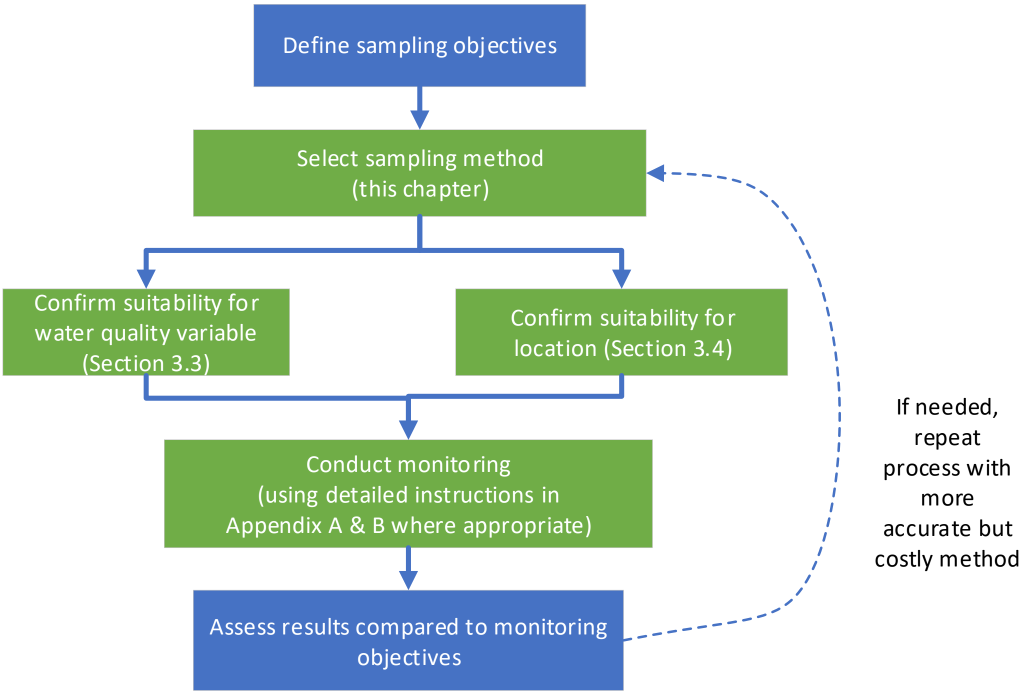

Figure 4-1: General process for determining sampling methods for urban waters. Boxes shown in green are covered in this guidance.

The following schematics (Figure 4-2 to Figure 4-4) outline the suitability of sampling methods based on four common sampling objectives. For each objective, different sampling methods are presented graphically in a layout that represents their suitability for providing data that accurately represents the sampling event. Commentary within each section discusses the limitations and advantages of each method. The four monitoring objectives are as follows:

1. Objective 1: Compare water quality to guidelines, standards or limits based on mean or median concentration.
2. Objective 2: Compare water quality to guidelines, standards or limits based on maximum concentration.
3. Objective 3: Compare contaminant concentrations between multiple locations, within a single stream or catchment, or between catchments.
4. Objective 4: Measure EMC or event-based mass loads at one or more locations within a catchment or in separate catchments.

4.2 Objective 1: Compare water quality to guidelines based on mean/median concentration.

This section outlines possible sampling methods for objectives that require comparison of stream or stormwater quality to water quality guidelines or standards that are based on a mean or median concentration during an event or multiple events[13]. This may be relevant to a single location or to multiple locations. Examples of situations where this objective would apply are:

- Christchurch City Council's (CCC) Environmental monitoring programme for their Comprehensive Stormwater Network Discharge Consent for Otautahi/Christchurch City and Te Pataka o Rakaihautu/Banks Peninsula requires wet weather monitoring at 26 stream locations for water quality variables including metals, and comparison of these concentrations to ANZ water quality guidelines (ANZG 2019) and Land and Water Regional Plan standards.
- Greater Wellington Regional council wish to assess whether zinc concentrations in any of the urban streams exceed ANZ water quality guidelines during storm events and have potential to cause toxicity.
- An industrial site needs to assess compliance with a consent condition specifying a mean TSS concentration of 50 mg/L in the stormwater discharge.
- An industrial site needs to assess compliance with a consent condition specifying a mean total nitrogen concentration of 1 mg/L in the creek downstream of the point of stormwater discharge.

The key consideration for this objective is that the samples collected adequately represent the *entire* storm event. Samples should be collected throughout an event, rather than only at key points in the event (e.g., first-flush, peak and recession, rather than only first-flush).

[13] Note that this differs from the objective of calculating a median to compare to a NPS-FM National Objectives Framework (NOF) attribute; the latter requires a *long-term* median from sampling over a long duration, including at baseflow.

Figure 4-2 illustrates that DGTs and autosamplers are the most appropriate sampling methods for objective 1 (as shown by their location to the right in the figure) because these methods either integrate the concentrations or collect multiple samples across the entire event. Of these two methods, autosamplers have higher cost than DGTs, particularly where multiple locations are to be monitored.

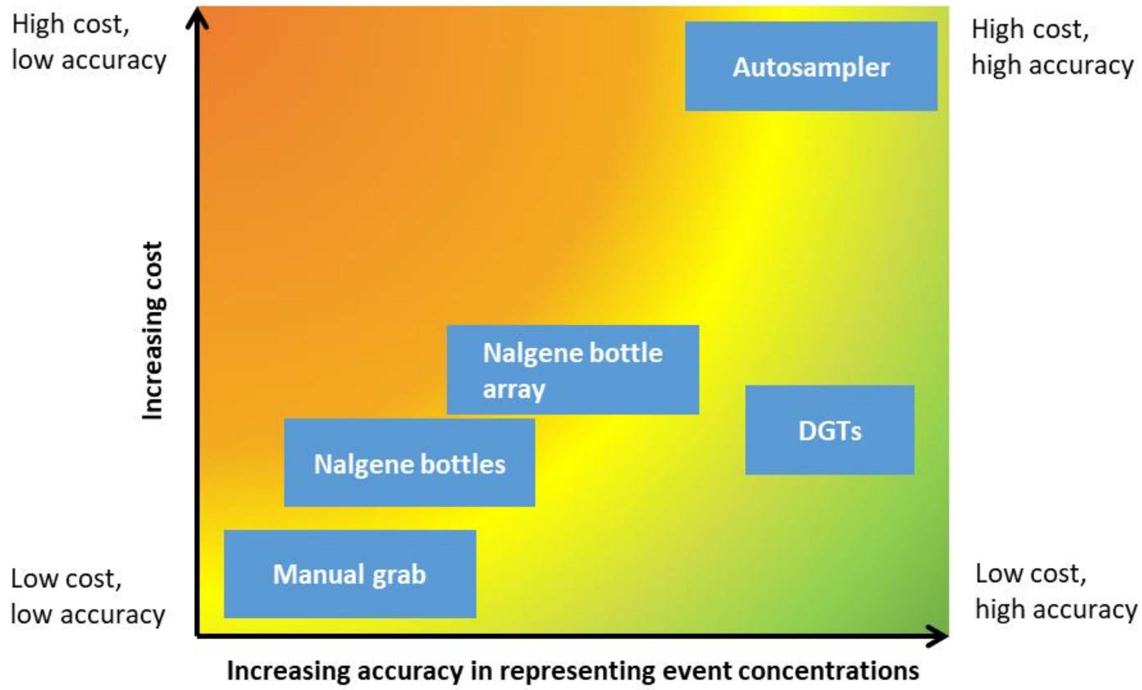

Figure 4-2: Matrix of sampling method suitability for Objective 1: Compare water quality to concentration-based guidelines, standards or limits based on mean/median values. .

DGTs provide a time-weighted average concentration that accurately represents the concentrations during the period of deployment. As they accumulate contaminants as soon as deployed, to measure event concentrations DGTs are best deployed and removed as close to the event start and end as feasible. The DGT concentration is suitable for comparing to an "average" limit where dissolved concentrations are of interest. For metals, DGTs measure the "labile" component, which more closely reflects the bioavailable concentrations (but may not include all dissolved metals) and is suitable for comparing to water quality guidelines for toxicity. DGTs are available for measuring a range of key water quality variables, all of which are dissolved contaminants. Other sampling methods are therefore required for indicator bacteria and sediment, or sediment-associated contaminants.

Autosamplers will provide a good representation of either mean or median concentrations as they can collect multiple samples throughout an entire event. Median (or mean) concentrations will be accurately represented as long as the samplers are programmed to collect sufficient samples (e.g., > 20) and the samples are well-spaced throughout the event. Autosamplers can be programmed to collect either time-based or flow-based samples to allow measurement of either time-weighted average or EMCs. Costs of analyses can be reduced by compositing samples prior to analysis and if samples are collected by flow-weighted sampling, this will provide an EMC.

A manual grab sample or single Nalgene bottle is generally unsuitable for this objective because a single sample will not provide a good indication of the mean or median concentration throughout an event. Manual grab samples could be used for initial screening for contaminants with low variability in storm events such as nitrate-N in some locations. Nalgene bottles may be suitable for flashy catchments or with large distances to the sites of interest but again, are suitable only for initial screening for contaminants with low variability. Because the bottles are filled on the rising limb of an event, samples could over-estimate the event mean concentrations of many contaminants (and under-estimate concentrations of contaminants that decrease with flow).

Multiple grab samples or Nalgene bottles collected during an event would provide better representation of the event if samples are well-spaced throughout the whole event. Note that this can be difficult to achieve with Nalgene bottles even when placed at increasing heights above the baseflow: if the flow rises very rapidly at the start of the storm event, all bottles may fill within a few minutes and this is outside the control of the sampling team. As Nalgene bottles do not collect on the falling limb of a storm, or during any peaks subsequent to initial peaks that filled the bottles, samples do not represent the full event mean or median and will over-estimate the event mean concentrations of many contaminants. Collecting multiple manual grab samples requires personnel to be on site for many hours, potentially outside normal working hours and can add significant cost.

For this objective, multiple storm events should be sampled, including a range of different event durations, rainfall depths and intensities and antecedent conditions. The number of events depends on the variability of the contaminant of interest (see Table 2-2) and may range from 3 to >10. When high confidence in the results is required, a larger number of events should be sampled (e.g., >8).

Hypothetical example of sampling for this objective

As a condition of their global stormwater consent, Christchurch City Council (CCC) need to undertake wet weather monitoring twice per year for multiple contaminants, including TSS, nutrients, metals and bacteria. Monitoring is rotated every 5 years around 5 major river catchments, each with 2 to 9 sampling locations for water quality. Samples must be collected after >3 mm rainfall occurs. Due to the large number of sites, and the low number of events required, autosamplers were not considered feasible. As there is a wide variety of contaminants to analyse, DGTs are not feasible. Nalgene bottle arrays were selected as the sampling method of choice.

Nalgene bottle arrays were deployed at the 9 sites prior to a forecast rain event. Bottles were deployed at heights just above the baseflow water level, to an estimated peak water level (based on hydrological data from one site in the catchment). Samples were collected during an overnight rainfall event of 6 mm.

At each site, the collected samples were combined to provide a composite across the rainfall event. Samples were then divided and transferred into the appropriate bottles for analysis and transported to the laboratory. The data obtained was then compared to the water quality guidelines specified in the consent.

4.3 Objective 2: Compare to water quality guideline or standard based on maximum concentration

This section outlines possible sampling methods for objectives that require comparison of stream or stormwater quality to water quality guidelines, standards or limits based on a maximum concentration. Examples of situations where this objective might apply include:

- Auckland Council wants to assess whether dissolved zinc concentrations in urban streams are below the US EPA acute criteria during storm events.

- NZTA needs to assess compliance with a consent condition of a maximum of 100 mg/L of TSS in the stormwater discharge during motorway construction.
- An industrial site has a consent limit of 1 mg/L of TN in their stormwater discharge.
- Invercargill City Council has a consent condition requiring further investigation if ammoniacal-N concentrations in a stream exceeds 1 mg/L.

The key sampling consideration for this objective is to ensure that *multiple discrete samples* are collected during the event. At a minimum this should include the first-flush (meaning here the initial part of the storm event, usually within the first 1-2 hours of rainfall) and the peak flow, as some contaminants typically demonstrate maxima during first-flush and others during flow peaks (see Section 2.2.3). However, in reality, event maximum concentrations have been observed at most points in a hydrograph, including during the flow recession. The more samples collected the better in order to detect this maximum. Samples can't be composited for the analysis of maximum concentrations and so methods that average across time (such as DGTs) are also not suitable for this objective.

Figure 4-3 indicates that a Nalgene bottle array and autosamplers are the most appropriate sampling methods for objective 2 as both enable multiple discrete samples to be collected during the event, which increases the likelihood of capturing the maximum concentration.

Multiple Nalgene bottles can be deployed to collect multiple discrete samples during an event. Bottles should be deployed at heights that would collect, at a minimum, the first-flush and peak flow. This is best achieved by deploying at multiple heights (i.e., more than 2) as it is difficult to predict a peak water level for a forecast flow event. For this objective, it is best to install a water level instrument (such as a pressure transducer) as well to provide information on the stream hydrograph.

Autosamplers have higher costs associated with them, primarily for installation of the sampler and water level instruments required. Autosamplers should provide a good representation of either maximum concentrations when programmed to collect sufficient samples (e.g., > 15) and when samples are collected discretely, rather than as composites.

For both methods, costs can be reduced by selecting only some samples for laboratory analysis. For TSS, collected samples can be examined visually to determine which should be analysed. For other contaminants, the water level information can be examined to determine which samples represent first-flush and which represent peak flow. However, for initial storm events, it may be safest to analyse most or all of the collected samples until contaminant dynamics are understood.

Single manual grab samples and Nalgene bottles are generally not recommended as it is very easy to miss the peak flow or maximum concentration when collecting a single sample. DGTs are also not suited to capturing maximum concentrations as they provide a time-weighted average concentration for the period of deployment which will under-estimate the maximum concentration.

Multiple storm events should be monitored to determine the maximum across events. The number of events depends on the desired reliability, and on the variability of contaminants of interest, but should be around 5 to 10. More events may be required when using the Nalgene bottle array because in some events where flow rises rapidly samples are collected over a very small period of time (e.g., within minutes). Sampling worst-case storm events would reduce the required number of events, and sampling should target storm events after a long dry period; very large storm events; and short-duration high intensity events.

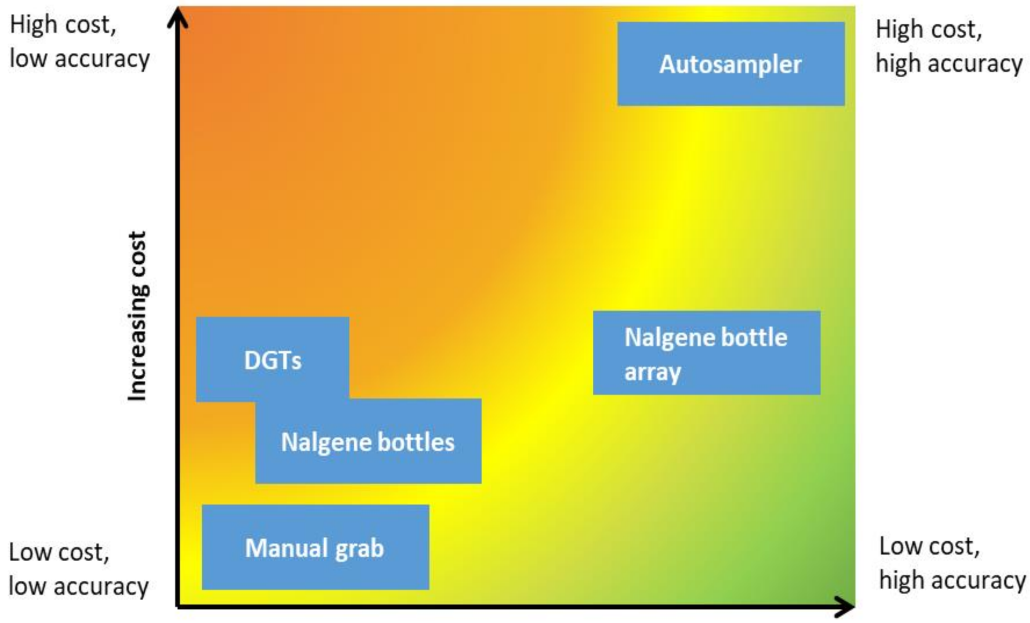

Figure 4-3: Matrix of sampling method suitability for Objective 2: Compare to guidelines, standards or limits based on maximum concentration. .

> **Hypothetical example of sampling for this objective**
>
> An industry's consent for stormwater discharges from its site requires sampling four times per year for the first year to assess compliance with a condition of "no more than 100 mg/L of TSS in the discharge". There are three discharge points from the site to be sampled and the operators do not wish to use autosamplers due to the cost of installation and hire. DGTs are not appropriate for assessing maximum concentrations, manual grab sampling is not suitable for after-hours events and collection of a single sample is not acceptable to the regulatory authority. Nalgene bottle arrays are selected as the sampling method of choice to provide multiple samples.
>
> Prior to a forecast storm event >20 mm, they installed four Nalgene bottles at each of the stormwater outlets. More than four bottles are not necessary at these sites due to the size of the discharges and would block the pipe outlets. The bottles were deployed at increasing heights from immediately above the base of the pipe, up to the top of the pipe.
>
> At two of the sites all four bottles filled and at the third site only three bottles filled. All bottles were inspected visually and either one or two bottles for each site were sent for TSS analysis. The maximum TSS concentrations reported for each site was compared to the consent condition to assess compliance and showed non-compliance at one location. The upstream catchment was investigated and a source of sediment input identified.

4.4 Objective 3: Compare concentrations between multiple locations

This section outlines possible sampling methods for objectives that require comparison of contaminant concentrations between different locations such as upstream and downstream of a discharge or tributary; at multiple sites within a single catchment; or multiple sites in separate catchments. Examples of situations where this objective might apply include:

- Greater Wellington Regional Council wish to collect information on water quality within the Hutt River and Wellington Harbour catchment to support Regional Plan-related processes.
- Auckland Council wishes to compare nitrate-N concentrations predicted from a water quality model with those measured in the Waitemata Harbour catchment to verify the model's outputs.
- Environment Canterbury wish to determine the major sources of *E. coli* within the Heathcote River catchment.
- A consent holder needs to assess whether a stormwater treatment wetland is removing 75% of contaminants.
- Otago Regional Council wishes to assess the success of water sensitive urban design (WSUD) methods applied in a new subdivision near Lake Wanaka by comparing to a subdivision without WSUD methods.

The key consideration for this objective is that data are *comparable between sites*. The *relativity* of contaminant concentrations between sites is of more importance than the absolute concentration across a storm event. This means that the sampling does not have to reflect the entire storm event as long as either 1) the same point on the hydrograph is being sampled, or 2) sufficient samples are collected to represent a comparable period of the storm hydrograph. For upstream / downstream studies (e.g., inlet and outlet of a stormwater retention pond; or upstream and downstream of a discharge), it may be possible to collect samples at a very similar point in the hydrograph. However, for sites that vary in size and location (e.g., comparing multiple different tributaries to a stream or locations in different catchments) it is probably unclear what points in a hydrograph are comparable and more samples would be required (e.g., to ensure the majority of the event is sampled).

Figure 4-4 illustrates that Nalgene bottle arrays, DGTs and autosamplers are appropriate sampling methods for objective 3; each of these methods enables either many samples to be collected or a mean concentration to be determined across the event.

DGTs are ideally suited to comparing between sites as they provide an average across the deployment period and so avoid issues associated with only capturing parts of the hydrograph. In most cases, data collected using DGTs will be entirely comparable provided the deployment periods do not differ substantially. However, DGT copper concentrations are highly influenced by water characteristics, including dissolved organic carbon (DOC). Where DOC concentrations vary between sites, DGT copper would not be a suitable indicator of all dissolved copper, reflecting the labile copper only. This is primarily a concern in organic-rich streams, and DGTs are likely to be suitable for comparing between most stormwater sources.

Autosamplers would provide a good comparison between sites, where sites are sampled comparatively with many samples collected across the hydrograph. Samples can be composited to reduce the costs of analysis and samples can be analysed for most contaminants. However, there is a high cost involved in installing autosamplers, particularly for studies sampling many locations.

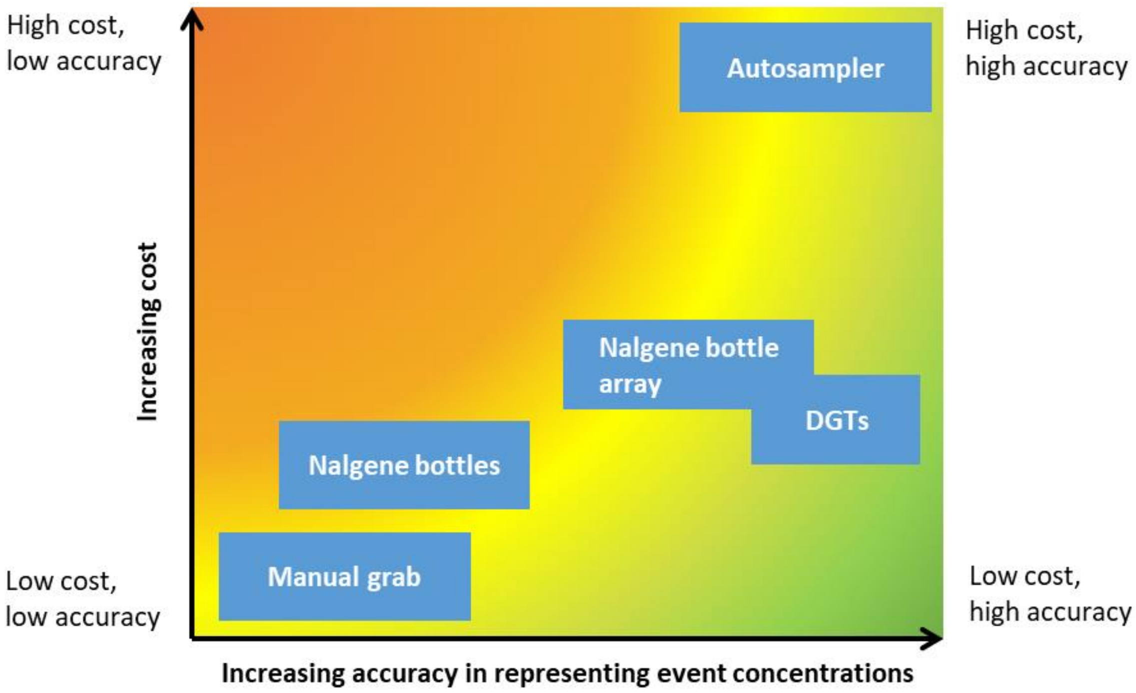

Figure 4-4: Matrix of sampling method suitability for Objective 3: Comparing concentrations measured at multiple locations.

Manual grab samples are not recommended because it is very difficult to ensure that samples are collected at the same point on the hydrograph and are therefore comparable across sites, as required for this objective. Manual grab samples are only suitable for initial screening of contaminants with low variability throughout a storm event (e.g., nitrate-N) and where large differences are expected between locations.

Single Nalgene sampling bottles could be used in upstream / downstream studies where these can be deployed to sample at the same point on the hydrograph (e.g., both deployed at 30 mm above stream baseflow in locations upstream and downstream of a stormwater outlet). This arrangement depends on equivalent stream channel widths at each location. Where stream channel width, or inlet and outlet pipes differ in their geometry, it would be more difficult (though not impossible) to determine the water level at each site that equates to an identical change in flow.

Multiple storm events should be sampled. The exact number of events required will depend on the specific objective. For building or validating a water quality model, a limited number of events may be sufficient. For assessing contaminant sources, a larger number of events with differing characteristics may be required as some sources may be more prevalent during different events. Sampling to assess the effectiveness of stormwater treatment systems should be undertaken over multiple events, including both large and small events, as treatment performance can differ with event size and duration. When sampling at many locations in separate catchments, differences in rainfall intensity between catchments may affect the contaminant concentrations, as well as the land use in the upstream catchment and other influences and therefore a larger number of events may need to be sampled.

Hypothetical example of sampling for this objective

Greater Wellington Regional Council (GWRC) has modelled water quality in Te Awarua-o-Porirua Harbour catchment as part of their work to implement the NPS-FM. The modelling includes sediment, nutrients, metals and bacteria as all are key contaminants for freshwater and for the downstream harbour. The model was developed from limited monitoring data and they wish to assess whether the predictions are realistic.

Because of the large number of sites, autosamplers are not suitable. DGTs can be used for the dissolved metals and nutrients but requirement for sediment and bacteria data necessitates using Nalgene bottles as well.

Prior to a forecast storm event of >20 mm, GWRC installed DGTs for metals, phosphorus and nitrate-N and 3 Nalgene bottles at 12 locations across the catchment, mainly near steam mouths. The bottles were deployed at increasing heights from 30 mm above the baseflow water level to 150 mm above baseflow. Temperature loggers were included at two locations and water level loggers at six. Samples collected with the Nalgene bottles were analysed as discrete samples. The hydrological data were inspected to assess whether bottles were comparable.

The concentrations of metals, nitrate-N and phosphorus from the DGTs were compared to the equivalent concentrations predicted from the model, with the emphasis on the relative difference between sites using each method. The TSS and bacteria concentrations from the Nalgene bottles were compared between sites and to the model predictions, with the focus on identifying large discrepancies between the two methods.

4.5 Objective 4: Measure EMCs or event-based mass loads at one or more locations.

This section outlines possible sampling methods for objectives that require assessment of event mean concentrations (EMCs) or loads, in one or more different locations, which may be within a catchment or in separate catchments. Examples of situations where this objective might apply include:

- Auckland Council wish to assess sources of key contaminants into the Tamaki Estuary, a location with degraded sediment quality and ecological health.
- Environment Southland wish to determine major sources of contaminants to the New River Estuary as part of studies for NPS-FM implementation.
- Christchurch City Council wish to estimate catchment copper and zinc loads at multiple locations to compare against the equivalent loads calculated in the application for their Comprehensive Stormwater Network Discharge Consent.
- Hawke's Bay Regional Council needs to estimate DRP loads from Havelock North township to compare to a catchment limit calculated to ensure DRP concentrations in Karamu Stream meet water quality objectives.

The key considerations for this objective are that the samples collected adequately represent the *entire* storm event *and hydrological data* are collected. Therefore, sampling methods that enable multiple samples to be collected will provide more confidence in the data than those that collect only a few samples (Figure 4-5). Furthermore, samples should be collected throughout an event, rather than only at key points in the event (e.g., first-flush, peak and recession, rather than only first-flush).

Hydrological data are important because load is the product of concentration and volume. Flows in urban water systems can change rapidly and vary by 1000x or more. Accurate measurement of flows is essential for studies seeking to accurately quantify contaminant loads discharged to receiving waterbodies, however for other studies an estimate of flow or volume may be sufficient. Flow measurement may require some form of water level control (such as a weir) along with measurement of change in stage height (water level); or an ultrasonic flow meter which measures velocity and stage (e.g., water level is easier to measure with a pressure transducer).

Figure 4-5 illustrates that autosamplers are the best sampling method for objective 4, with Nalgene bottle arrays and DGTs acceptable under some circumstances. Autosamplers, when used in combination with water level instrumentation, can be programmed to collect flow-weighted samples which can be readily composited to provide an EMC, and used with hydrological data to calculate loads. A wide variety of contaminants can be measured in the water samples, therefore enabling load calculations for multiple contaminants of interest.

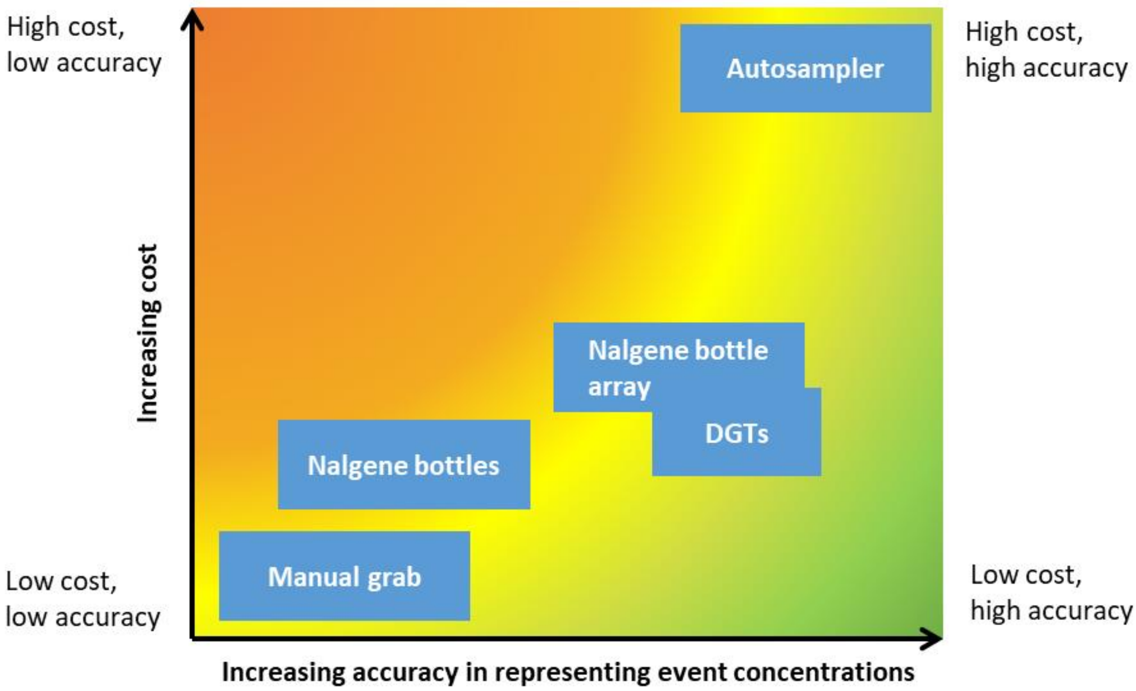

Figure 4-5: Matrix of sampling method suitability for Objective 4: Measuring EMCs or loads at one or more locations.

Multiple grab samples or multiple Nalgene bottles collected during an event could provide good representation of the event provided samples are well-spaced throughout the event (from the initial rise to peak water level). As noted previously, it can be difficult to achieve such spacing during some (especially large) storm events. As Nalgene bottles collect samples on the rising limb only, this method would over-estimate the EMC for most contaminants. A load based on sampling with Nalgene bottles could be calculated from the volume during that part of the event. This would under-estimate the total *event* load, but this may be sufficient information in some cases (e.g., if a load estimated this way exceeds a limit, this could trigger installation of an autosampler for further sampling or investigations within the upstream catchment).

DGTs provide a *time-weighted* average concentration, not a flow-weighted concentration which is needed for calculating loads. However, in practise, there is often only a minor difference between flow-weighted and time-weighted concentrations. DGTs would be accurate for nitrate-N and phosphorus but measure only labile metals and would therefore under-estimate the dissolved load for some metals (e.g., copper). If the objective is to compare loads between locations, then using a time-weighted average, combined with an estimate of water flow, may be satisfactory – at least for initial screening and for *comparing* loads between sub-catchments rather than for calculating an absolute load.

As suspended sediment concentrations during trials of Nalgene bottles were frequently very high and well above samples collected with an autosampler (see section 5.2.3) if calculation of sediment loads is the primary objective, an alternative approach is recommended – such as using a turbidity sensor to continuously monitor turbidity, coupled with sampling using an autosampler to develop a relationship between suspended sediment and turbidity (see www.nems.org.nz for detailed guidance). This approach obviously incurs additional instrumentation costs.

Manual grab samples or single Nalgene bottles are generally not recommended for this objective as a single sample does not provide a good indication of the EMC. If a very large number of storm events are sampled, the data may approximate the long-term site mean concentration from which a load can be calculated – however this may require sampling more than 30 events for TSS (fewer for other contaminants). Nalgene bottles collect samples on the rising limb so may over-estimate long-term averages for many contaminants (and under-estimate concentrations of contaminants that decrease with flow) and therefore also over-estimate the load.

Multiple storm events should be monitored to determine EMCs or loads. The number of events depends on the required confidence in the results and the specific objective. Greater reliability is required when comparing to a catchment limit or to calculate loads entering a downstream receiving environment such as an estuary, as the *absolute* load is of importance – and at least 8 to 12 events are recommended. Similarly, more events would be required to determine metrics such as a long-term median EMC or annual contaminant load. Fewer events may be acceptable when the specific objective relates to comparing between locations and the *relativity* of loads is more important than the absolute load. Even in this case, at least 3 and ideally 5 events would be monitored because the relative loads at each location / from each catchment may differ between events due to differences in rainfall or catchment characteristics. More events may need to be targeted when using the Nalgene bottle array, as samples are collected over a very short time period (e.g., within minutes) during events where flow rises rapidly (i.e., the data from this sampling may have limited use).

Hypothetical example of sampling for this objective

Environment Southland (ES) wish to identify the major sources of nitrate-N into the New River Estuary, which is rapidly degrading and showing signs of eutrophication. The upstream catchment includes urban and rural streams. The rural streams are regularly monitored, however data are lacking for the urban streams, especially during wet weather events.

Because of the large number of sites, autosamplers are not suitable. DGTs can be used for nitrate-N and are therefore the sampling method selected for this objective.

Prior to a forecast storm event >10 mm, ES installed DGTs at eight locations including five key urban streams. DGTs were installed underwater near the mouths of the streams, upstream of saline areas (as nitrate-N DGTs are not suitable for monitoring saline waters) and above water at the three major stormwater outlets that discharge directly to the estuary. Ultra-sonic doppler flow recorders were installed in each stream and water level recorders installed at each stormwater outlet. Temperature loggers were only included at one stream and one stormwater location as all sites are very close together and drain catchments with similar rainfall characteristics.

The concentrations of nitrate-N from the DGTs was multiplied by the total storm event volume, as calculated for each site from the flow or water level data, to estimate loads. This indicated that the loads from stormwater outlets was minor compared to the streams. The sampling was repeated again for a storm of 26 mm with the same outcome.

PART 2: PROJECT SAMPLING TRIALS

5 Phase 1 sampling device trials

This chapter summarises the results of the first phase of the project, where five different sampling devices were deployed alongside autosamplers to assess their comparability in measuring storm event concentrations of selected water quality variables. The methods used in trialling the devices are described in Section 5.1 and the results are presented and discussed in Sections 5.2 to 5.4.

5.1 Field, laboratory and data analysis methods

5.1.1 Introduction

This section outlines the two sites where the majority of the testing was conducted; the sampling methods used; laboratory methods to prepare and analyse samples, and the data analysis methods. The testing was run alongside existing monitoring projects to maximise the number of storm events during which the sampling methods could be tested. Table 5-1 summarises the testing conducted in Phase 1.

Table 5-1: Sampling methods tested.

Device	Sampling method	Contaminant
Nalgene Storm Water Sampler bottles (Nalgene bottles)	Grab sample, total or dissolved contaminants	Suspended solids, indicator bacteria, nutrients and metals
Siphon sampler bottles	Grab sample, total or dissolved contaminants	Suspended solids, indicator bacteria, nutrients and metals
DGTs	Integrating, time-weighted average labile concentrations	Cadmium, copper, nickel, lead and zinc; phosphate, nitrate-N and ammonium
Chemcatcher for metals	Integrating, time-weighted average concentrations	Cadmium, copper, nickel, lead and zinc
SorbiCell	Integrating, flow-weighted average dissolved concentrations	Cadmium, copper, nickel, lead and zinc; nitrate-N + nitrite-N (NOx-N), dissolved phosphorus

5.1.2 Test sampling sites

The devices were tested at two primary locations: a stormwater outlet and an urban stream, both located in west Auckland. These sites were selected as they both had autosamplers already installed and being used for other projects, enabling comparison with the DGTs and Nalgene bottles. A stormwater site at Timothy Place in Auckland was used for additional testing.

Akatea Road stormwater site

The Akatea Road stormwater outlet (Figure 5-1) receives stormwater from an 8.9 ha catchment with industrial land use. The monitoring site was located at the outlet which was configured with a temporary plywood weir to control water level. During normal conditions there is little or no flow through the outlet, however during moderate to large storm events, the flow can be over 100 L/s.

Figure 5-1: Location of Akatea Road stormwater monitoring site and image of stormwater outlet.

Whau Creek site

The Whau Creek is an urban stream in west Auckland which drains into the Whau River estuary. The monitoring site was located immediately upstream of Blockhouse Bay Road (Figure 5-2) and has an upstream catchment of 470 ha at this point. The catchment land use is low to medium density residential. The stream is typical of low gradient urban streams in Auckland City that are primarily fed by stormwater, with rapid response to rainfall. The baseflow is approximately 10-20 L/s, with peak flows over 1,000 L/s during storm events (NIWA, unpublished data).

Figure 5-2: Location of Whau Creek at Blockhouse Bay Road stream monitoring site and image of stream.

5.1.3 Field methods

Water level control and instrumentation

The two sites were already set-up for flow measurement and recording. Both had a weir[14] with an upstream water level measurement instrument consisting of a stilling well with float and

[14] The Whau Creek site is part of Auckland Council's hydrometric network.

counterweight-driven Hydrologger, programmed to calculate instantaneous discharge from the water level. This allowed the collection of flow-proportional water samples using ISCO 3700 automatic samplers. The intake to the sampler at the Akatea Road site was located near the exit point from the stormwater pipe outlet so as to collect samples at a point of relatively high-velocity, well-mixed flow. The intake to the sampler in the Whau Creek was located on the true left bank, adjacent to the water level intake pipe. Water temperature was continuously measured at each site.

Automatic sampler

Water samples were collected at each site using the automatic sampler on a volume-proportional basis with sampling intervals determined based on the forecasted rainfall duration and depth. At each sampling interval, approximately 1 L of water was collected from the stream or stormwater channel. Acid-washed polyethylene bottles were used in order to avoid the potential contamination of samples by metals associated with the use of glass (Batley 1989) and reduce adsorption of metals contained in the water to the sample bottles. Clean bottles were transported to the site capped and gloves worn when placing in the autosampler and removing the lids.

Water samples were collected on conclusion of each sampling event, usually within 24 hours (36 hours maximum) of the first samples being collected. To minimise the time between collection of the first water sample and (time-sensitive) analysis of faecal indicator bacteria, water samples were sub-sampled while on site and placed into a small chilly bin and delivered directly to a nearby laboratory for testing.

Nalgene bottles

Mounting units for the Nalgene bottles were constructed and installed at both sites. At the Whau Creek site, a timber mounting unit was designed with space for up to eight bottles to be mounted at increasing heights, allowing multiple samples to be taken during a single storm event. At the Akatea stormwater site, the stainless steel mounting unit had space for up to three bottles only. The bottles were mounted onto the unit using cable ties, all at the same height as the water level that triggers the autosampler. Gloves were worn at all times when handling the bottles to minimise possible sample contamination.

Following the storm event, the bottles were retrieved from the mounting unit, the funnel intake system removed, bottles capped and placed into a chilly bin with cooling blocks for transport to the laboratory.

Though designated for single-use purposes, we found that the Nalgene bottles performed well over multiple events and cross-contamination could be minimised if all parts were thoroughly washed in between uses in a lab-grade dishwasher (and acid-washed if sampling for metal analysis, with the exception of the rubber seal).

Figure 5-3: Mounting equipment for Nalgene sampling bottles at Whau Creek site (left) and Akatea Road site (right).

DGT sampling device

DGTs for metals (product code LSNM-NP) were purchased from DGT Research, United Kingdom[15]. DGTs for nutrients (nitrate-N, ammoniacal-N and DRP) were supplied by University of South Australia.

For the stream site, the DGTs were deployed in an acrylic plastic holder mounted at a water depth that ensured they remained submerged at all times (Figure 5-4 left). The holder was mounted so that the membrane surface of the DGTs was vertical, to minimise sediment deposition on the membrane, which could affect contaminant uptake rates (British Standard 2011); and in line with the direction of stream flow to ensure optimal water flow past the face of the DGT.

Figure 5-4: Holders for DGTs for monitoring of stream water (left) and stormwater (right).

Although the stormwater monitoring site had a permanent body of water, and DGTs could be maintained wet in that water during the deployment, the intention was to test these as if the pipe was dry during baseflow. The DGTs were deployed in a custom-designed and made housing (or trough, Figure 5-4 right) that sat above the water's surface during dry weather flow and was inundated at storm flows. The DGTs were mounted vertically in this trough to minimise sediment deposition on the membrane, which could affect contaminant uptake rates. To ensure that the DGTs remained wet prior to the water level rising to inundate the trough, the DGTs were covered with a weak electrolyte solution (0.01M NaCl). All equipment used in the troughs, to attach the DGTs or to attach the trough was either stainless steel or acid-washed plastic. DGTs were deployed prior to a

[15] DGTresearch.com

storm event, but as close as possible to its commencement. DGTs were deployed in triplicate to gauge measurement precision. All DGTs were transported to the sampling sites within the sealed plastic bags as supplied, with gloves worn at all times when handling them. The time of deployment was recorded to the nearest minute.

DGTs were removed as close as possible to the conclusion of a storm event. For the stream site, this required that the flow had subsided to a level where it was safe to enter the water. The DGTs in their holders were retrieved and the time of collection recorded to the nearest minute. The extent of biofouling was noted and photographed (British Standard 2011) to record the potential for reduced metal uptake and underestimation of stream concentrations. Each DGT was rinsed thoroughly with Milli-q water and the integrity of each device examined and noted, for example any scratches or ruptures in the membrane. Each DGT was then placed into labelled zip-lock bags and stored in a chilly bin with cooling blocks and transported to the laboratory.

Modified siphon sampler bottles

Methods for deployment of the modified siphon sampler bottles were similar to those for the Nalgene bottles. At the Whau Creek site, the bottles were mounted in the stream (Figure 5-5, left) with their intake tubing height set to the water level at which the autosampler is triggered. Similarly, at the Akatea Road stormwater site (Figure 5-5 right), the bottles were placed with their intakes at the same height as the water level that triggers the autosampler. Gloves were worn at all times when handling the bottles to minimise possible sample contamination.

Following the storm events, the bottles were retrieved from the mounting unit, the intake system was removed and the bottle capped for transport. Bottles were placed into a chilly bin with cooling blocks and transported to the laboratory.

Figure 5-5: Modified siphon sampler bottles mounted to frame in Whau Creek (left) and at Akatea Road stormwater site (right).

Chemcatcher sampling device

Chemcatchers for metals were only used at the Whau Creek site where they were deployed in a similar manner to the style of housing as the DGTs (Figure 5-6), and mounted at a water depth that ensured they remained submerged at all times. As for the DGTs, the housing was mounted so that the membrane surface of the Chemcatcher was vertical to minimise sediment deposition. Gloves were worn at all times when handling the Chemcatchers.

Chemcatchers were deployed prior to a storm event, as close as possible to its commencement. The time of deployment was recorded to the nearest minute. The devices were transported in a chilly bin in zip-locked bags to avoid contamination or drying during transport and prior to deployment.

Chemcatchers were retrieved as soon as possible after the conclusion of the sampling event and the time of retrieval recorded to the nearest minute. The extent of biofouling was noted and photographed. Each Chemcatcher was rinsed with thoroughly with Milli-q water, the integrity of each device examined, and any damage noted (e.g., any scratches or ruptures in the membrane). Each Chemcatcher was placed into labelled zip-lock bags and during transport to the laboratory, the samplers were stored in a chilly bin with cooling blocks.

Figure 5-6: ChemCatcher samplers after deployment in Whau Creek.

SorbiCell sampling device

For the stream site, the SorbiCells were deployed using the Sorbisense accessory WW-50 housing (Figure 5-7). According to the manufacturer's instructions, this housing provides the most reliable and reproducible results for the Sorbicell samplers but requires at least 30 cm of water depth. Water pressure above the sampler and housing drives the flow through the Sorbicell sampler. Prior to field deployment, the air-hose was connected to the WW-50 housing and a sufficient length of tubing connected to this to ensure it reached well above the water level (including water level at storm flow). The Sorbicells were then carefully inserted into the WW-50 housing and the housing was hung from the intake pipe for the permanent water level recorder at the site, ensuring they were well below the water's surface.

For the stormwater site, the SorbiCells were deployed using the steel ball mounting in the source tracking kit purchased from the manufacturer (Figure 5-7). The ball mounting option does not require a water depth of 30 cm or more, and was therefore considered suitable for placing in stormwater drains, manholes and pipes. The SorbiCells in the steel balls were immersed into the stormwater pipe outlet immediately in front of the pipe outlet underwater in the first storm event and above the water in the second event (Figure 5-8).

Figure 5-7: Mounting options for Sorbicells for monitoring of stream water using WW-50 (left) and stormwater using steel ball or plastic mounting (right). [Sorbisense Limited]

Figure 5-8: Sorbicell deployed in steel ball at the Akatea Road stormwater site.

For both sites, the SorbiCell devices were transported to site in a chilly bin in their supplied foil bags and transportation tubes (Figure 5-9) to avoid contamination or drying during transport and prior to deployment. To deploy the Sorbicells, they were removed from their package on site, the protection caps removed from the transportation tubes and the cartridges pre-wet with Milli-Q water (Figure 5-9). At each deployment, the time (to the nearest minute) of deployment was recorded, along with the SorbiCell serial numbers and water level.

Following the storm events, the WW-50 housings at the stream site were removed from the water, a plug removed from the base and the volume of water within the housing was measured and recorded. The SorbiCells were then removed from the mounting and placed into the transportation tubes and the protective caps refitted. At the stormwater site, the SorbiCells in the steel ball mountings were removed from the water, and the SorbiCells removed from the mounting and then placed into the transportation tubes as above. All SorbiCells were placed into labelled zip-lock bags and placed into a chilly bin with cooling blocks. Time of retrieval was recorded to the nearest minute.

 

Figure 5-9: SorbiCell sampler, protective cap and transportation tube with red cap (left). Pre-wetting of SorbiCell using syringe with Milli-Q water (right).

5.1.4 Quality control procedures

Field blanks for the Nalgene bottles were used to assess potential contamination for faecal indicator bacteria. Field blanks comprised Nalgene bottles filled with ultra-high purity water, taken into the field. A test was undertaken with the bottles to assess the potential for growth of bacteria in collected water samples if not immediately retrieved. Nine stream water samples were collected using Nalgene bottles and were either immediately capped (3 samples) or left in place in the stream and retrieved either the following morning (19 hours after collection) or the subsequent day (43 hours after collection). All samples were analysed for *E. coli*.

Laboratory and field blanks for the DGTs were used to assess potential contamination at each stage of the field study. Laboratory blanks were DGTs that had not left the laboratory and were analysed alongside each batch of samples, to measure the metals present in the DGTs and introduced during analysis. Field blanks comprised DGTs taken into the field, removed from their packaging and then replaced into the bag. One field blank was analysed with every batch of samples. A method blank was also assessed using DGTs deployed in the trough used at the stormwater site, but deployed in a location where it received no water flow. This was to test contamination from the trough and from dust and other deposition.

All samplers were deployed in triplicate for most events to provide a measure of the precision of each device.

5.1.5 Laboratory methods

Water samples were processed immediately on collection of the samples from the field sites and sent to the laboratories for analysis within 24 hours of sample retrieval. DGTs were stored in the refrigerator up to several weeks until there was a larger batch to dispatch for laboratory analysis.

The autosampler collected up to 24 bottles which were combined for analysis to reduce the costs. For the Akatea stormwater site, the bottles were combined into samples that represented the "first-flush" and the remainder of the event. This combination was due to needs for Auckland Council's (AC) Whau catchment contaminant study monitoring project, which Phase 1 of this Envirolink project was aligned with. For the Whau Creek site, bottles were combined in some events and measured discretely in others, depending on the needs of AC's project.

The water samples from the autosampler were analysed by Hill Laboratories for total and dissolved metals (copper and zinc), nutrients (ammonia-N (NH_4-N), nitrate-N (NO_3-N), nitrite-N (NO_2-N), dissolved reactive phosphorus (DRP)), total suspended sediment using standard analytical methods; and by Aqualab for *E. coli* using the Colilert method (9223B, (APHA 2012)).

Samples from the Nalgene bottles were assessed for the same list of contaminants, though not all contaminants were assessed in each storm event.

The DGT samplers were extracted by Hill Laboratories in Hamilton using the methods prescribed by the manufacturers, and the extracts measured for copper and zinc or for nitrate-N, ammoniacal-N and DRP.

5.1.6 Data processing

Analysis of the extract from the DGT gel provides a concentration of metals from which the time-weighted average water concentration can be calculated. Concentrations of each metal in the blanks (specific to each batch) were subtracted, then the mass of metal accumulated in the resin gel layer (M) was calculated using Equation 5-1:

$$M = Ce\frac{(V_{HNO_3} + V_{gel})}{fe}$$ **Equation 5-1**

where Ce is the concentration of metals in the 1M HNO_3 elution solution (in µg/l), $VHNO_3$ is the volume of HNO_3 added to the resin gel, Vgel is the volume of the resin gel (0.15 ml), and fe is the elution factor for each metal.

Next the metal concentration in the water column was calculated using Equation 5-2:

$$C_{DGT} = \frac{(M\Delta g)}{(DtA)}$$ **Equation 5-2**

where Δg is the thickness of the diffusive gel (0.078 cm) plus the thickness of the filter membrane (0.014 cm), D is the diffusion coefficient of metal in the gel, t is deployment time (in sec) and A is the exposure area (A=3.14 cm^2).

Diffusion coefficients were obtained from the DGT research website (https://www.dgtresearch.com/diffusion-coefficients/).

Similar methods were used for calculation of ammoniacal-N, nitrate-N and DRP with assistance from the device supplier.

5.1.7 Analysis and evaluation of sampling results

The results of the trials were assessed in terms of the accuracy of the sampling methods, by assessing quality assurance data and comparing to autosampler data; and the precision of the results, by assessing variability among replicates.

Contaminant concentrations measured in the Nalgene bottles were compared to concentrations in the samples collected by the autosampler at a water level that most closely matched the water level of the Nalgene bottles (usually the first sample) or, for the Akatea site, the composite of the first-flush. Contaminant concentrations calculated using DGTs were compared to time-weighted average concentrations (TWAs) calculated from concentrations in discrete samples collected by the autosampler and the elapsed time between samples. In some events, including all events at the Akatea site, this was not possible and only event mean concentration (EMC) data were available for comparison with the DGT results. Analysis of TWA and EMC data calculated for other sites showed that there was minimal difference between these two averages, particularly in comparison to the difference between storm events and between sites. Accordingly, EMCs could be reasonably adopted as surrogate for TWAs where the latter were not available.

The results are compared graphically in sections 5.2 and 5.3, by plotting the contaminant concentrations from the Nalgene bottles and DGTs against concentrations from the autosamplers. A 1:1 line is used to show where identical results would plot, and dotted lines are used to indicate an area that relates to a factor of 2 or less difference between the two methods. While somewhat arbitrary, values falling inside the dotted lines are considered to be reasonable estimates of the 'true' concentration, as measured by the autosampler.

The repeatability of the results (or method precision) was assessed by calculating the coefficient of variation of replicate results, calculated as the standard deviation divided by the mean concentration.

5.2 Nalgene storm water sampler bottle results

5.2.1 Quality control samples

Nalgene bottles filled with ultra-high purity water (Milli-Q) contained no measurable *E. coli* (three replicates <1 MPN/100 mL), even when stored unrefrigerated and placed in a stream for up to 43 hours (three replicates <1 MPN/100 mL).

Sampler bottles filled with stream water and left in the stream for up to 43 hours showed minimal growth of *E. coli* (Table 5-2). The water level ranged from 0.07-0.28 m during this time and the bottles would have been out of the water for most of the period. Water temperatures ranged from 13-17°C and air temperatures ranged between overnight minima of 11-13°C and daytime maxima of 19-20°C. This indicates that the bottles are suitable for sampling for faecal indicator bacteria, even if bottles cannot be retrieved immediately and samples analysed within 24 hours. However, this finding may not be valid in the middle of summer when air temperatures or water temperatures are warmer, particularly in locations with minimal stream shading.

Table 5-2: *E. coli* in stream water Nalgene bottle samples retrieved immediately, the subsequent morning or two days following sample collection. .

	Hours elapsed between collection and retrieval	*E. coli* (mean of three replicates)	Change over time
Immediate analysis	0	8,360	-
Following morning	19	8,877	6% increase
Two days later	43	7,825	6% decrease

5.2.2 Measurement precision

The coefficient of variation (CV) for the triplicate Nalgene bottles was quite high, often around 50% (meaning there is about a factor of two difference between samples). For some water quality variables, notably suspended sediment (SS) and *E. coli*, the variation was up to or more than 100%. In some cases, it appeared that the bottles were accumulating sediment once filled. The rubber seal of the bottles needs to be correctly seated to ensure the bottle seals once it has collected its sample. The high variation observed in this project suggests that when the intention is to compare between sites (or to guidelines), the bottles are best suited as a screening tool to check for suspected large differences in SS concentrations between sites.

Table 5-3: Mean CV (and range in brackets) of samples from triplicate deployment of Nalgene bottles.

	SS (n=7)	Nitrate-N (n=6)	*E. coli*	DRP (n=6)
Stormwater	36 (22 – 46)	16 (0 – 43)	55 (30 – 98) (n=4)	34 (0 – 66)
Stream	65 (21 – 128)	5 (1 – 10)	31 – 52 (n=2)	36 (0 – 87)

5.2.3 Comparison to autosampler results

The suspended solids concentrations were frequently much higher in the Nalgene bottles compared to the autosampler and there was considerable variance between replicates (Figure 5-10). This may be due to collection of larger, heavier particles in the Nalgene bottles that are not able to be taken up through an autosampler's pump[16]. In any case, based on the findings of our deployments, we recommend that where SS are of interest, Nalgene bottles are used for screening purposes only.

For *E. coli*, the Nalgene bottle and autosampler results generally agreed well in the range 100 to 3,000 *E. coli* /100mL (Figure 5-10). At higher counts, as found in the stream, there was poor agreement between the two methods. This may be due to slight differences in the timing of sample collection between the two methods, the high variability in *E. coli* counts within the stream and – possibly in part – the inherent 'noisiness' of microbial data (Muirhead & Meenken 2018). Although the Nalgene results did not appear accurate (relative to the autosampler results) at very high concentrations, the bottles still appear suitable for distinguishing between waters with low FIB counts (e.g., 100-500 *E. coli* /100 mL, below or near recreational guidelines); moderate FIB associated with diffuse bacteria sources; and very high bacteria counts (e.g., > 5000-10,000 *E. coli* /100 mL), such as those associated with sewage contamination.

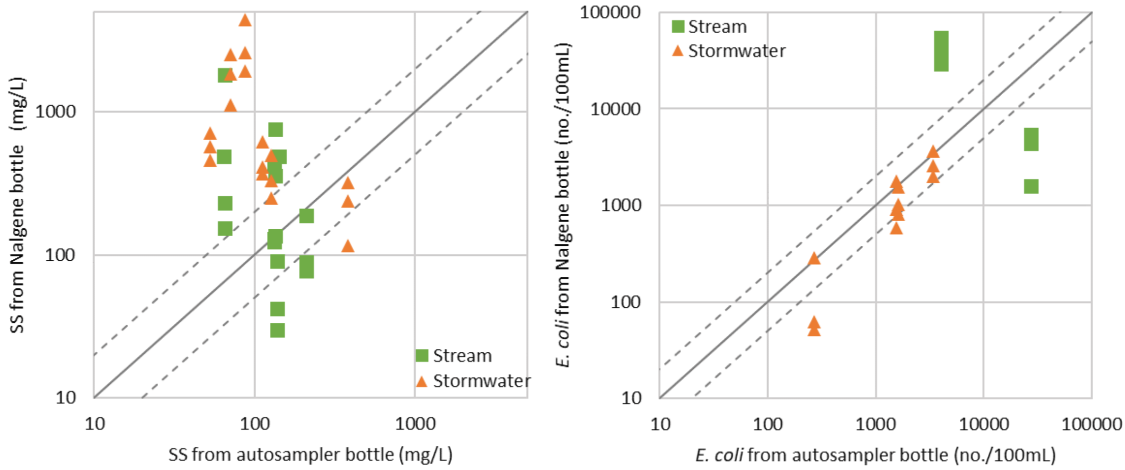

Figure 5-10: SS (left) and *E. coli* (right) concentrations as measured in Nalgene bottles and in autosampler bottles. The solid diagonal line represents the 1:1 line where the data would be if exactly the same result was measured with both methods. The dashed lines indicate a factor of 2 difference: ideally results fall within the dashed lines. Note the logarithmic scale applied to both axes.

There was good agreement in the nitrate-N and DRP results between the Nalgene bottles and autosamplers for most of the stream and stormwater site sampling events (Figure 5-11). The lowest stream DRP result (near 0.001 mg/L) represents a concentration below the laboratory's detection

[16] See Semadeni-Davies (2013) for a comprehensive review in relation to stormwater sampling.

limit of 0.004 mg/L and there is considerable uncertainty in this measurement. In both these events, the other two Nalgene bottles had concentrations comparable to those from the autosampler.

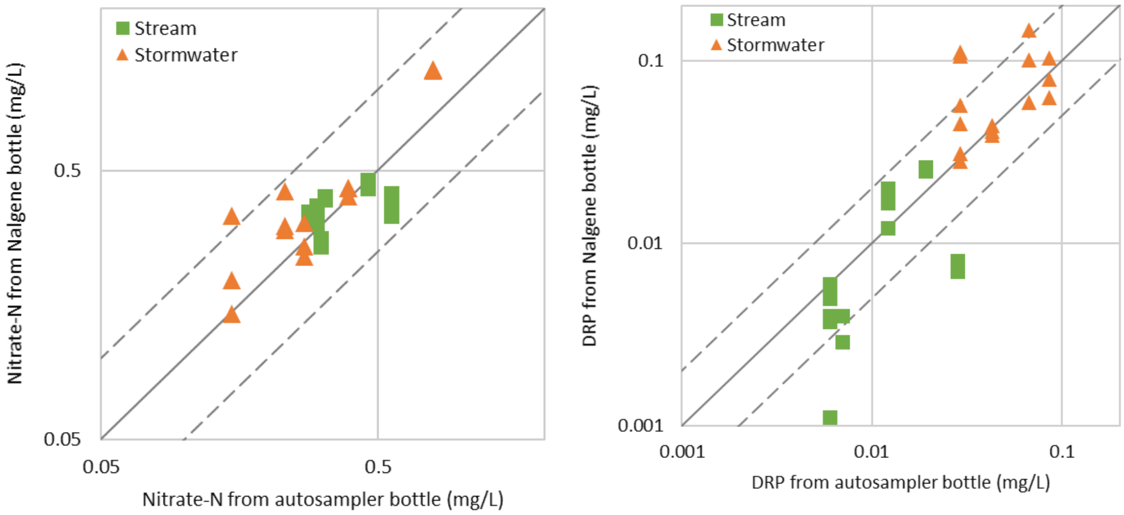

Figure 5-11: Nitrate-N (left) and DRP (right) concentrations as measured in Nalgene bottles and in autosampler bottles. The solid diagonal line represents the 1:1 line where the data would be if exactly the same result was measured with both methods. The dashed lines indicate a factor of 2 difference: ideally results fall within the dashed lines. Note the logarithmic scale applied to both axes.

Total zinc concentrations appeared to be similar in both the Nalgene and autosampler bottles, whereas total copper was at times higher in the Nalgene bottles, particularly for the stormwater samples (Figure 5-12). For the dissolved metals (Figure 5-13), copper concentrations were lower in the Nalgene bottles, particularly in the stormwater samples. Dissolved zinc concentrations were much closer between methods, particularly for the stream samples which had lower zinc concentrations. The greater variance in the stormwater samples may be due to differences in the timing of sample collection and the greater variability in dissolved zinc concentrations in stormwater, compared to stream water and compared to dissolved copper.

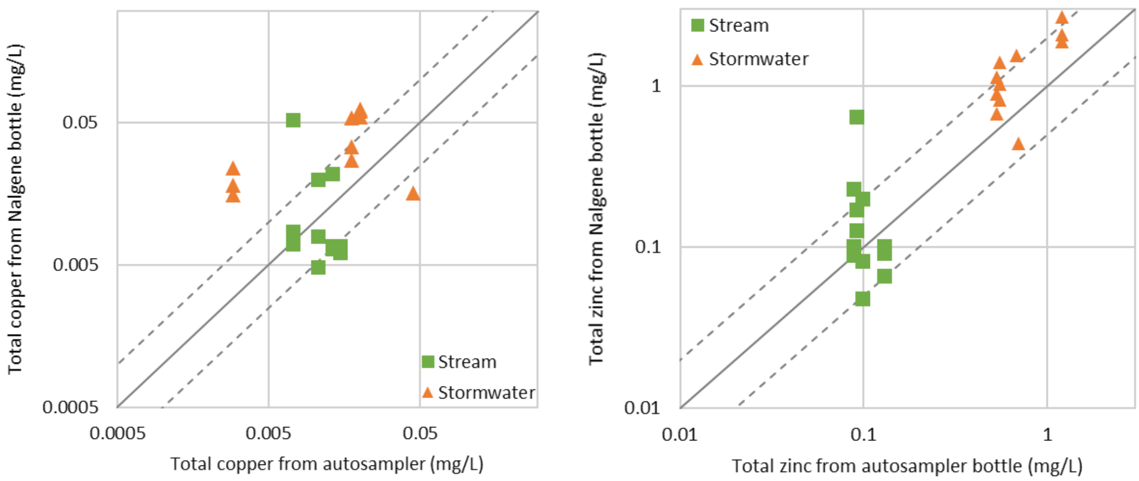

Figure 5-12: Total copper (left) and zinc (right) concentrations as measured in Nalgene bottles and in autosampler bottles. The solid diagonal line represents the 1:1 line where the data would be if exactly the same result was measured with both methods. The dashed lines indicate a factor of 2 difference: ideally results fall within the dashed lines. Note the logarithmic scale applied to both axes.

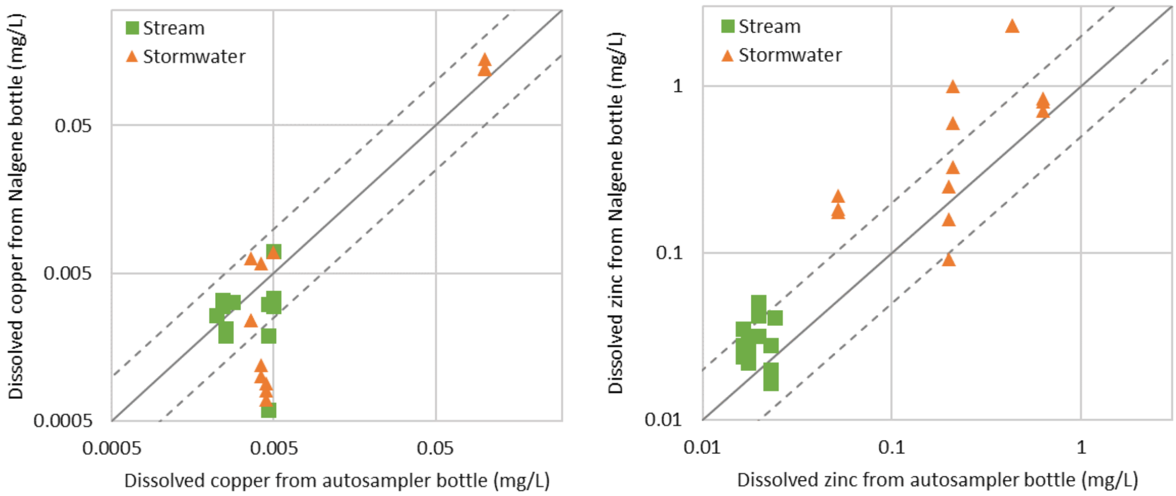

Figure 5-13: Dissolved copper (left) and zinc (right) concentrations as measured in Nalgene bottles and in autosampler bottles. The solid diagonal line represents the 1:1 line where the data would be if exactly the same result was measured with both methods. The dashed lines indicate a factor of 2 difference: ideally results fall within the dashed lines. Note the logarithmic scale applied to both axes.

5.3 DGT results

5.3.1 Quality control samples

Quality control sample results (laboratory, field and trough blanks) are shown in Table 5-4. The laboratory blanks contained zinc at measurable concentrations, of around 0.025 to 0.049 mg/L in the extract. This is about 10x lower than was found in DGTs deployed in the Whau Creek and at least 100x lower than found in DGTs deployed at Akatea Road. DGTs contained copper at lower concentrations, frequently below the detection limit of 0.0025 mg/L for the DGT extracts. The maximum copper concentration measured in the blanks was 0.0087 mg/L which was around 5x lower than that measured at the stream site.

Table 5-4: Metals concentrations in extracts of laboratory blanks, field blanks and trough blanks compared to samples. Range of data shown, metals in µg/L in 1 mL gel extract.

Blank type	Cadmium	Copper	Lead	Nickel	Zinc
Lab blank	<0.25 – 0.76	<2.5 – 0.87	0.6	5 – 6	35 – 49
Field blank	<0.25 – 1.3	<2.5 – 124	<0.5 – 2.7	<2.5 – 39	48 – 230
Trough blank	2 – 14	28 – 168	0.9 – 3.9	13 – 102	170 – 840
Stormwater DGTs	<0.25 – 2.4	32 – 220	1.2 – 11	12 – 121	3400 – 60,000
Stream DGTs	<0.25 – 1.4	20 – 146	0.5 – 40	12 – 132	410 – 3,600

Concentrations of zinc in field blanks were approximately double the concentrations in laboratory blanks. The mean (and median) zinc concentration in the field blanks was 0.09 mg/L, with a concentration range from 0.05 to 0.23 mg/L. The upper values are close to concentrations that might be measured in a DGT deployed in a clean stream for a short time or at baseflow. Copper concentrations were variable, sometimes remaining below detection but up to 0.12 mg/L in the extract of one field blank – as high as might be found in extracts from stormwater samples. The median copper concentration in the field blanks was <0.0025 mg/L.

The field blanks indicated there is potential to contaminate the DGTs if not handled extremely carefully. Therefore, field blanks should be collected at all times when using DGTs and any contamination taken into account in final calculations of copper and zinc concentrations.

The ‘trough’ blank (DGTs deployed in the trough in a location that did not receive stormwater flow) contained metals at concentrations higher than the field blanks. This is unsurprising as the DGTs were exposed for 71 hours and subject to dry and wet deposition. The concentrations of copper in these ‘trough’ blanks were within the range that might be measured in some stormwater discharges however zinc concentrations in the blanks remained well below what would be expected in stormwater. This suggests some caution should be applied when using troughs to measure copper in stormwater. Although a trough system like the one used in this project could in theory be used to sample stream water at high flow only (i.e., by deploying the trough above the baseflow water level), we do not recommend this strategy due to the high potential for contamination of the DGTs during the baseflow period. Metal concentrations in streams (even urban streams) are lower than in stormwater and the level of contamination in the trough blanks is within the range that might be encountered in DGTs deployed in urban streams for short durations.

5.3.2 Measurement precision

DGTs were deployed in triplicate on 12 occasions (sites x events) in Phase 1. For zinc, the mean CV was 8% and ranged from 2 to 18% and for copper, the mean CV was 10% and ranged from 4 to 24%. There was good agreement between replicates for almost all occasions, with CV ≤10% for 8 out of 12 events. Higher variation between replicates for one metal was not necessarily associated with higher variation in other metals, suggesting the variance is due to factors other than the absorption by the DGT. Minor damage such as dents in the membrane did not appear to affect the uptake of metals, however recording this in the field is useful for understanding any outlying results received.

5.3.3 Comparison to autosampler results

Concentrations of zinc in the DGTs were very similar to those measured in water collected by the autosampler (Figure 5-14), for both stormwater and stream water. This was true across a wide range in concentration, from 6 µg/L to over 3000 µg/L (3 mg/L). At times the DGT zinc concentrations were higher than zinc concentrations in the water samples. This difference was unexpected as DGTs measure labile zinc (a subset of total dissolved zinc). For the stormwater samples this may be due to delays between the cessation of the storm event and recovery of the DGTs, during which time they are exposed to the stormwater remaining in the trough (unlike prior to the event, where they are in a clean fluid). This does not explain discrepancies for the stream deployments however, and this could simply reflect variability in the water concentrations and the error associated with sampling using an autosampler.

For stormwater, the DGT copper concentrations agreed well with those in water collected by the autosampler (Figure 5-14). However, for streams, the DGT copper concentrations were mostly lower than those measured in the water samples collected by the autosampler (Figure 5-14). This is not unexpected. Copper binds strongly to dissolved organic carbon (DOC) and the bound copper is not easily taken up by a DGT. Compared to zinc, a much narrower concentration range was found for copper in the stormwater and stream samples, from just over 1 µg/L to 45 µg/L.

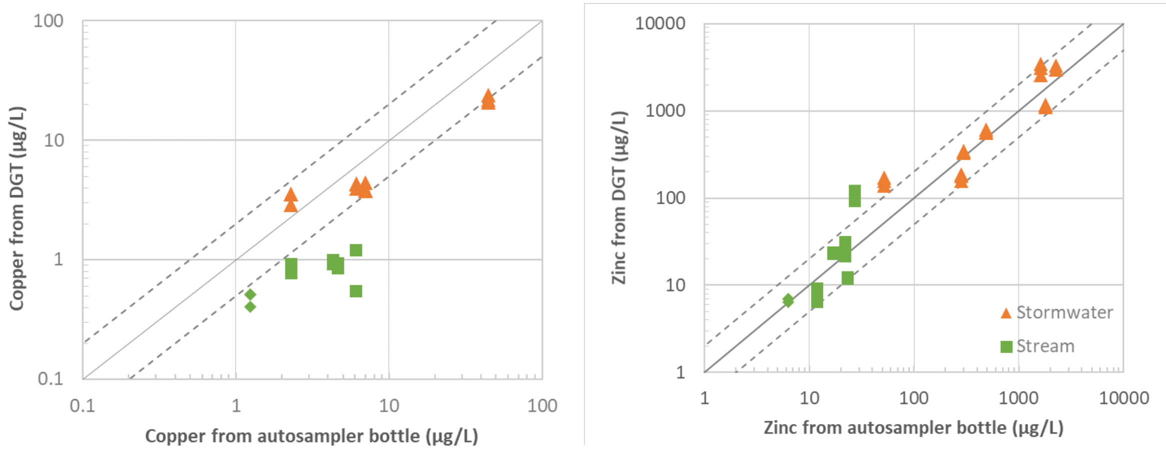

Figure 5-14: Copper (left) and zinc (right) concentrations as measured by DGTs and by autosampler. The solid diagonal line represents the 1:1 line where the data would be if exactly the same result was measured with both methods. The dashed lines indicate a factor of 2 difference; ideally results fall within the dashed lines. Note the logarithmic scale applied to both axes.

5.3.4 Additional tests

Mixed media DGTs (those suitable for a wider range of metals and also phosphorus) were also trialled alongside the metal-only DGTs at the Whau Creek site. These devices produced very similar results to the metal-only DGTs, suggesting they are equally suitable for measuring metals if phosphorus is also of interest.

Nutrient DGTs from a research batch were trialled but high ammoniacal-N and DRP concentrations were measured in the blanks relative to the concentrations found in the stream. Nitrate-N concentrations in the DGTs agreed reasonably closely with those measured in samples collected by the autosampler (Figure 5-15), however these DGTs were tested in only one storm event for stormwater and two for streams so further testing may be justified before using these DGTs to quantify absolute concentrations.

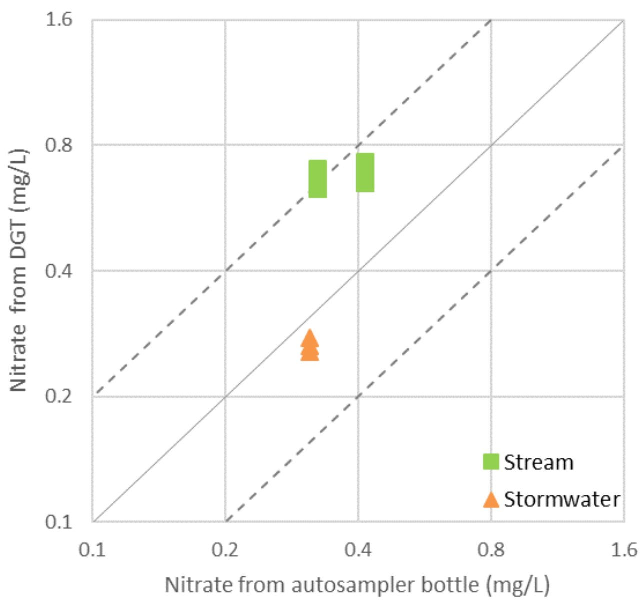

Figure 5-15: Nitrate-N concentrations as measured by DGTs and by autosampler. The solid diagonal line represents the 1:1 line where the data would be if exactly the same result was measured with both methods. The dashed lines indicate a factor of 2 difference; ideally results fall within the dashed lines. Note the logarithmic scale applied to both axes.

5.4 Other devices

5.4.1 Modified siphon sampler bottles

The trials of the modified siphon sampler bottles indicated that the original design was prone to leakage as the bottles are oriented on their side. An inadequate seal between the bottle and lid allowed water to leak out which resulted in increased concentrations of sediments and other particulate-related contaminants. Samples were therefore analysed for dissolved metals and nutrients instead of total, although SS and *E. coli* were also measured. The bottles were replaced with a different type that had a better seal which prevented leakage of the collected samples and trialled again in a further event. The precision was comparable to that of the Nalgene bottles (Table 5-5).

Table 5-5: Coefficient of variation of samples from triplicate modified siphon sampler bottles. Mean and range of CV shown. N = 4 for all contaminants except *E. coli* (n=1 for stormwater, n=2 for stream); dissolved zinc and copper at stormwater site (n=3).

	SS	*E. coli*	Nitrate-N	DRP	Dissolved zinc	Dissolved copper
Stormwater	27 (11 – 51)	30	33 (4 – 73)	38 (11 – 61)	30 (24 – 36)	47 (27 – 70)
Stream	43 (6 – 94)	51 – 86	23 (6 – 81)	32 (15 – 49)	30 (10 – 46)	15 (7 – 30)

The SS concentrations in the siphon sampler bottles were generally well above those measured using the autosampler (Figure 5-16), which may be at least partly due to issues with sample leakage as described. For dissolved contaminants, there was much better agreement between the two methods (Figure 5-17 and Figure 5-18). This method showed promise for use in locations with insufficient depth for a Nalgene bottle, however more testing is required with the redesigned model to assess reproducibility and accuracy.

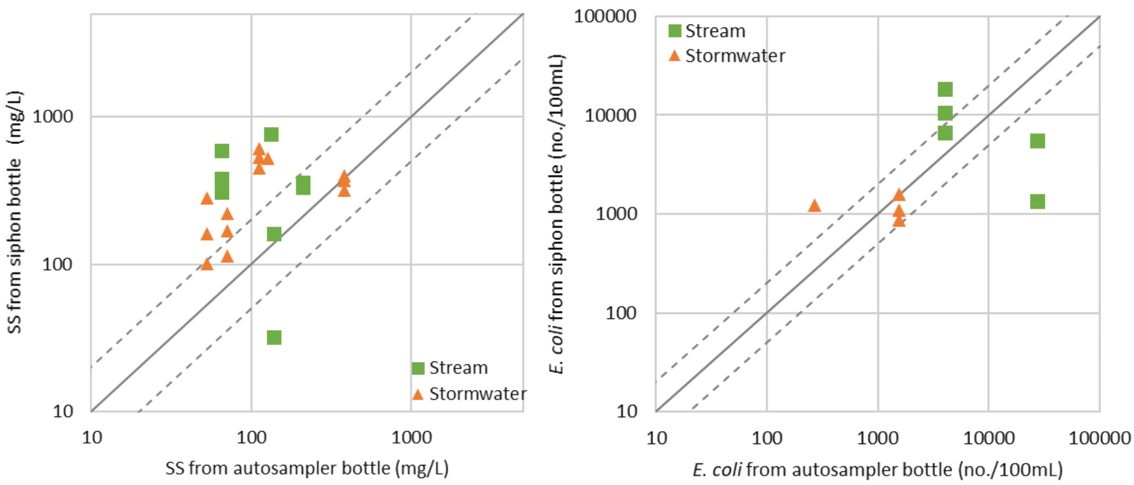

Figure 5-16: Suspended solids (left) and *E. coli* (right) concentrations as measured in siphon sampler bottles and by autosampler. The solid line represents the 1:1 line where the data would be if exactly the same result was measured with both methods. The dashed lines indicate a factor of 2 difference; ideally results fall within the dashed lines. Note the logarithmic scale applied to both axes.

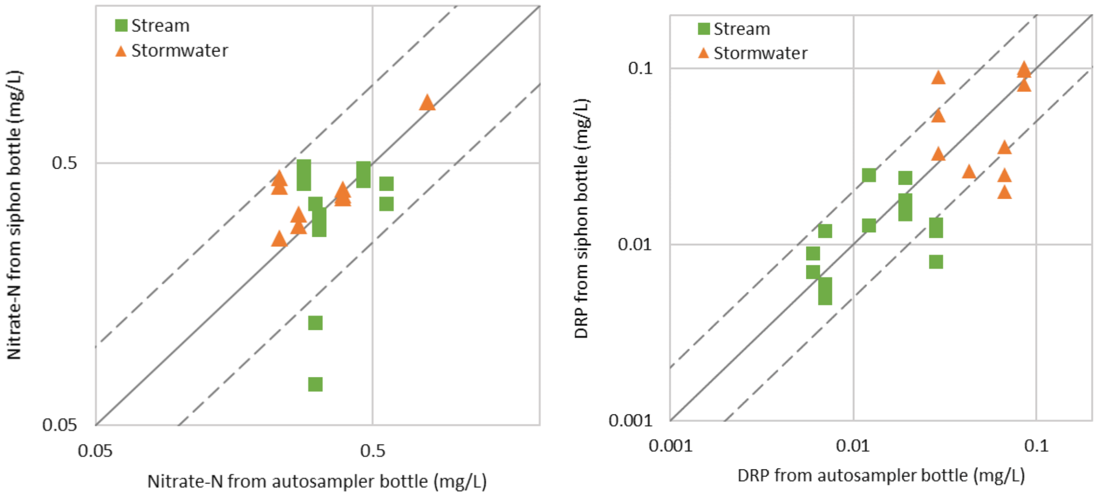

Figure 5-17: Nitrate-N (left) and DRP (right) concentrations as measured in siphon sampler bottles and by autosampler. The solid diagonal line represents the 1:1 line where the data would be if exactly the same result was measured with both methods. The dashed lines indicate a factor of 2 difference; ideally results fall within the dashed lines. Note the logarithmic scale applied to both axes.

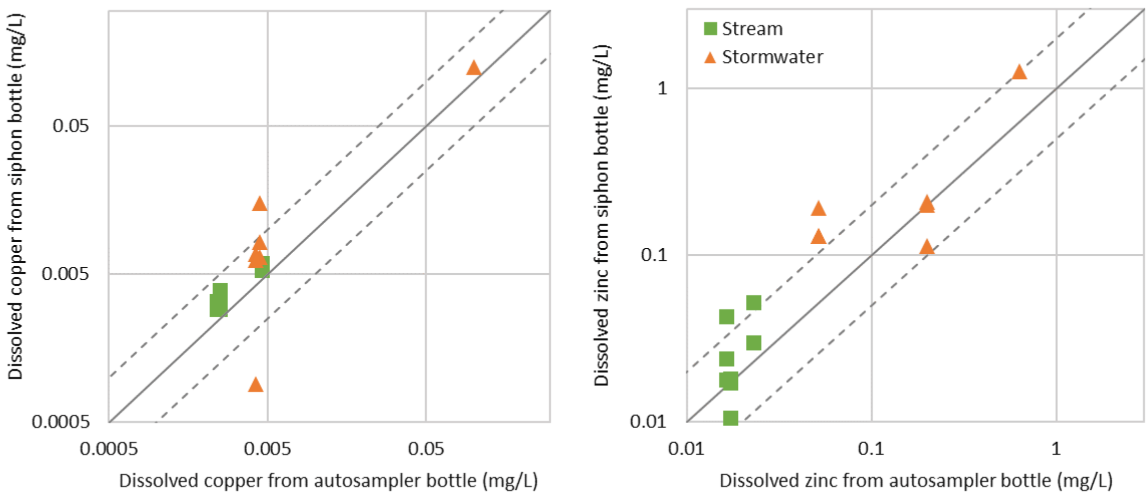

Figure 5-18: Copper (left) and zinc (right) concentrations as measured in siphon sampler bottles and by autosampler. The solid diagonal line represents the 1:1 line where the data would be if exactly the same result was measured with both methods. The dashed lines indicate a factor of 2 difference; ideally results fall within the dashed lines. Note the logarithmic scale applied to both axes.

5.4.2 ChemCatcher passive sampling device

ChemCatcher samplers were trialled in Whau Creek during two storm events only. The zinc concentrations agreed well with those obtained from the autosampler (Figure 5-19). The copper concentrations from the ChemCatchers were slightly lower than those from the autosampler, similar to the DGT results.

ChemCatchers require information on the water velocity for the in-water calculation (Allan et al. 2008) and therefore they are not as well suited as DGTs to sites where the velocity is unknown or changes. Because of these disadvantages, no further ChemCatchers were deployed.

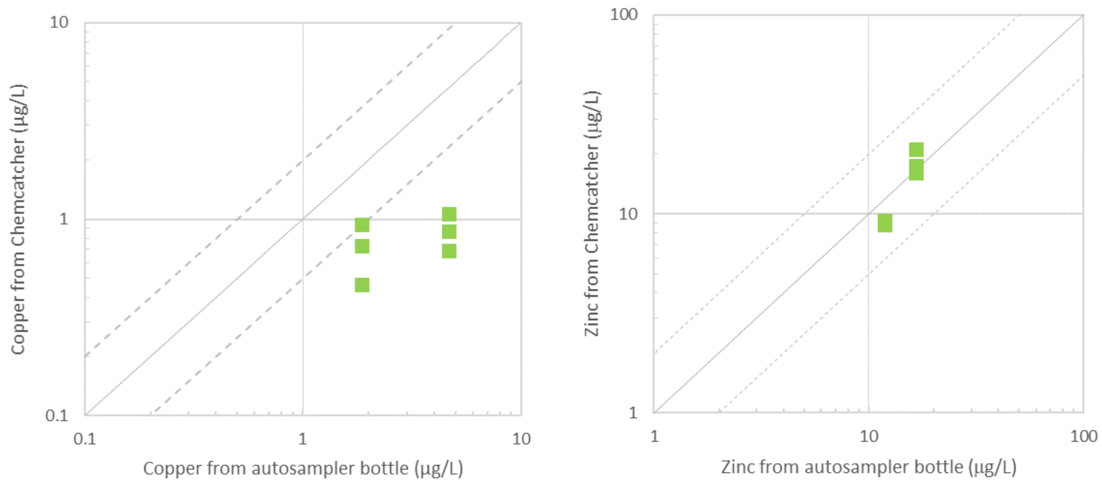

Figure 5-19: Copper (left) and zinc (right) concentrations as measured by ChemCatchers samplers and by autosampler. The solid diagonal line represents the 1:1 line where the data would be if exactly the same result was measured with both methods. The dashed lines indicate a factor of 2 difference; ideally results fall within the dashed lines. Note the logarithmic scale applied to both axes.

5.4.3 Sorbicell passive sampling device results

Metals were measured in the Sorbicell devices at the stream and stormwater site for two storm events each (Table 5-6). At the stormwater site, there was insufficient flow through two of the three sampling tubes to accumulate metals and calculate in-water concentrations. An alternative way of deploying the sampler tubes (above the water, immediately in front of the stormwater pipe) was used in the second deployment and metal concentrations were measurable in each. When there was sufficient flow through the tubes, the copper and zinc concentrations in the Sorbicell tubes were often very close to those measured by the autosampler (Figure 5-20). The concentrations measured by these samplers are the dissolved concentration and may also include metals attached to fine particles (Birch et al. 2013) (cf the *labile* concentration measured by DGTs).

Table 5-6: Metal concentrations as measured from Sorbicell samplers deployed in two storm events. Concentrations in µg/L.

Site	Event	Replicate	Copper	Lead	Zinc
Stream site (Whau Creek)	1	1	3.8	<0.3	9.6
	1	2	1.7	0.25	7.9
	1	3	1.3	<0.2	5.4
	2	1	1.1	<0.2	7.8
	2	2	2.0	0.49	8.8
	2	3	<1	<0.6	11
Stormwater site (Akatea Road)	1	1	*Insufficient flow through sampler tube*		
	1	2	*Insufficient flow through sampler tube*		
	1	3	7.6	<2	13
	2	1	4.8	1.8	160
	2	2	6.1	1.4	180
	2	3	7.3	1.1	260

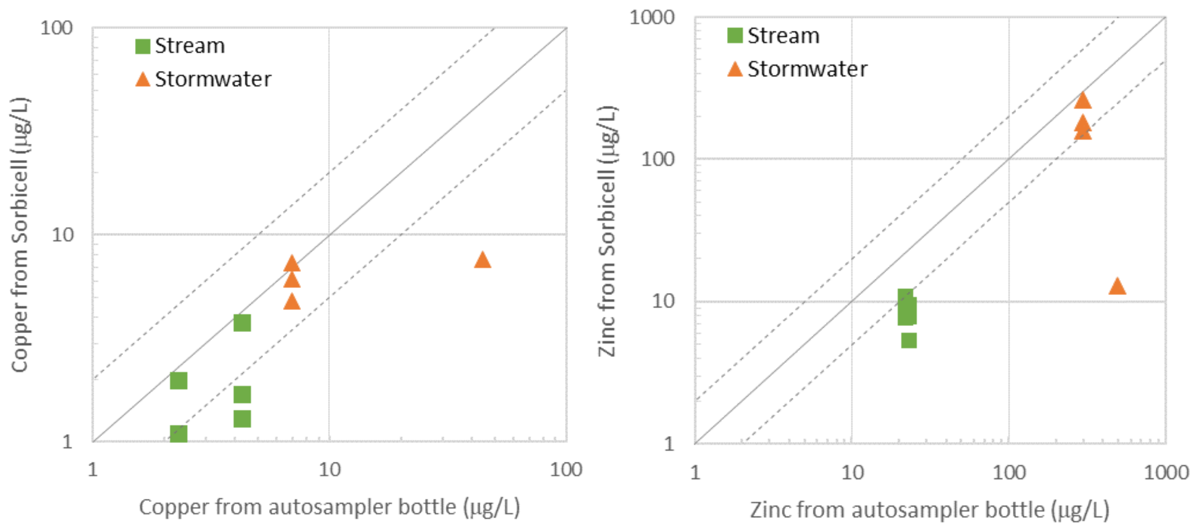

Figure 5-20: Copper (left) and zinc (right) concentrations as measured by Sorbicells and by autosampler. The solid diagonal line represents the 1:1 line where the data would be if exactly the same result was measured with both methods. The dashed lines indicate a factor of 2 difference; ideally results fall within the dashed lines. Note the logarithmic scale applied to both axes.

Sorbicell samplers for nitrate-N and phosphorus were also trialled during two storm events at each site. The results for all sampling tubes indicated very little flow through several of the tubes deployed at the Akatea Road site, indicating that the way the samplers were deployed was not suitable for this event. There was more flow through the samplers at the Whau Creek site, as also noted in the field when measuring the water retained in the WW-50 housing. However, there was no measurable nitrate-N or phosphorus in any of the tubes analysed. This may be partly due to the delay in time between collection of the devices and analysis, which required shipping to Denmark.

Because Sorbicell devices must currently be analysed in Denmark, they are only suitable for contaminants that are stable once collected. Nutrients collected by Sorbicells are not stable; whereas the metals are stable for weeks to months. The devices have potential uses for metals, although the cost of analysis may remain prohibitive. The results suggest the Sorbicell devices could be useful for measuring dissolved metal concentrations, particularly copper. This would be useful for stormwater monitoring, where the labile (or bioavailable) concentration is not relevant as toxicity is more usefully measured within the stream receiving environment. However, the sampling tubes need to be affixed in a manner that ensures they receive sufficient flow throughout a storm event. In stream locations, the WW-50 housing can be used, however these are expensive to purchase (although reusable) and in some storm events there was sediment deposition on the tubes, introducing some doubt in their ability to sample the water column consistently throughout a storm event in such locations. If an improved deployment configuration can be developed then these devices would warrant further trials for monitoring metal concentrations. Because of the disadvantages shown during these initial deployments, no further devices were deployed.

5.5 Practical considerations

A key consideration in the suitability of these devices for urban stream and stormwater sampling relates to their ease of use. Devices that are too complex to use without advanced training, require substantial site-specific modifications, or frequently fail, are less useful than simple methods that work dependably in a wide range of different locations. This section evaluates the practical strengths and weaknesses of the five devices.

The Nalgene bottles were easy to deploy with minimal training, all deployed bottles collected water samples and there was no loss of bottles held in place simply using cable ties. The bottles do require a water depth of 250 mm, which reduces suitability for deploying within stormwater pipes. However, because they can be used within catchpits (although not tested in that way in this project) and at a stormwater outlet, they could be deployed up or downstream of a stormwater pipe and therefore would be suitable for many stormwater applications. If bottles are washed for re-use, it is essential that the rubber seal is correctly seated prior to re-use. Furthermore, Nalgene bottles collect water samples that can be analysed for almost any contaminant of interest.

By contrast, the modified siphon sampler is suitable in more shallow locations, with a minimum depth ~150 mm. The prototype bottles require a flat edge to connect to and because of the space required with their horizontal arrangement, it may be difficult to deploy multiple bottles in a single location without creating a barrier to flow, particularly for a stormwater outlet. Further testing is required to assess contamination or contaminant loss from the materials used in these bottles.

The DGTs were easy to install in stream locations and did not need a great depth of water to ensure coverage. Biofilms were noted on the devices even after a 2-3 day deployment, suggesting short duration (<7 days) deployments would be more appropriate for urban streams (consistent with the goals of sampling storm events). The troughs configuration was suitable for stormwater applications and allowed sufficient flow past the gel area to provide uptake of the metals. Measurement of water temperature at each location improves the accuracy in calculating the in-water concentration however estimates of this based on nearby sites would be sufficient if high accuracy is not required. A limiting factor for DGTs is that they only sample a limited range of contaminants and only for the dissolved fraction. Furthermore, different DGTs are required for different contaminants, which adds to the cost when undertaking studies with multiple contaminants of interest.

The ChemCatchers were larger in size than the DGTs and therefore require a larger plate and greater water depth for deployment (although still less than 250 mm). Due to their larger size, they were not suitable for a trough-style holder for deployment in stormwater locations. The ChemCatchers were also easily damaged (Figure 5-21) and had a higher purchase cost than the DGTs.

Figure 5-21: Chemcatcher sampler after deployment in stream showing complete rupture of protective filter membrane.

The Sorbicells were relatively easy to install in stream locations within the WW-50 housings, however these were expensive to purchase and hold only one Sorbicell at a time, so multiple housings are required to deploy replicates. The samplers have a narrow surface area, and this can clog up with sediment which then reduces the flow of water through the sampler. In the stormwater location, the mounting on ball-bearings did not ensure flow through the device. Whilst the amount of flow through the device can be calculated after sampling (from the tracer salts in the device) this does not offset the disadvantage of diminished flow.

5.6 Synthesis

The Phase 1 sampling method trials demonstrated the potential uses of different methods in sampling urban streams and stormwater. The Nalgene bottles and DGTs were easy to use, cost-effective and generally robust when compared to data from autosamplers, except for suspended solids (SS) in the Nalgene bottles and copper in the DGTs. Copper concentrations measured with DGTs reflects the bioavailable concentration rather than the “total dissolved” concentration and therefore this method may not be appropriate for all monitoring objectives. The variance in the SS measured by the Nalgene bottles indicates that care should be taken when using these for particulate-associated contaminants (e.g., SS and total phosphorus).

Metals measured with the Sorbicell samplers demonstrated good agreement with the autosampler results. This method includes all forms of dissolved metals and would therefore be more appropriate for sampling related to source identification. However, Sorbicell samplers were more difficult to use and ensure adequate flow through the tubes. In addition, these samplers are considerably more expensive to analyse than water samples or DGTs and consequently they were not recommended for further (Phase 2) trials within this project. The Chemcatcher metal concentrations showed good agreement with the autosampler results for dissolved zinc, but a weaker agreement for dissolved copper. They were more difficult to handle and less suitable for a stormwater application due to their size. Moreover, with a slightly higher cost, there were no advantages with Chemcatchers over DGTs and consequently they were not recommended for further (Phase 2) trials. The testing of the modified siphon sampler bottles suggested similar performance to the Nalgene bottles, once the design was modified to prevent leakage. However, further testing is required of these samplers before their use can be recommended in monitoring projects.

Overall, two sampling devices – Nalgene bottles and DGTs – were selected for testing by regional council staff in Phase 2 of the project. These trial deployments are presented next in Chapter 6.

6 Phase 2 sampling device trials

6.1 Introduction

In Phase 2 of the project, Nalgene stormwater sample bottles (Nalgene bottles) and DGTs were deployed by regional council staff in urban locations in Wellington, Southland, Hawke's Bay and Canterbury. The objectives of this phase were to test the draft written and video sampling instructions; provide council staff with an opportunity to use the sampling devices under the guidance of NIWA staff; and to test the devices across a broader range of urban environments. The trials were designed by council staff in consultation with NIWA and field work was typically undertaken by council science and/or monitoring staff. This chapter presents the trials of the four regions, along with a subset of the results of a further study independently conducted by Bay of Plenty (BoP) Regional Council to use DGTs to monitor metals in urban streams across the entire Bay of Plenty region.

This chapter describes each of the trials, including background on the trial locations, the methods used to trial the devices, the results obtained and the findings of the study. The latter section evaluates the usefulness of the devices and any practical considerations regarding their use in different environments.

6.2 Porirua Stream catchment, Porirua

6.2.1 Background

Porirua Stream is a highly urbanised stream within the Wellington region and is the major freshwater input to the Onepoto Arm of Te Awarua-o-Porirua Harbour. Previous monitoring based on routine grab and (limited) wet-weather sampling with autosamplers has demonstrated that concentrations of dissolved copper and zinc exceed water quality guidelines at some sites (Milne & Morar 2017, Milne & Watts 2008). Greater Wellington Regional Council (GWRC) decided to trial Nalgene bottles and DGTs for metals at selected locations in this catchment to complement some previous grab sampling of selected tributaries carried out to investigate metal sources. The primary aim was to assess if these sampling devices could be used more widely to identify metal source 'hotspots'. Other contaminants were also of interest, including suspended sediment and nutrients.

6.2.2 Sampling methods

Nalgene bottles (two at each site), DGTs (in triplicate) and a TidbiT® temperature logger (Onset Ltd) were deployed in-situ at GWRC's Porirua Stream at Town Centre flow recorder monitoring site, where an autosampler and turbidity sensor were already installed. Nalgene bottles and DGTs were also installed in the lower reaches of two tributaries – Mitchell Stream and Kenepuru Stream (Figure 6-1).

The height at which to deploy the Nalgene bottles in Porirua Stream at Town Centre was determined by analysis of stream water level records, and was set at heights associated with peak flows during small storm events (e.g., 5-20 mm rainfall over 24 hours). For the two tributaries, there was no information on the water levels during storm events, so the bottles were simply set arbitrarily at 100 mm and 200 mm above baseflow at each site.

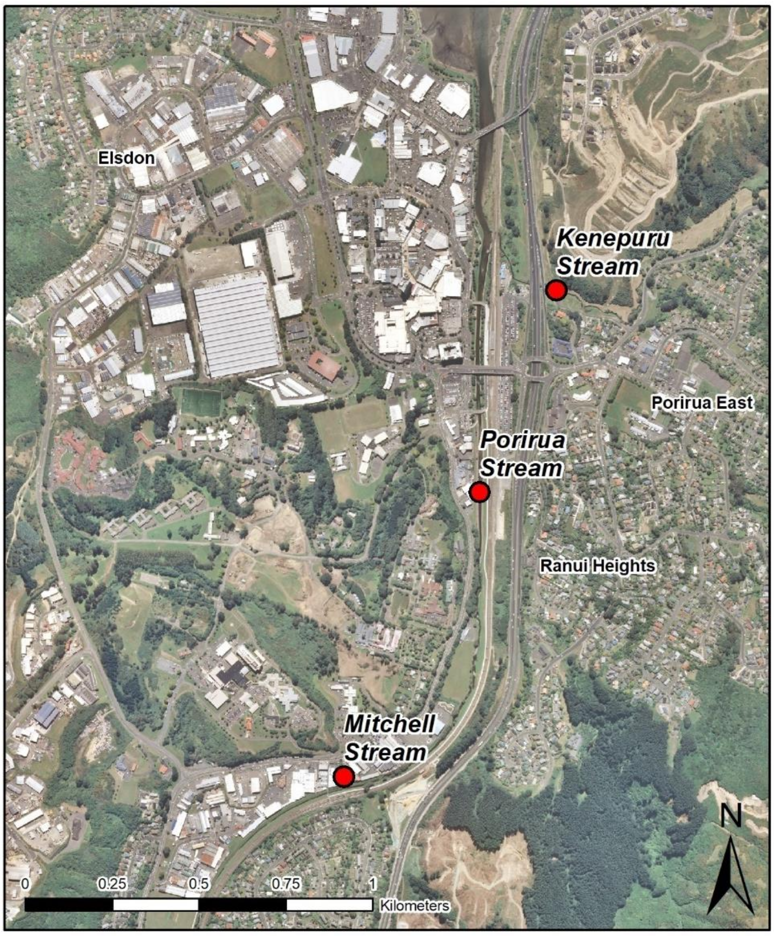

Figure 6-1: Sampling locations in Porirua Stream and tributaries Mitchell Stream and Kenepuru Stream.

The DGTs were deployed on 24 October 2018 for approximately 48 hours, which included about 36 hours of baseflow, then a rain event of 10 mm over 12 hours where the flow in Porirua Stream (as measured at GWRC's Porirua Stream at Town Centre site) increased from about 0.4 m^3/s to nearly 9 m^3/s. DGTs were deployed in Kenepuru Stream for a second period from 26 October 2018 to 31 October 2018 (approximately 5 days) which included about 3 days of baseflow and two rain events of approximately 20 mm and 10 mm lasting about 12 hours and 6 hours, respectively.

6.2.3 Sampling results

The Nalgene bottle samples returned very high concentrations of suspended sediment at all three sites, with high variability between the two samples from Kenepuru Stream (Table 6-1). The nitrate-N concentrations were slightly lower than median concentrations recorded from 12 months of grab sampling in these streams but within the reported range (Milne & Morar 2017). The pattern observed for the Nalgene bottles of lower concentrations in Mitchell Stream, mid-range in Kenepuru Stream and highest concentrations in Porirua Stream was consistent with that identified from previous grab sampling.

The DGT results (Figure 6-2) showed that the Mitchell Stream site recorded the highest zinc concentrations during the deployment and this was the only site where the current default ANZ water quality guideline (ANZG 2019) for zinc of 8 µg/L (not adjusted for site-specific water hardness)[17] was exceeded. This one-off result is in contrast to results from the earlier grab sampling that showed median zinc concentrations were higher in Porirua Stream than Mitchell Stream (Milne & Morar 2017).

[17] At the time of this report, this is the same value as ANZECC (2000).

Table 6-1: Nalgene bottles water quality results for Porirua Stream and two tributaries collected on 25 October 2018.

Stream	Bottle height (mm)	Suspended Sediment Concentration (mg/L)	Total N (mg/L)	Nitrate-N + Nitrite-N (mg/L)	Total P (mg/L)	Dissolved copper (µg/L)	Dissolved zinc (µg/L)
Mitchell Stream	100	850	7.7	0.16	1.75	2.6	42
	200	400	2.8	0.19	0.87	3.3	28
Kenepuru Stream	100	280	1.8	0.62	0.33	1.9	13
	200	1,630	5.2	0.23	1.56	3.0	16
Porirua Stream	400	490	2.8	0.78	0.58	2.6	35
	500	490	3.1	0.55	0.62	3.2	41

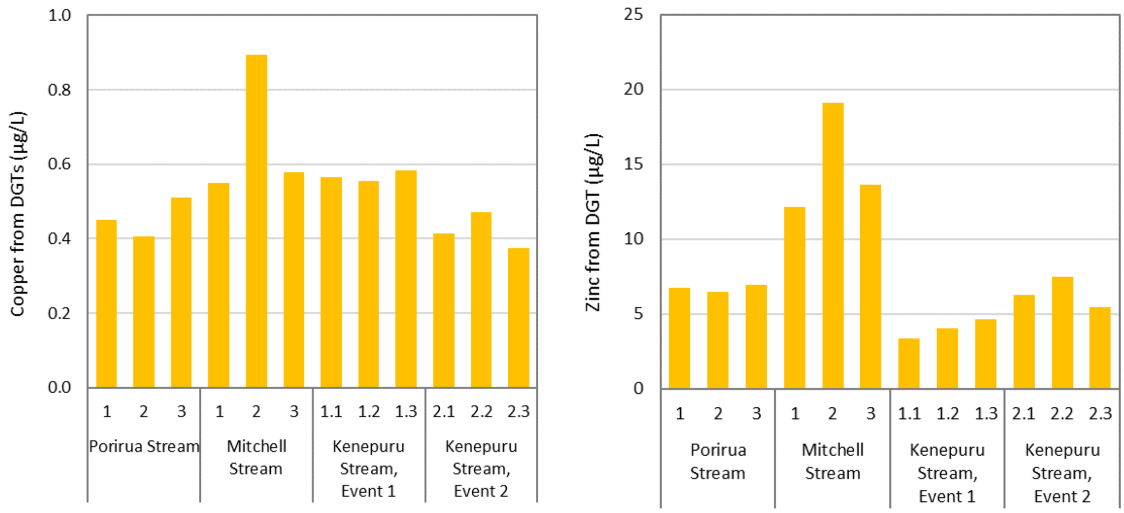

Figure 6-2: Copper (left) and zinc (right) concentrations from DGTs deployed in triplicate in Porirua Stream and tributaries over 24 to 26 October 2018 and 26 to 31 October 2018 (Kenepuru Stream only).

6.2.4 Trial findings

The zinc concentrations obtained using DGTs, integrated across the storm event, provided increased certainty for comparing between sampling locations and investigating sources. The devices were easy to deploy in these locations demonstrating to GWRC their potential use for sampling at multiple locations within a catchment.

6.3 Otepuni Creek, Invercargill

6.3.1 Background

Otepuni Creek is an urban stream in Southland that runs through the middle of Invercargill City and discharges into the lower Waihopai River as the river joins the New River Estuary. The headwaters extend to the east of the city where the catchment is flat and dominated by pastoral land use, including dairy farming. Environment Southland has a water quality monitoring site in the lower creek close to its confluence with the Waihopai River. The data at this site indicate poor water quality, with high *E. coli*, nitrate-N and DRP concentrations and low visual clarity[18]. Invercargill City

[18] https://www.lawa.org.nz/explore-data/southland-region/river-quality/waihopai-stream/otepuni-creek-at-nith-street/

Council (ICC) has monitored copper and zinc at three locations in the stream and the data indicate a general increase from upstream to downstream, with higher concentrations during wet weather than dry (Fountain et al. 2016). However, the monitoring to date has been restricted to total metals with no assessment of the dissolved or bioavailable component.

Environment Southland wished to trial both Nalgene bottles and DGTs to understand whether they would be suitable devices for catchment investigations and for assessing contaminants from stormwater discharges into the stream.

6.3.2 Sampling methods

Environment Southland staff deployed single Nalgene bottles attached to waratahs at three locations in the stream, including a site immediately upstream of the urban area (Figure 6-3 and 6-4, left), for measurement of suspended sediment concentration (SSC) and *E. coli*. Bottles were also attached to the grill of two major stormwater outlets discharging into the stream (Figure 6-4,right). The Nalgene bottles and DGTs were installed on the morning of 4 December 2018 for expected rain in the afternoon and/or overnight. DGTs for metals and nitrate-N were deployed (in triplicate) at only the upstream and downstream site and at one stormwater outlet. A TidbiT® temperature logger was installed at one stream site. Grab samples were collected from the upstream and downstream Otepuni Creek sites during DGT deployment and retrieval for analysis of dissolved organic carbon (DOC).

Figure 6-3: Sampling locations in Otepuni Creek and at two stormwater outlets.

At the middle and downstream site, the minimum height for Nalgene bottle deployment was dictated by the tidal nature of the stream at that point; heights were selected of 45 mm and 35 mm above the tidal range at the middle and downstream site, respectively. The upstream site is not affected by tides and the bottle was deployed at a height of 60 mm above the baseflow stream level.

The Nalgene bottles were removed the next morning and the DGTs were removed after a further day (deployment of 43 hours). Approximately 14 mm of rain was recorded at the Invercargill Airport climate station from 4 pm on the afternoon of deployment to the next morning, including a period of 5.8 mm per hour for 2 hours. There was no further rain before the DGTs were removed. The DGT deployment therefore covers a small rain event and some period of baseflow after the event.

 

Figure 6-4: Nalgene bottles deployed on a waratah in Otepuni Creek (left) and attached to the grill of a stormwater outlet (right). [Photos: Nuwan DeSilva]

6.3.3 Sampling results

The Nalgene bottle results indicated an increase in SSC and indicator bacteria from the upstream to downstream sites, as previously shown in data from grab sampling. *E. coli* concentrations in the stormwater discharges were also high (Table 6-2), suggesting these are likely sources of bacteria to the lower reaches of the stream.

The DGT zinc concentrations were within the range measured by ICC for total zinc and were well above the ANZ (ANZG 2019) default guideline value for 95% protection (8 µg/L, not adjusted for site-specific water hardness) at the downstream site. DGT copper concentrations increased somewhat downstream and were higher in the stormwater outflow, but remained below water quality guidelines at all three sites. This likely reflects the high concentrations of DOC in the Otepuni Creek, measured at 15-18 mg/L in the grab samples.

The DGT nitrate-N concentrations were similar at the two sites tested and consistent with concentrations measured during wet weather flows by ICC (Fountain et al. 2016).

Table 6-2: Water quality in Otepuni Creek and two stormwater outlets.

	"First-flush" from Nalgene bottles		Time-weighted average from DGTs		
	Suspended sediment (SSC, mg/L)	*Escherichia coli* (cfu / 100mL)	Nitrate-N (mg/L)	Copper (µg/L)	Zinc (µg/L)
Otepuni upstream	< 10	2,700	0.97	0.30	6.4
Otepuni mid	19	2,000	Not sampled	Not sampled	Not sampled
Otepuni downstream	154	18,000	0.95	0.44	34
Stormwater outlet 1	73	13,800	Not sampled	0.70	42
Stormwater outlet 2	220	27,000	Not sampled	Not sampled	Not sampled

6.3.4 Trial findings

The results of the trial were consistent with results from manual grab sampling programmes conducted over several years, suggesting the methods are suitable for the council's purposes. The DGTs provided a better assessment of the bioavailability of copper and zinc than the current ICC monitoring data. The latter suggested that both copper and zinc concentrations exceed water quality guidelines whereas the concentrations from the DGTs suggest potential for toxicity from zinc only.

The Nalgene bottles were deployed at different heights above the water's surface and the largest height was at the upstream site. When sampling at multiple sites in a single stream, it would be best to deploy all bottles at the same height above the water level (assuming sites have similar stream widths and flow) or slightly higher as you move from upstream to downstream, to account for increased flows (and water level) at the downstream site.

The water level at the most downstream location varies with tide and therefore the Nalgene bottles were deployed above the high tide level to prevent filling during high tide. In locations like this, the part of the storm sampled depends on the timing of the storm in relation to the tide. If the storm event coincides with low tide, the sample would be collected during a peak flow, as a large rise in water level would be required to fill the bottle. But if the storm event coincides with high tide, the sample may be collected during the initial parts of the storm, as a smaller rise in water level is required to fill the bottle. In such locations it is difficult to deploy bottles to target a storm event related water level. However, if these sites cannot be avoided, water level instruments should be deployed alongside the bottles. This record can be used to determine the point of the event that the bottle sampled.

The trial highlighted difficulties in sampling stormwater outlets adjacent to streams. In some locations, the stream flow increases to the height of the stormwater outlet to “drown out” the outlet. When DGT troughs are deployed in such circumstances, it may not be clear whether the flow is coming from the stream or the stormwater outlet. Sampling may need to be undertaken at a location further up in the stormwater network. This is less likely to be an issue for the Nalgene bottles when deployed to fill with initial flows from the outlet as these should remain sealed when the stream level rises.

A further potential complication revealed in this trial concerns using these methods in macrophyte dominated streams; macrophytes that wash off during storm events can be entrained on the waratahs and potentially block the inlet of the Nalgene bottle or restrict flow to the DGTs. It is recognised that in many streams this will be unavoidable, and therefore any macrophytes on the devices during retrieval will need to be noted and assessed for the likelihood of interfering with the devices.

6.4 Urban streams in Napier and Hastings

6.4.1 Background

Although Hawke's Bay Regional Council (HBRC) monitor many of their urban streams, there is no routine monitoring for metals; the only information available is from short-term surveys. These surveys suggested that Ruahapia Stream has very high metal concentrations compared to other streams in the Hawke's Bay region. The HBRC wanted more information to help assess potential toxicity to aquatic biota.

6.4.2 Sampling methods

HBRC staff undertook sampling in three different streams in Napier and Hastings (Figure 6-5). The catchment of Ruahapia Stream includes an area of industrial land use, while the catchment of Georges Drain includes primarily residential land use and Karamu Stream comprises mixed rural and urban land use. The sampling was undertaken twice, with the first deployment on 22 February 2019 for 4 days and the second on 26 March 2019 for 7 days. Both deployments included a period of approximately 24 hours of storm flows with the remainder at baseflow.

Figure 6-5: Sampling locations in Georges Drain, Napier (left); and Ruahapia Stream and Karamu Stream, Hastings (right).

In each stream, two Nalgene bottles were attached to waratahs at different heights. The height of the Nalgene bottles was selected with the aim of sampling from the early stage of the storm (after a small rise in water level, 30-160 mm) and a peak flow (130-420 mm). The deployments heights were based simply on field observations around the likely water level reached during events. In the second event, the upper bottle in Karamu Stream did not fill as it was deployed above the maximum water level reached during that event. Nalgene bottle samples were analysed for total suspended solids (TSS) and total metals.

DGTs for metals and nitrate-N were deployed (in duplicate for the first event and in triplicate for the second event) at each site. Water level and temperature loggers were also installed at each site. For the second event, grab samples were collected at deployment and retrieval and analysed for dissolved copper, zinc, nitrate-N and DOC.

6.4.3 Sampling results

The Nalgene bottle sample results showed much higher concentrations of TSS and total metals in Ruahapia Stream than in either Georges Drain or Karamu Stream (Figure 6-6). Metal concentrations were lowest in Karamu Stream. The pattern between the two samples collected was different for each stream: in Georges Drain, sediment and metal concentrations were higher in the bottle deployed at a greater height; whereas in Ruahapia Stream, TSS and copper concentrations were lower in the bottle at greater height while zinc concentrations did not change. This suggests that the copper may be more closely associated with the sediment and higher flows, whereas zinc may exhibit a first-flush. More sampling would be required to confirm if this is the case.

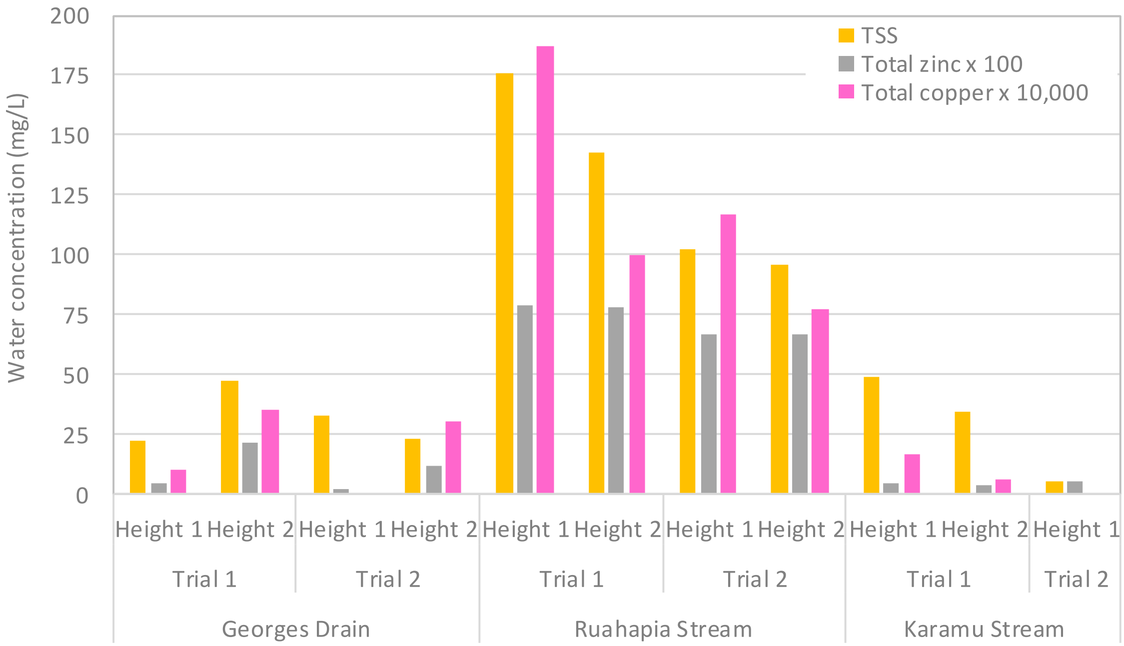

Figure 6-6: Suspended solids, zinc and copper concentrations in Nalgene bottle water samples from three Hawke's Bay urban streams.

The DGT results confirmed the pattern of highest copper and zinc concentrations in Ruahapia Stream, followed by Georges Drain and Karamu Stream (Figure 6-7). In the second trial, DGT zinc concentrations were about the same as those in grab samples collected at deployment and retrieval, reflecting that the three streams were at baseflow for most of that deployment. DGT copper concentrations were lower than the water samples. The DGT metal concentrations measured in Ruahapia Stream were above default ANZ water quality guidelines (for 95% level of protection) for both copper and zinc (1.4 µg/L and 8 µg/L, respectively, not adjusted for site-specific hardness) during at least one deployment.

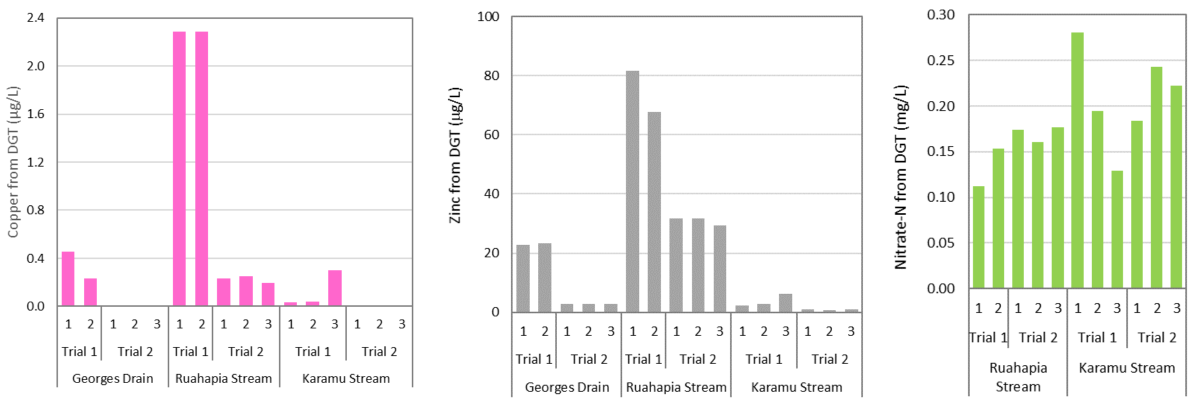

Figure 6-7: Copper (left), zinc (middle) and nitrate-N concentrations measured in DGTs deployed in three Hawke's Bay streams in February and March 2019.

The DGTs deployed at Georges Drain did not contain measurable nitrate-N, possibly because of saline influence at the site (nutrient DGTs do not work in brackish or saline waters). Furthermore, the DGTs were all above the water's surface on retrieval. Analysis of the water level logger data showed that the water level at this location fluctuates considerably (Figure 6-8), suggesting the possibility that the DGTs were exposed to the air multiple times during the deployment, causing them to dry out and reduce nitrate-N uptake to concentrations that could not be reliably quantified. This drying out most likely reduced metal uptake as well.

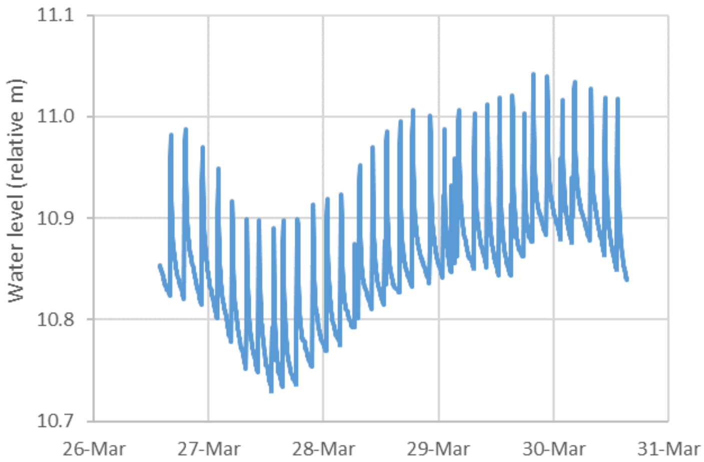

Figure 6-8: Sub-daily fluctuations in water level at the Georges Drain site.

6.4.4 Trial findings

Zinc and copper concentrations were much higher in Ruahapia Stream than in the other two streams sampled. Whilst the elevated metals in this stream had been previously identified, the use of DGTs – which are more reflective of bioavailable metals – highlights the potential risk to aquatic biota, which was not easily assessed from previous monitoring.

The practical learnings from this trial were three-fold. Firstly, if there is any chance that the waterbody of interest has saltwater influences, salinity should be measured prior to deploying DGTs for nitrate-N. Secondly, both the Karamu Stream and Georges Drain sites were very slow-flowing reaches, which are not ideal for DGT measurements. Such locations should be avoided where possible (for example sampling could have been conducted further upstream in Karamu Stream), or DGTs with multiple gel thickness could be used to improve data accuracy. Thirdly, knowledge of water levels is essential to ensure DGTs remain underwater throughout the deployment and to ensure bottles are not filled due to tidal fluctuations. If there is suggestion of tidal fluctuation, water levels could be measured for a brief time (e.g., over 24-48 hours to include several tidal cycles) prior to device deployment.

6.5 Avon River and tributaries, Christchurch

6.5.1 Background

Environment Canterbury collaborated with Christchurch City Council (CCC) to focus stormwater sampling efforts, including the trial of new sampling devices, in the Ōtākaro/Avon River catchment. Addington Brook and Riccarton Stream are two tributaries of the Ōtākaro/Avon River that routine monitoring has shown have high concentrations of contaminants, including metals, nutrients, sediment and *E. coli* – particularly during wet weather.

The objectives were to compare the concentrations of dissolved zinc, dissolved copper and phosphorus between the Riccarton and Addington tributaries, which are priority catchments for the Christchurch-West Melton Zone Committee; and gather data to assess the relative contribution of these contaminants from each of the tributaries to the Ōtākaro/Avon River.

6.5.2 Sampling methods

The sites selected for DGT deployment were near existing CCC monitoring sites within each tributary and at sites upstream and downstream of each confluence with the mainstem of the Ōtākaro/Avon River, within the Botanic Gardens (Figure 6-9). The DGTs were deployed on 28 May 2019 prior to a forecast rain event (forecast 10 mm, actual 1.4 mm) and left for a period of 7 days, which also included baseflow conditions and a large rain event (>90 mm) over Queen's Birthday weekend. The DGTs were analysed for dissolved zinc, copper and phosphorus.

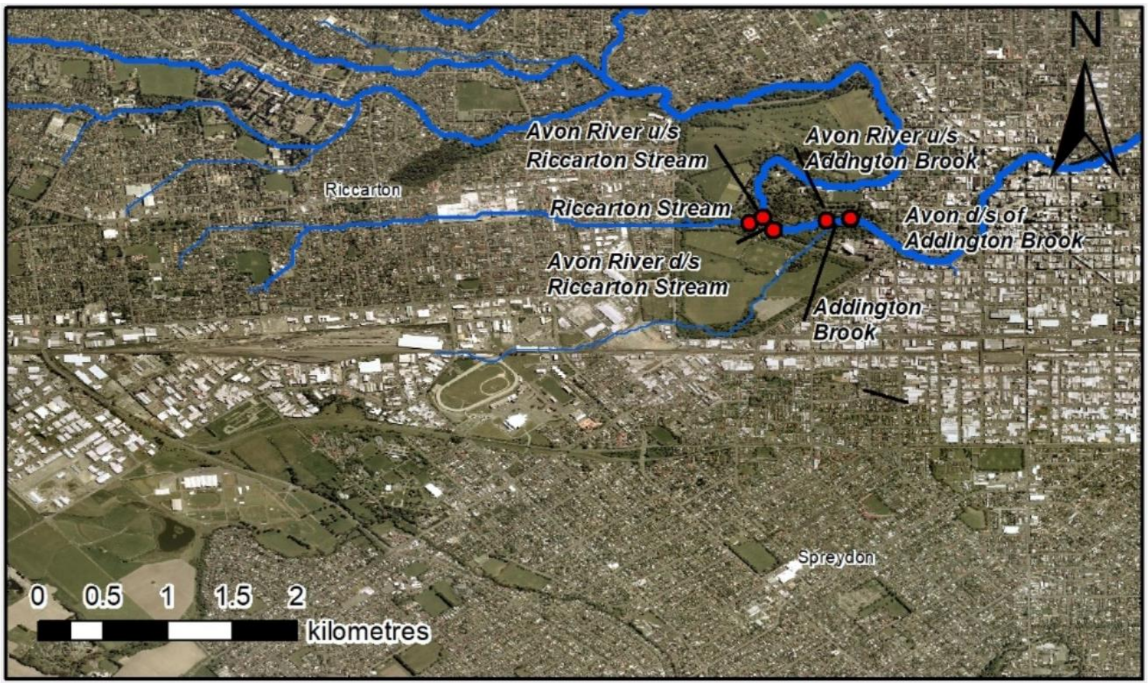

Figure 6-9: Sampling locations in the Avon River and its tributaries, Riccarton Stream and Addington Brook.

6.5.3 Sampling results

Higher concentrations of copper, zinc and phosphorus were measured in the two tributaries (Riccarton Stream and Addington Brook) compared to the Avon River at locations upstream and downstream of these tributaries (Figure 6-10 and Figure 6-11). In particular, zinc concentrations in the Avon River seem to be influenced by the two tributaries and were at higher concentrations downstream of each tributary than upstream (Figure 6-10). Phosphorus concentrations were more variable between replicates.

In the two tributaries, zinc concentrations measured by the DGTs were above ANZ default guidelines of 8 µg/L and also above the hardness modified trigger value of 29 µg/L used by CCC in the Avon River catchment (Margetts & Marshall 2018). Copper concentrations were below both default guidelines and hardness modified trigger values.

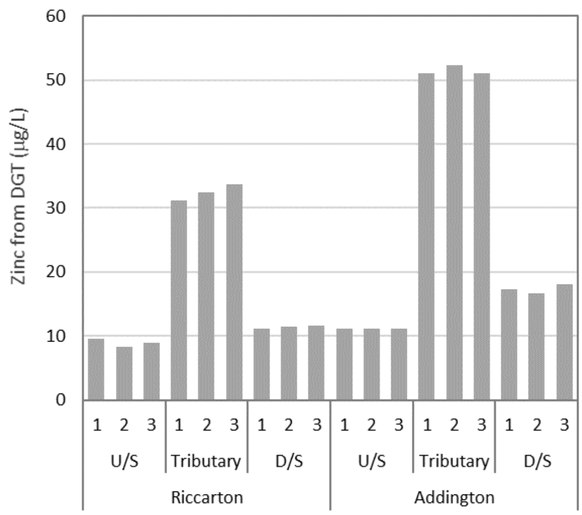

Figure 6-10: Copper (left) and zinc (right) concentrations measured in DGTs deployed in the Avon River and two tributaries in May 2019.

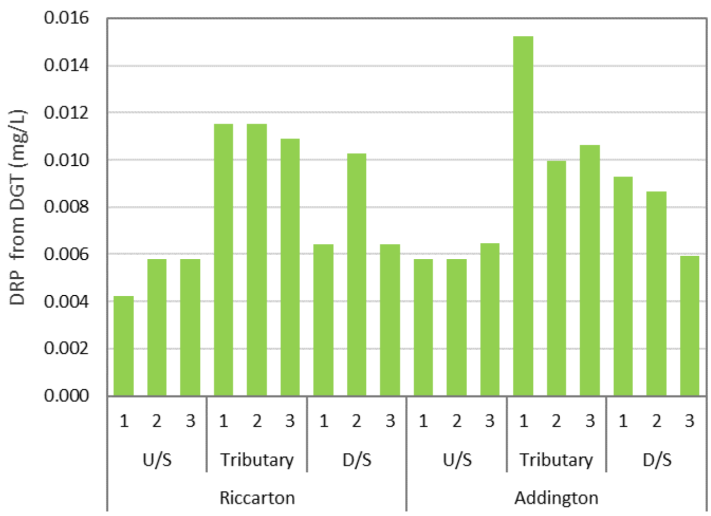

Figure 6-11: Phosphorus concentrations measured in DGTs deployed in the Avon River and two tributaries in May 2019.

6.5.4 Trial findings

The zinc results in the two tributaries were similar to those measured previously by CCC during monthly grab sampling (Margetts & Marshall 2018). Concentrations in the Avon River were also within the range observed at sites nearby. The use of the DGTs, integrating across the deployment period rather than a single grab sample during an event, provided Environment Canterbury staff with confidence that the results of higher concentrations (especially for zinc) downstream of the tributaries were genuine (and not simply due to sampling different parts of the hydrograph).

Phosphorus concentrations were more variable between the replicate DGTs and were also affected by high phosphorus concentrations in the blank extracts (1.1 mg/L) that were over 50% of the concentration of some sample extracts (1.8-3.4 mg/L). By contrast, copper and zinc concentrations in the blanks were less than 50% of that in the samples with lowest concentrations, and less than 30% of the median concentration measured (10% for zinc). This trial was the first time using these DGTs and the extraction and analysis process. Before these DGTs are used routinely, the source of this phosphorus in the blanks should be identified and ideally reduced.

6.6 Urban streams in Tauranga

6.6.1 Background

Within the Bay of Plenty, urban growth is occurring at a high pace, particularly in Tauranga City. Without sufficient mitigation measures, there is a risk that stream ecosystems will degrade with ongoing urban development (Suren pers. comm. 2019)[19]. As part of its State of the Environment monitoring programme, Bay of Plenty Regional Council (BoPRC) monitor macroinvertebrate fauna at eight urban stream sites. The results of this monitoring have shown that ecological health is degraded when compared to streams draining other land uses. A potential cause of this is toxicity associated with metals derived from stormwater – copper and zinc – however there is very little information on metal concentrations in these streams to assess this (Suren pers. comm. 2019).

A study was established by BoPRC to deploy DGTs in urban streams and non-urban control sites to quantify copper and zinc concentrations. In addition, stream bed sediment samples were collected from each site and copper and zinc were measured in these as a further measure of metal contamination.

The aim of the work was to provide a broad synoptic survey of ecological, sediment and water quality conditions in the selected urban streams. The survey might also identify potential hot spot areas of high copper and zinc contamination that may require more in-depth targeted studies to determine the source of any hotspots.

6.6.2 Sampling methods

Prior to a forecast rain event, DGTs were deployed (in duplicate at two sites and in triplicate at the remainder) at nine locations (Figure 6-12) over a period of two days (5 and 7 May 2019). The devices were left for approximately nine days during which 10-12 mm of rain fell (as recorded at the Tauranga Airport climate station). The DGTs were then retrieved and analysed for copper and zinc.

6.6.3 Sampling results

The DGT results indicated copper and zinc concentrations were low (below analytical detection) at the sites upstream of the urban areas. Copper concentrations were also low at many of the urban sites. There were three streams with much higher zinc concentrations than others, measuring 7.7 to 13 µg/L, close to or above the default ANZ water quality guideline of 8 µg/L. This suggests the potential for toxic effects in these streams. Further sampling is required to confirm if this is the case.

6.6.4 Trial findings

The DGTs were found to be relatively simple to deploy and very good consistency in results was found between the duplicates and triplicates. However, only a single field blank was used for this trial and this contained both copper and zinc at concentrations similar to those in DGTs from the upstream control sites. This study was the largest trial of DGTs, spanning nine sites in Tauranga and sites in other parts of Bay of Plenty and demonstrated the need for more guidance on the number of field blanks to use.

Reinforcing bar was used to deploy the DGT holders and in some cases the holders rotated around and became perpendicular to the flow, indicating that y-shaped waratah posts are more suitable for this task.

[19] Dr Alastair Suren, Freshwater Scientist, Bay of Plenty Regional Council.

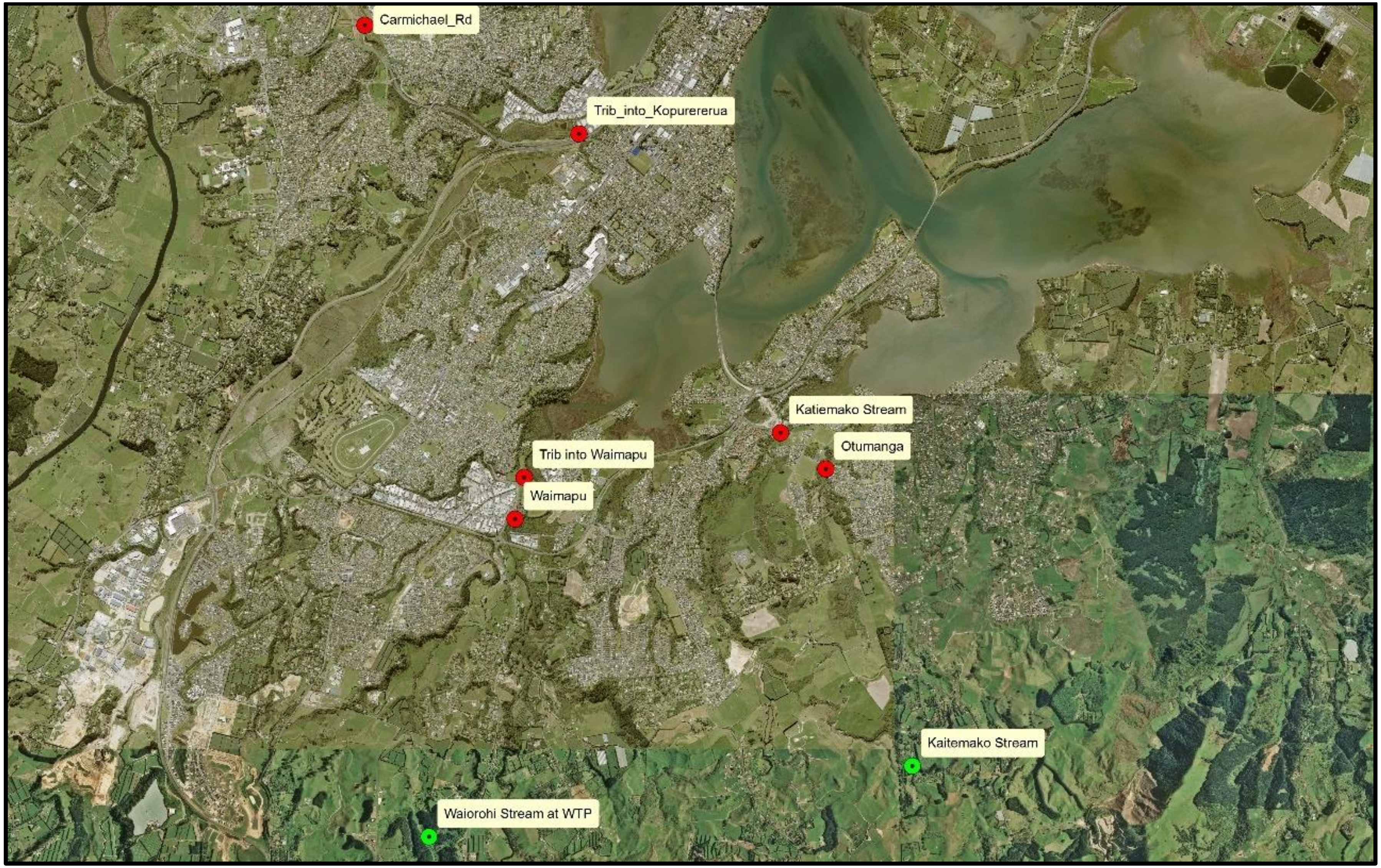

Figure 6-12: DGT sampling locations in Tauranga. Red markers indicate urban stream sites and green markers indicate upstream control sites. Map supplied by BoPRC.

Table 6-3: Median copper and zinc concentrations from DGTs deployed in duplicate or triplicate in urban and control stream sites in Tauranga during May 2019. ND = not detected (concentration in sample DGT less than in blanks).

Sampling location	Copper (µg/L)	Zinc (µg/L)
Control sites, upstream of urban areas		
Kaitemako Stream	ND	ND
Waiorohi Stream at WTP	ND	ND
Urban streams		
Downstream in Owens Park	ND	1.4
Katiemako Stream	ND	1.3
Otumanga Stream	ND	9.1
Stream on Carmichael Rd	ND	0.18
Kopurererua Tributary	0.20	7.7
Waimapu Tributary	0.17	12.8
Waimapu Stream	ND	ND

In many locations it was difficult to find reaches with moving water, due to the flat topography and proximity to the coast, which is common for many of New Zealand's (lowland) urban areas. This results in more uncertainty in the data for these sites, which could be reduced (if desired) by using DGTs with multiple gel thicknesses (although this comes with additional cost).

The DGT deployment was carried out in conjunction with a stream bed sediment survey. In combination, the information has provided BoPRC with a good characterisation of the state of metal concentrations in urban streams. Both methods provide an integrated approach to sampling, rather than representing a single snapshot in time. The two methods are complimentary as DGTs may have increased uncertainty in low gradient waters, but stream sediments are typically more homogenous here. Conversely, DGTs would have higher certainty in upper stream reaches, where sediments are frequently more heterogenous and less comparable.

6.7 Synthesis

The Phase 2 trials provided an opportunity for several regional councils to use the sampling devices and gather information on selected urban environments. Feedback provided on the Nalgene bottles and DGTs was used to refine the guidance that was presented in Part 1 and the appendices of this document.

7 Summary

Stormwater discharges are a major influence on water quality in urban streams. Stormwater contains a wide range of contaminants, depending on the land use and the specific activities undertaken within the catchment, but the typical contaminants of concern for an aquatic receiving environment are sediment, nutrients, copper, zinc and faecal indicator bacteria. The concentrations of these contaminants in both stormwater and streams vary considerably from location to location and are weakly related to the amount of impervious surface in a catchment. Contaminants also vary considerably according to stream or stormwater flow, with many contaminants present at higher concentrations during high flows, or demonstrating a first-flush, with higher concentrations during initial stages of a storm event. The season, antecedent conditions, rainfall depth and intensity, event duration and time since onset of rainfall all influence contaminant concentrations.

This high variability necessitates sampling methods that are more intensive than monthly grab sampling, to provide data that is a) comparable between sites, b) comparable to water quality guidelines or c) suitable for calculating catchment loads. Manual grab sampling can be used in most locations and for most water quality variables but requires staff to be available on-site rapidly after rainfall begins and there is a clear disadvantage relating to samples being only a 'snapshot' in time of the varying concentrations. Nalgene bottles share this latter disadvantage but can be deployed prior to rain events, at pre-defined water levels (heights) to capture a defined part of a storm event and at increasing heights to collect multiple samples and capture temporal variability in concentrations. Nalgene bottles are not well-suited for tidal locations and cannot be used where flows do not change significantly during events (e.g., in a very wide flat stream). In contrast, DGTs provide a time-weighted average concentration, integrated across the entire deployment period. They can be used in many locations but are only suited to dissolved constituents. Automatic samplers can be used in many locations and are suited to most water quality variables, but have higher installation and operation costs.

Guidance on the selection of these methods has been provided for 4 key monitoring objectives:

Objective 1: Compare water quality to guidelines, standards or limits based on mean or median concentration.

Objective 2: Compare water quality to guidelines, standards or limits based on maximum concentration.

Objective 3: Compare concentrations between multiple locations, within a single stream, catchment or in separate catchments.

Objective 4: Measure Event Mean Concentrations (EMC) or loads at one or more locations within a catchment or in separate catchments.

For each of these objectives, the suitability of each sampling method was evaluated taking into account both accuracy and cost requirements. Autosamplers remain the most accurate method for many objectives but at higher cost. For the objective of comparing to water quality guidelines, DGTs can provide a cost-effective option for some contaminants of interest with accuracy that rivals autosamplers. For assessing maximum concentrations, an array of Nalgene sampler bottles deployed at increasing heights can be a cost-effective alternative to an autosampler with minimal loss in accuracy. For comparing between multiple locations, DGTs are a cost-effective and reliable option for some contaminants of interest; and a Nalgene bottle array used with hydrological data to select comparable samples, can be an efficient option for contaminants that cannot be measured by DGTs. For the assessment of EMCs or contaminant mass loads, autosamplers remain the most accurate option. However, for specific objectives where highly accurate information is not required, DGTs or Nalgene bottles, deployed along with hydrological instrumentation may provide sufficient information.

The trials showed that all five sampling devices could replicate the results from autosamplers for some contaminants but not for all. At times, Nalgene bottles demonstrated discrepancies for suspended solids (and other particulate-associated contaminants) but generally reasonable agreement for dissolved nutrients and metals. A major advantage of Nalgene bottles is their suitability for deployment in many locations and for analysis of multiple contaminants of interest. DGTs demonstrated high precision (low variation between replicates) and good agreement with autosampler concentrations for zinc; but poor agreement for copper in streams, especially in locations with high DOC. Further trials in additional locations confirmed these findings.

The other three devices trialled (a modified siphon sampler, ChemCatcher passive sampler and Sorbicell passive sampler) demonstrated potential use for stream and stormwater sampling based on agreement with the autosampler results. However, for each of these devices, there were practicalities relating to their deployment that currently restrict their further use, such as insufficient flow through the device, sampler damage or sample loss. If these practicalities can be overcome through further development, the devices may be suitable for monitoring urban waters.

Based on the trials of the devices and the guidance provided in this document, urban streams and stormwater can be sampled using methods that will provide the reliable data required for improved water management.

8 Further reading

<u>Grab sampling</u>

NEMS (2019). Water Quality Part 2 of 4: Sampling, Measuring, Processing and Archiving of Discrete River Water Quality Data. *National Environmental Monitoring Standards*. 85 p. http://www.nems.org.nz/assets/Documents/NEMS-60/Water-Quality-Part-2-Sampling-Measuring-Processing-and-Archiving-of-Discrete-River-Water-Quality-Data.pdf

<u>Nalgene bottles</u>

Charters, F. (2016). Stormwater contaminant load monitoring and modelling of the Addington Brook catchment. Environment Canterbury Regional Council Report No. R16/11. Christchurch. 85 p.

Poudyal, S.; Cochrane, T.A.; Bello-Mendoza, R. (2016). First-flush stormwater pollutants from carparks in different urban settings. Water (Journal of Water New Zealand) November/December 2016: 24-27.

<u>DGTs</u>

Brief background and guidance on use:

https://www.dgtresearch.com/background-and-theory-of-dgt/

https://www.dgtresearch.com/guides-to-using-dgt/

More technical details and guidance:

Davison, W. (ed.) (2016). Diffusive Gradients in Thin-Films for Environmental Measurements. *Cambridge Environmental Chemistry*. Cambridge University Press, United Kingdom. 297 p.

Jolley, D.; Mason, S.; Gao, Y.; Zhang, H. (2016). Practicalities of working with DGT. *In*: Davison, W. (ed.). Diffusive Gradients in Thin-Films for Environmental Measurements, pp. 263-290. *Cambridge Environmental Chemistry*. Cambridge University Press, United Kingdom.

Österlund, H.; Widerlund, A.; Ingri, J. (2016). Applications in natural waters. *In*: Davison, W. (ed.). Diffusive Gradients in Thin-Films for Environmental Measurements, pp. 123-145. *Cambridge Environmental Chemistry*. Cambridge University Press, United Kingdom.

Using DGTs in stormwater ponds:

Brydon, J.; Oh, I.; Wilson, J.; Hall, K.; Schreier, H. (2009). Evaluation of Mitigation Methods to Manage Contaminant Transfer in Urban Watersheds. *Water Quality Research Journal 44(1)*: 1-15.

Using DGTs in slow-flowing reaches:

Uher, E.; Tusseau-Vuillemin, M.H.; Gourlay-France, C. (2013). DGT measurement in low flow conditions: diffusive boundary layer and lability considerations. *Environmental Science-Processes & Impacts 15(7)*: 1351-1358.

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Uher, E.; Compere, C.; Combe, M.; Mazeas, F.; Gourlay-France, C. (2017). In situ measurement with diffusive gradients in thin films: effect of biofouling in freshwater. Environmental Science and Pollution Research 24(15): 13797-13807.

Automatic sampling

Fassman, E.A. (2010). Sampling Requirements and Reporting Statistics for the Proprietary Devices Evaluation Protocol Development. Prepared by UniServices for Auckland Regional Council. Auckland Regional Council Auckland Regional Council Technical Report TR 2010/001. Auckland. 137 p.

Gadd, J.; Semadeni-Davies, A.; Moores, J. (2014). Design of Stormwater Monitoring Programmes. Environment Southland NIWA Client Report. p.

Lee, H.; Swamikannu, X.; Radulescu, D.; Kim, S.J.; Stenstrom, M.K. (2007). Design of stormwater monitoring programs. Water Research 41(18): 4186-4196.

Ma, J.S.; Kang, J.H.; Kayhanian, M.; Stenstrom, M.K. (2009). Sampling Issues in Urban Runoff Monitoring Programs: Composite versus Grab. Journal of Environmental Engineering 135(3): 118-127.

McCarthy, D.T.; Harmel, D. (2014). Quality assurance /quality control in stormwater sampling. In: Quality Assurance & Quality Control Of Environmental Field Sampling, pp. 98-127.

9 Glossary of abbreviations and terms

ANZ	Australia New Zealand (guidelines for fresh and marine water quality)
CV	Coefficient of variation, a statistical measure of variability. Calculated by dividing the standard deviation by the mean.
DGT	Diffusive gradients in thin films
DOC	Dissolved organic carbon, a measure of the amount of dissolved organic matter in water (may be measured as DNPOC)
EMC, Event mean concentration	A frequently used statistic for reporting contaminant concentrations in stormwater, defined as the total contaminant load divided by the total runoff volume for any given event. When multiple samples are collected during a single event, this can be calculated using the formula: $EMC = \frac{total\ pollutant\ loading\ per\ event}{total\ runoff\ volume\ per\ event} = \frac{\sum_{i=1}^{n} C_i V_i}{V}$ Where *EMC* = event mean concentration in mg/L; C_i = pollutant concentration at time *i*, mg/L; V_i = runoff volume proportional to the flow rate at time *i*, in L; *V* = total runoff volume per event, L; and n = total number of samples during a single storm event
Elution factor	The proportion of the metal (or other contaminant) that is extracted using the extraction method. This differs for each metal and for the strength and amount of acid.
First-flush	When the mass of contaminant discharged during the initial part of the storm is higher than expected for that volume of water (i.e., disproportionately high) when compared to the remainder of a storm event
Flow-weighted mean or flow-weighted average	A flow-weighted mean is a measure of the average concentration over time and is relevant for comparing discharges between locations and in relation to downstream receiving environments. For a single event, this is identical to an EMC. A flow-weighted average concentration can be obtained by compositing all samples collected on a volume-proportional basis; or calculated from samples analysed discretely as above for an EMC.
Labile	For DGTs, labile refers to metals in the free form, not attached to inorganic or organic ligands (e.g., Cu^{2+}) and those that can rapidly convert to such form. This generally means metals that are not associated with large organic ligands (but are dissolved) or attached to particulates.
Manhole	Opening to a confined space (stormwater chamber in this case) within a piped system
Nalgene	Nalgene Storm Water Sampler bottle
PAHs	Polycyclic aromatic hydrocarbons; a group of more than 100 compounds that are comprised of multiple aromatic rings. Found in some petroleum products and as a product of combustion

SoE	State of the Environment – the typical name given to long-term water quality monitoring programmes operated by regional councils
SSC	Suspended sediment concentration, a measure of sediment within a water sample, measured by filtering the entire water sample
Stormwater outlet	End of a stormwater pipe or network where water leaves the built stormwater system and enters the natural environment, at a watercourse, lake or beach, pond etc
Tidal gates	Gate or valve device at the outlet of a pipe or channel to prevent water backflows from a watercourse or the sea from tidal effects
Time-proportional	Time-proportional sampling refers to samples collected at equal intervals in time. The mean of measurements of these samples provides a time-weighted average.
TPH	Total petroleum hydrocarbons, a term used for the mixture of hydrocarbons found in crude oil and other petroleum products
TSS	Total suspended solids, a measure of the amount of solids in solution in a water sample. Measured by filtering a sub-sample of the water sample
TWA, time-weighted average	TWA is used as a measure of the average concentration over time, and is used for assessing exposure (for ecological and human health risks). A DGT provides this average directly by integrating over time. When multiple samples are collected during a single event, this can be calculated using the formula: $TWA = \frac{\sum_{i=1}^{n} t_i C_i}{t}$ Where *TWA* = event mean concentration in mg/L; t = duration of event, L; t_i = duration of concentration *i*,; C_i = pollutant concentration at time *i*, mg/L; and n = total number of samples during a single event
Volume-proportional	Volume-proportional sampling refers to samples collected after equal intervals of water volume (calculated from the flow and elapsed time). The mean of measurements of these samples provides a flow-weighted average or EMC.
Wingwall	Wall at an inlet or outlet from a pipeline or culvert designed to prevent erosion of the surrounding soil. Usually made of concrete.

10 References

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Appendix A Instructions for Nalgene bottles

See also our instructional video on how to deploy Nalgene sampler bottlers in streams and stormwater outfalls: https://www.niwa.co.nz/sampling-urban-streams-stormwater

A1. Essential things to know about Nalgene Storm Water Sampler bottles

A1.1. What are Nalgene bottles?

Nalgene Storm Water Sampler bottles (Nalgene bottles, Figure A-1) are commercially produced bottles that collect a grab sample of water without the need for personnel on site. The bottles are deployed above the water level prior to a storm event, fill once water either flows over them (e.g., in the stormwater grate) or reaches the intake level when deployed into a stream or drain. They close off by means of a float valve or ball cock, preventing any further water from mixing with the sample.

The debris cassettes supplied with the bottles can be removed if there is a high chance of leaves and other suspended (organic) material clogging the inlet and preventing the collection of a water sample.

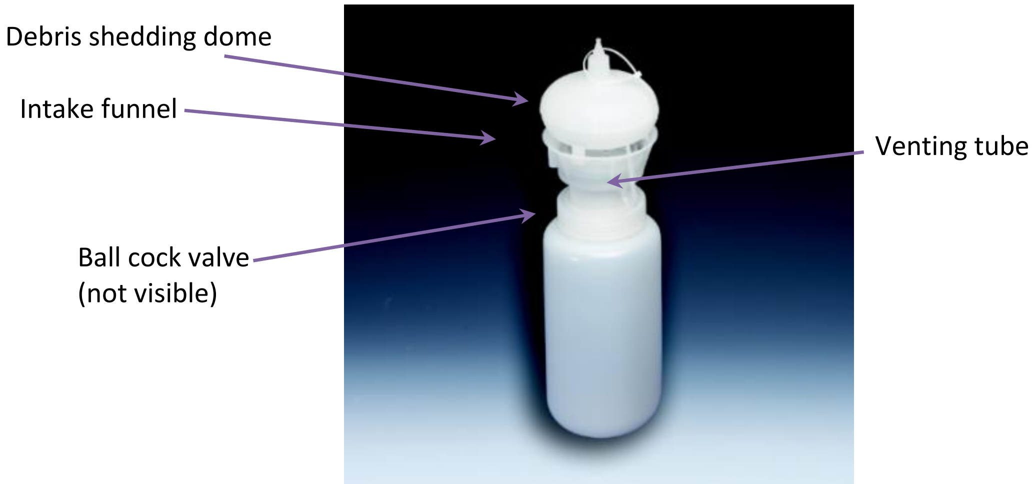


Figure A-1: Nalgene® Storm Water Sampler bottles. Image from Thermoscientific [20].

A1.2. How will a Nalgene bottle help me?

The sampler bottles collect a single 'grab' sample once the water level reaches the bottle intake level (Figure A-2a). They are designed for, and best suited to, collecting a sample from the first-flush in a stormwater location because they can be deployed well before a rain event, and at multiple locations. This avoids the requirement to rush out to a site as soon as rain begins or for multiple personnel when sampling multiple sites. The bottles can also be used for collecting samples at high flows in streams, and you could deploy a series of bottles at increasing heights to collect across the rising limb of a storm event (Figure A-2b).

[20] Nalgene storm water sampler with HDPE bottle. http://www.thermoscientific.com/content/tfs/en/product/nalgene-storm-water-sampler-hdpe-bottle.html?ca=stormwater

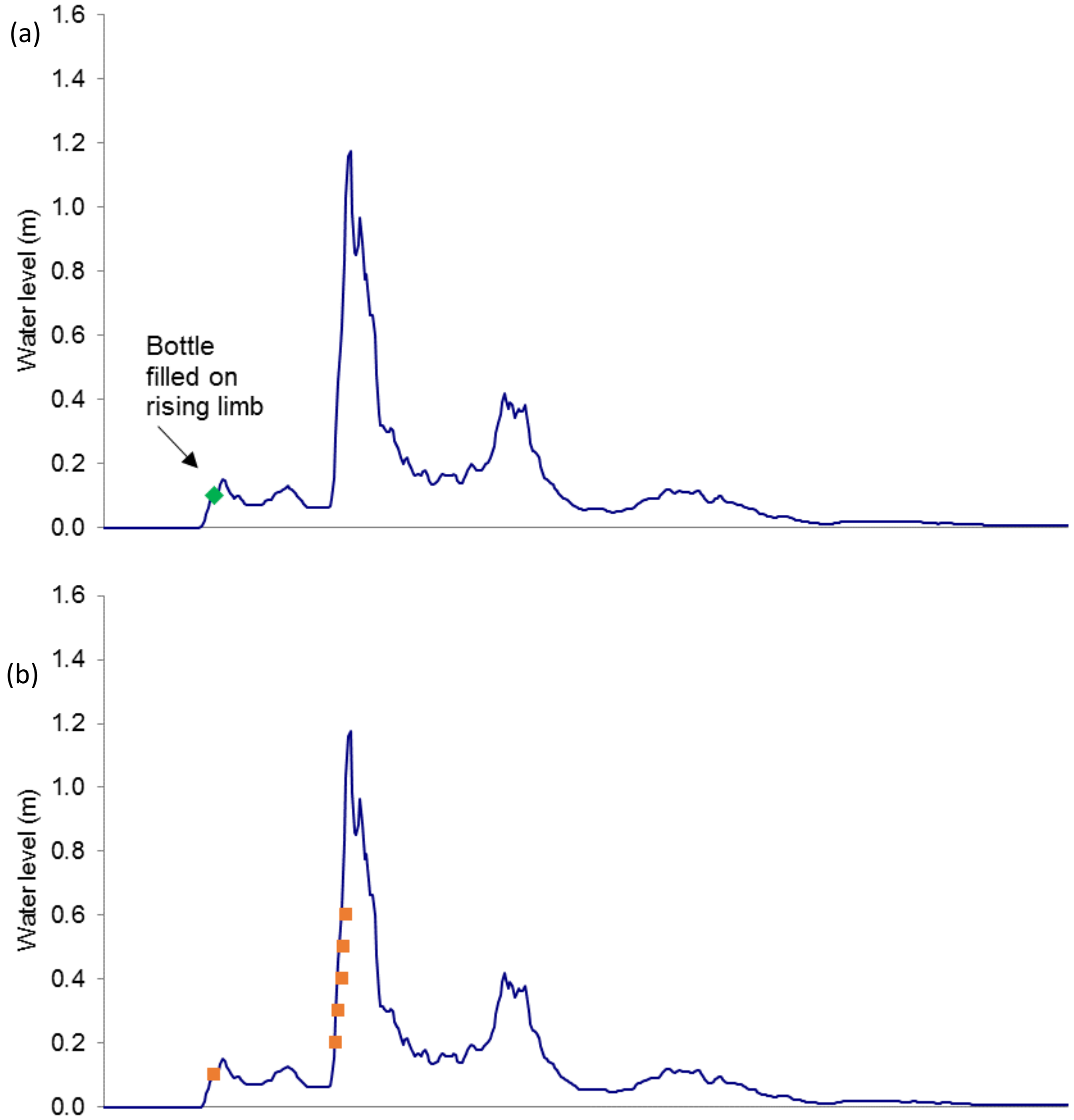


Figure A-2: Stormwater hydrographs indicating timing of a) single bottle deployed at a height of 0.1 m or b) multiple bottles deployed from 0.1 m to 0.6 m.

A1.3. How do you use a Nalgene bottle?

The bottles need to be deployed in the field prior to a rain storm. When the flow rises, they collect a grab sample and the ballcock valve closes. They then need to be retrieved and capped. The water sample retained can be shipped to a laboratory for analysis of any kind of contaminant. For organic contaminants, the plastic bottles can be replaced with glass bottles.

Figure A-3: Deployment in a stream showing the deployment height.

A1.4. Where can I use a Nalgene bottle?

- Streams, excluding those that have tidally-influenced flows.
- Stormwater drains.
- Stormwater pipes.
- Pumped stormwater discharges.

The bottles are not suitable for tidal locations as they could fill on an incoming tide, rather than with a storm flow.

A1.5. What else do I need to know?

Some key features of these bottles:

- The bottles are 1 L so they provide sufficient water volume for several analyses, but in very clean water they may not provide enough volume for TSS or SSC as well as many other analyses.
- Glass bottles can also be purchased which would be suitable for measuring organic contaminants such as hydrocarbons (TPH or PAHs) or pesticides.
- The bottles only fill on a rising limb, so they cannot sample the water quality at the end of a storm.
- Multiple bottles can be deployed at different heights to collect samples from first-flush and peak flow (highest water level).
- The bottles fill in about 3 minutes with the debris cassette in place.
- The bottles fill in less than 90 seconds with the debris cassette removed, so they represent a snapshot in time, just like manually collected grab samples.
- The intake funnel is ~250 mm above the base of the bottle, so the water depth in the stream, pipe or stormwater drain must rise to at least 250 mm to collect a sample, unless the bottle is partially buried (which can be done in a stream bed or drainage ditch).
- The grab samples collected are unpreserved water samples, so the samplers should be retrieved as quickly as possible, particularly for analysis of microbiological variables.

A2. Preparatory work

The level of detail in the descriptions below vary depending on the application. For applications that are expected to be the most commonly used, these instructions provide relatively complete information regarding how and when to implement this approach. For applications that are expected to be more rarely used, the details will depend on the specific situation and only general guidance is provided.

A2.1. Determine target water level

This section contains information on how to determine the water level for deployment at a stormwater site or in a stream.

A2.1.1. Stormwater deployment

In a stormwater application, the primary use of these bottles is often to sample the first-flush. The water level that is associated with the first-flush will be different in every location. However, as a rule of thumb, in a stormwater network location where there is no flow during dry weather, the target water level could be 20-100 mm. Some contaminants are associated with **peak** flow, so you could also sample at a higher water level as well.

Because the intake funnel is ~250 mm above the base of the bottle, if the bottle is on the base of a stormwater pipe, the water would need to rise to at least 250 mm to collect a sample. In smaller pipes and drains, a rise of 250 mm is unlikely to reflect the first-flush. Therefore, the bottle may need to be deployed at a stormwater pipe outlet, where it can be positioned below the invert of the pipe. In a soft-bottom stormwater drain, the bottle could be partially buried, ideally within a mounting tube to prevent soil or sediment entering the bottle during deployment. When sampling peak flows, it may be appropriate to deploy the bottle at the base of the pipe or drain.

A2.1.2. Stream deployment

There is not always a clear first-flush effect in streams, due to the (generally) larger catchment sizes. However, peak contaminant concentrations, often do occur in the early part of a storm event and on the rising limb. Peak flows can be associated with peak concentrations for other contaminants, such as suspended solids. Sampling in a stream may therefore target either (or both) of these hydrological conditions by deploying bottles at the appropriate height.

In a stream, the water level that relates to a first-flush or peak flow will depend on the size of the stream and its catchment. This section provides guidance on how to determine this water level, in cases with and without hydrological data. In the absence of hydrological data, it is difficult to assess the target water level as every stream and site will respond differently to rainfall. Furthermore, it will be impossible to confirm the point in the storm event at which a bottle filled. We *highly recommend* deploying a water level logger alongside the bottles. Note that because every site will respond differently, a water level recorder in a nearby site or stream may not provide any indication of the water levels at the monitoring site.

If there is a requirement to only sample larger storm events, e.g., > 5 mm depth over 24 hours, then the target water level will either need to be above the level reached during a small event, or the bottles will need to be deployed immediately before the storm, to avoid filling during a small event. In this case, it would be difficult to determine the height in the absence of hydrological data.

With hydrological data

The most reliable way to determine the target water level is to examine a historical hydrograph of water level from the site of interest. This is easiest if there is a permanent water recorder station at the site of interest. If not, a low-cost water level logger (such as a Hobo U20L) could be deployed for a few events prior to the anticipated sampling events. In this case, the logger should also be retained in the stream during sampling events.

Once this data is in hand, you can examine the hydrograph of previous events and determine the water level that relates to the first 30 minutes of a storm event. This is a rough rule of thumb consistent with the rule of 30 minutes being first-flush in a stormwater location, assuming that the streams being monitored are from relatively small catchments, with considerable impervious surfaces and reticulated systems that rapidly delivers stormwater to the streams. The water level after 30 mins is likely to be slightly different for all events, so choose one that is either similar to the event you are expecting or is from a relatively small event (i.e., not a major flood).

To target the peak flow, check the water level at peak flow for storms of similar characteristics (rainfall depth and duration) to that predicted for your target storm event.

The deployment height of the bottle is therefore the target water level minus the baseflow water level at the time of deployment.

With no hydrological data

The best approach would be to visit the site during a rain event and note how quickly the water level rises from baseflow and to what level. Select a water level that is above the baseflow and is rapidly reached in even a small storm (rather than only reached at peak flows).

The second, and a much poorer option, would be to guess, and simply deploy the bottle approximately 20-100 mm above the baseflow water level. This approach does risk the bottle filling unexpectedly, for example, in the case of a small discharge to the stream from someone hosing pavements if that results in a sufficient water level rise.

A2.2. Mounting considerations

A2.2.1. Mounting tube

A mounting tube for the bottles (Figure A-4) can assist with deployment. This is particularly recommended if the bottle needs to be buried, for example in a dry stormwater drain.

Figure A-4: Mounting tube for the sampler bottles.

A2.2.2. Mounting in streams and rivers

The following factors should be considered:

Flow: Just as a grab sample should be collected from a flowing section of water, ideally a run section and never in a pool or backwater, these bottles should be deployed in a run section.

Point sources and dead zones: The deployment location should be away from the immediate influence of point sources, tributary stream and drain confluences and dead zones (e.g. backflow eddies) that will not have completely mixed in the river channel.

Water depth: The bottles should be deployed at a height that relates to your target water level (see Section A2.1.2). Except for in large streams, you probably need to place samplers in a section of the stream that is deep enough for the bottles to be partially submerged during baseflow. If the bottles are completely above the water, it will require a water level rise of 250 mm before a sample is collected. If the stream bed is soft, the bottle base could be pushed into the stream bed slightly to obtain the correct height. If the stream bed is concrete, then you could have a problem and you might want to choose a different site.

Attachment: The easiest deployment is to bang a waratah into the stream bed and either hose-clip or cable tie the bottles to the waratah. Ensure that the cable ties are threaded through a hole in the waratah so that they do not move up and down. If the waratah doesn't have many holes in it, the mounting stake that comes in the mounting kit can be attached to the waratah to provide finer scale height variation. On the bottles, it is best to use multiple cable ties, located around the neck and around the body of the bottle (Figure A-5). A thin rope or cable tie should be put through the hole on top of the debris deflector dome and loosely attached to the waratah to ensure that this is not lost at high flows.

Figure A-5: Stormwater sampler bottle attached to a waratah stake in a stream, deployed as individual or multiple bottles at different heights.

A2.2.3. Mounting in stormwater networks

Dead zones: The deployment location should have a steady flow but not be too turbulent.

Water depth: The bottles should be deployed at a height that relates to your target water level (see Section A2.1.1). You may need to find a spot that is just downstream of the pipe outlet, rather than inside the pipe, to ensure that the bottle intake is at the desired height.

Attachment: Every stormwater deployment is likely to be slightly different and methods will need to be adapted for each. Some suggestions for attachment methods are provided here (Figure A-6).

In a drain: use the mounting tube, attach to a waratah and partially bury in the bed of the drain (see video at 6:29, https://f1.media.brightcove.com/12/665001591001/665001591001_4758702678001_1159728607001.mp4?pubId=665001591001&videoId=1159728607001)

In a stormwater pipe: use a steel pipe with threaded rod inside which can be extended to brace against the top and bottom of the stormwater pipe, with the sampler bottle attached at the desired height (Figure A-6a & b).

In a stormwater grate: hang the bottle from the stormwater grate, on the upstream side of the grate to ensure that water enters the bottle (see video around 4:30, https://f1.media.brightcove.com/12/665001591001/665001591001_4758702678001_1159728607001.mp4?pubId=665001591001&videoId=1159728607001)

For a more permanent (frequently used) installation, a piece of timber with an angle bracket could be dynabolted into the concrete stormwater structure, such as the side of a culvert, and the bottles can then be attached to this at the desired height (see Figure A-6d).

Figure A-6: Bottles mounted (a) with an extendable threaded rod; (b) close up of the threaded rod; (c) using existing steel mesh on a stormwater outlet; and (d) to a piece of steel angle, dynabolted to the side of a stormwater outlet wingwall.

A2.3. Equipment and field record forms

Equipment lists are provided in Sections A3.1 and A4.1 below, specific for deployment and retrieval. The equipment required differs depending on the location of deployment, either in a stormwater pipe / drain or in a constantly-flowing stream. Check that you have all the equipment needed prior to your field trip.

A standard field form should be used to record field visit metadata, including essential information on the timing of deployment. An example form is provided in Attachment 1. This form provides a record that verifies the location and timing under which deployment was carried out, along with other factors that may influence the data being collected. This record is also essential for later reconciliation with water quality results received from the laboratory.
A photograph of the deployment site also provides a useful record.

A2.4. Health and safety

Collection of field measurements and water samples from rivers has some elements of danger that should be considered in a Health and Safety Plan, prepared in accordance with your own organisational processes. Safe access to routine monitoring sites in all weather conditions is particularly important. Special attention to safety is needed when sampling of rivers is conducted from the shore, a bridge, a boat or by wading during high, swift and/or turbid conditions. Only trained personnel shall be involved in fieldwork and suitable lone worker procedures are required if lone work is unavoidable. Appropriate personal protection equipment, such as hi-visibility clothing and floatation aids, should be provided to ensure safety. Gloves should be worn when sampling all river waters, from pristine to heavily contaminated. This is to protect samples from potential contamination and the sampler from potential harm. For further guidance on safety precautions when collecting discrete water samples refer to the NEMS Code of Practice Safe Acquisition of Field Data In and Around Fresh Water. http://www.nems.org.nz/assets/Documents/NEMS-12/Safe-Aquisition-of-Field-Data-in-and-Around-Fresh-Water-v11.pdf

When sampling for metals in summer, ensure that sunscreen being used is not a zinc-containing formula. The very high zinc content of these sunscreens has potential to easily contaminate samples.

A3. Field deployment

A3.1. Equipment list

Gear list for deployment
Clean stormwater sampler bottles
Ruler to measure deployment depth
Disposable, powder-free nitrile, latex or vinyl gloves
Medium cable ties and long cable ties
Side-cutters or scissors for snipping cable ties
Field sheets and pencils
Additional equipment depending on deployment options
Waratah & waratah hammer
Mounting tube and spade
Pete's pipe, spanner and wrench (pipe wrench, vice grips or strong pliers); hose clamps
2x G-clamps
Waders (chest or thigh, depending on stream depth) and rope

A3.2. Preparation and transport

If Nalgene bottles have been washed for re-use, check that the black rubber gasket is correctly seated to ensure the bottle seals once a sample has been collected.

Nalgene bottles should be transported in a clean environment, e.g., inside large zip-lock plastic bags, or lidded bins.

A3.3. Deployment

A3.3.1. Stream deployment

Install the bottle(s) on a waratah placed at a suitable location in the stream, as follows.

1. Install waratah or other mounting structure in the stream, usually by hammering into stream bed. If the stream bed is concreted, look for a location to attach on the stream bank such as on a gabion basket.
2. Put on disposable gloves (powder-free), to be worn at all times when handling the bottles.
3. Using a long and thick cable tie, thread cable tie through a hole in the waratah, then around the body of the bottle until it holds loosely.
4. Adjust the height of the bottle to the desired height, using the ruler to measure from the water surface to the intake; or from the stream bed to the intake, depending on how you have calculated your desired intake water level.
5. Thread another cable tie through an appropriate waratah hole at the height around the neck of the bottle.
6. Tighten all cable ties to ensure the bottles cannot move vertically or spin. Snip tails from cable ties to reduce collection of debris.
7. Add a final cable tie to the top of the debris shedding dome and loosely attach to the waratah. This is to ensure this part of the bottle is not lost during a storm event even if it pops off.
8. Thread a rope through a top hole of the waratah and fix firmly to something on the stream bank. This provides additional security of the equipment in case of a large storm.

A3.3.2. Stormwater pipe deployment

Install the bottle(s) inside the stormwater pipe, as follows.

1. Using a threaded rod and pipe, with the sharp end of the pipe at the invert of the stormwater pipe, wind the threaded rod until it reaches the obvert of the stormwater pipe and tighten.
2. Attach the bottle to this pipe with hose clamps or cable ties, adjust to the correct height and tighten.

A3.3.3. Stormwater pipe outlet deployment

Install the bottle(s) below the pipe outlet, using clamps if it is a perched outlet, or with waratahs.

1. Attach clamps to the bottom of the stormwater pipe or stake waratah into ground downstream of outlet.
2. Cable tie (or hose clamp) your bottle to the clamps.

A3.3.4. Stormwater drain deployment

If the stormwater drain contains constant flow during dry weather, follow instructions above for stream deployment.

If the stormwater drain is dry during dry weather but flowing to only a low water depth during wet weather, you can bury the mounting tube in the drain and insert the bottles into this.

1. Calculate depth of hole: this is 290 mm minus your target water level
2. Dig a hole to depth as calculated in step 1.
3. Using a hose clip or cable tie, attach the mounting tube near the bottom of the mounting stake with the tube on the open “V” side of the stake.
4. Insert the mounting tube & stake in the hole with the tube on the upstream site and backfill, ensuring mounting kit remains vertical
5. Check height from ground level to bottom of the holes in the side – this should equal the target water level.
6. Put on disposable gloves (powder-free), label the stormwater sampler bottle with the site name and date, and insert sampler bottle into the buried mounting kit.
7. Replace upper grated end cap, making sure to snap the end cap into the engagement holes.
8. Make sure the red plug is inserted into the upper grated end cap to prevent clean rainwater entering the tube.

A3.4. Records

The field sheet attached in Appendix A, or similar, should be filled in, with particular attention to the heights deployed.

A4. Field retrieval

A4.1. Equipment list

Gear list for retrieval	
Zip-lock bag containing the lids for each bottle	
Chilly bin packed with frozen slicker pads	
Disposable, powder-free nitrile, latex or vinyl gloves	
Side-cutters or scissors for snipping cable ties	
Ruler to measure bottle height	
Camera	
Field sheets and pencils	
Stormwater drain application (above water during dry weather)	Stream water application (underwater during dry weather)
Small spade	Elbow length gloves
	Waders

A4.2. Retrieval steps

A4.2.1. Stream retrieval

1. Put on disposable gloves with elbow length gloves on top for retrieval.
2. Wading into the stream, measure the depth from the water level to the intake funnel.
3. Use side cutters to snip cable ties attaching debris domes.
4. Hold the body of the bottle securely with one hand and use side-cutters to snip cable ties attaching bottle to the waratah.
5. Unscrew the bottle intake funnel / dome and cap with a clean lid.
6. Check label on bottle is still present and legible.
7. Remove waratah if not using again.

A4.2.2. Stormwater pipe or outlet retrieval

1. Put on disposable gloves for retrieval.
2. Measure the distance from the intake funnel to the base of the stormwater pipe to check if it moved during the event.
3. Use side cutters to snip cable ties attaching debris domes.
4. Hold the body of the bottle securely with one hand and use side-cutters to snip cable ties attaching bottle.
5. Unscrew the bottle intake funnel / dome and cap with a clean lid.
6. Check label on bottle is still present and legible.
7. Remove all equipment used to attach bottle in location.

A4.2.3. Stormwater drain retrieval

1. Check height of tube – measuring from bottom of intake holes to ground level.
2. Remove the grated end cap from the tube (insert a pen or screwdriver into one of the end cap engagement holes).
3. Put on disposable gloves.
4. Remove the stormwater sampler bottle from the tube.
5. Unscrew the bottle intake funnel / dome and cap with a clean lid.
6. If using site again, leave mounting tube in place, otherwise remove it.

A4.3. Sample transport and handling

During transport to the laboratory, the bottles should be stored in an insulated container with cooling blocks.

Samples should be transferred to laboratory-supplied bottles appropriate for the contaminants of interest. The samples should be shipped to the analytical laboratory as soon as possible, with appropriate chain of custody documentation and laboratory request forms.

The Nalgene bottles can then be retained and washed for future uses.

Attachment 1: Field Record Form

Water Quality Data Sheet – Stormwater Sampler Deployment & Retrieval

Site details

Site Location Code	Description

	Deployment	Retrieval
Date		
Person recording data		
Person deploying samplers		

Sampler details

Sample codes	Location	Deployment height & reference	Time deployed (NZST)	Time retrieved (NZST)	Observations

Appendix B Instructions for DGTs

See also our instructional video on how to deploy DGTs in streams and stormwater outfalls:

https://www.niwa.co.nz/sampling-urban-streams-stormwater

B1. Essential things to know about DGTs

B1.1. What is a DGT?

DGT (diffusive gradients in thin films) are small, simple passive sampling devices (Figure B-1) that accumulate dissolved substances and provide a time-weighted average (TWA) concentration over the deployment period. They do not require any power supply to work and are small enough (~40 mm in diameter) to be deployed in many locations.

The DGTs have three layers:

- A membrane filter to keep out solid particles;
- A diffusive gel layer which controls the diffusion of solutes; and
- A binding layer or gel, which selectively binds the solutes of interest.

DGTs are available for metals (cationic and oxyanions), some nitrogen and phosphorus species, and selected polar organic compounds. For metals, the binding layer is Chelex, which binds trace metals more strongly than major cations. This allows the metals to accumulate over the deployment period to higher concentrations, thus enabling measurement of trace concentrations in water. The devices have been used extensively in rivers and streams though somewhat less in stormwater.

Figure B-1: DGT device for sampling water. Photo credit Stuart Mackay, NIWA.

B1.2. How do you use a DGT?

The DGT devices need to be deployed in the field for several hours to weeks to accumulate contaminants. They then need to be retrieved and shipped to a laboratory where they are disassembled under clean conditions, the contaminants are extracted from the binding layer, and the accumulated mass of contaminants is measured by routine methods. This mass, along with water temperature and the length of time deployed, is used to calculate the time-weighted average concentration in the waterbody.

B1.3. How will a DGT help me?

A DGT continuously absorbs and concentrates dissolved contaminants from the water column and provides an indication of the in-stream concentration throughout the entire period the DGT device was installed (Figure B-2). It does not provide any information on peak concentrations or the range in concentrations throughout a storm.

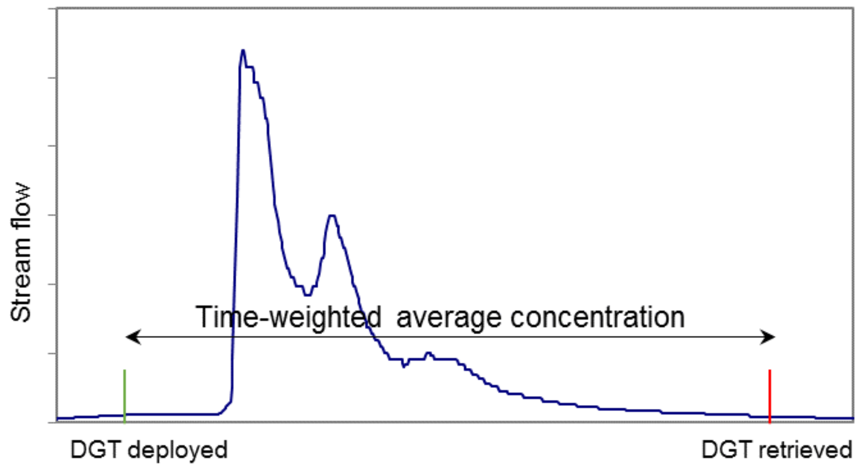


Figure B-2: Example stream hydrograph showing period of DGT measurement.

B1.4. Where can I use a DGT?

- Streams, including those tidally-influenced (depending on the variables being measured);
- Stormwater drains;
- Stormwater pipes;
- Pumped stormwater discharges.

B1.5. What else do I need to know?

Some key features of DGTs:

- DGTs can be damaged by sharp objects (e.g., sticks, scissors) which can pierce the outer membrane layer. Treat them carefully prior to deployment.
- DGTs must not dry out, either before or during deployment, as this will affect the ability of the gel to take up contaminants.
- At least one field blank and one laboratory blank need to be included with each batch of samples (where a batch is ≤10 and ≤4 sites).
- You can contaminate a DGT through incorrect handling, just as you can contaminate a water sample. Gloves (powder-free) need to be worn at all times when handling. Zinc-containing sunscreen should be avoided when sampling for metals.
- To calculate water concentrations, you need to know the water temperature during deployment. Ideally this is recorded at the location. Inaccuracies of > 2°C will give an error of more than 5% (see Section B3.1).
- You need to record the length of time the DGT was deployed (underwater), see Section B3.3.
- At this stage, we recommend deploying DGTs in duplicate (with at least one site in triplicate) to enable the identification of outlying results (for example from a damaged DGT).

- DGTs can be stored in the refrigerator after deployment for several weeks prior to sending to the laboratory. Therefore it is safe to retrieve DGTs on a Friday, and refrigerate over the weekend.

B2. Preparatory work

The level of detail in the descriptions below vary depending on the application. For applications that are expected to be the most commonly used, these instructions provide relatively complete information regarding how and when to implement this approach. For applications that are expected to be more rarely used, the details will depend on the specific situation and only general guidance is provided.

B2.1. Selecting and purchasing DGTs

DGTs can be purchased from DGT Research, based at Lancaster University, who provide these for research and commercial purposes. The DGTs are produced in China and generally shipped about 3 weeks from order. There are many different types available, including multiple types for the same contaminants, with different gels and requiring different extraction methods. The DGTs that are recommended for use in NZ in stormwater and urban stream applications are listed in Table B-1 with their codes for clarity when ordering.

Table B-1: DGTs commercially available from DGT Research suitable for stormwater and urban stream applications. .

DGT code	Water quality variables measured
LSNM-NP	Metals incl. Cd, Cr, Cu, Fe, Ni, Zn
LSNX-NP	Phosphorus, metals & metalloids (wide range incl. As, Cd, Cr, Cu, Fe, Ni, Zn)
LSNN-AP	Nitrate-N

DGTs have an expiry date that is typically about 3 months after purchase. Within this period the DGTs are not expected to dry out when stored refrigerated. They may still be suitable for use after expiry, however the devices should be carefully checked to ensure they are not dry. The filter membrane should have good contact with the cap and if there is any visible gap then the gels have dried out and need to be either revived (instructions at dgtresearch.com) or discarded.

B2.2. Site selection and mounting considerations

This section contains information on considerations when selecting a site, and for positioning and mounting the equipment at the selected site.

B2.2.1. DGT holders

In stream and stormwater deployments, DGT holders are recommended (Figure B-3). In marine deployments, DGTs can be simply deployed on a rope using nylon threaded through the DGT back plates.

Figure B-3: Housings for DGTs for monitoring of stream water (a) and stormwater (b).

B2.2.2. Mounting in streams and rivers

The following factors should be considered:

Flow: A constant flow of water is required past the face of the DGT. Therefore, the device should be deployed in a flowing reach of stream (run or riffle) and never in a pool or backwater. Excessive turbulence, particularly bubbles should be avoided.

Point sources and dead zones: The deployment location should be away from the immediate influence of point sources, tributary stream and drain confluences and dead zones (e.g. backflow eddies) that will not have completely mixed in the stream channel.

Water depth: The DGTs should ideally be deployed at mid-depth of the stream. They should not be sitting on or directly above the stream bed. They should also be at a depth that ensures they will remain underwater for the duration of deployment. Pay close attention to this in locations where the water level is affected by the tide or downstream control structures such as pumps to ensure they remain underwater during all parts of the tidal (or pumping) cycle.

Attachment: The acrylic holder can be cable-tied to a permanent structure within the stream, such as a heavy log or tree root, or an intake pipe at a water level recording site, as long as these are in a flowing reach of stream and oriented as required. Alternatively, a waratah may be banged into the stream and the holder can be cable tied to the waratah at the required depth and orientation.

Orientation: The DGTs should be deployed in an acrylic plastic holder that is mounted at a depth to ensure that the DGTs are always submerged. The holder should be mounted in line with the stream flow to optimise flow past the face of the DGTs. The holder should not be placed inside any other object (such as a minnow trap) which might reduce the flow and affect contaminant uptake. The holder should be mounted so that the membrane surface of the DGTs is vertical, to minimise sediment deposition on the membrane, which can also affect contaminant uptake rates[21].

[21] British Standard (2011). Water quality - Sampling. Part 23: Guidance on passive sampling in surface waters (ISO 5667-23:2011). 23 p.

B2.2.3. Mounting in stormwater networks

The following factors should be considered:

How to keep the DGT wet: For a stormwater location that is dry except during storm conditions, such as a stormwater pipe or drain, DGTs should be deployed in a housing to keep the DGTs wet prior to the storm commencing. DGTs can be deployed in the NIWA-designed and made trough housing which holds clean fluid during dry weather flow and is rapidly inundated at storm flows. The DGTs should be mounted vertically in this housing, to minimise sediment deposition on the membrane, which could affect contaminant uptake rates.

Dead zones: The deployment location have a steady flow past but not be too turbulent.

Water depth: The DGT housing can be placed on the pipe floor or wall. Ensure that it is not deployed too high – it should be underwater for most of the storm event, not just for the very peak flow.

Attachment: The trough housing needs to be attached to a solid structure, such as the side of the culvert or the bed of the stormwater pipe. For a temporary installation, extendable pipe can be used with the DGT trough attached to that (see Figure B-4a). For a more permanent (frequently used) installation, a piece of timber could be dynabolted into the concrete stormwater structure, and the DGT trough screwed into this at the desired height (see Figure B-4b).

Orientation: The DGT housing should be oriented with its longest dimension parallel to the stream flow. Stormwater will flow in one end, past the three DGTs and then out the other end. This is to optimise flow past the face of the DGTs.

All equipment used in the housings, to attach the DGTs or to attach the housings, should be stainless steel or acid-washed plastic.

Figure B-4: DGT trough holder mounted to (a) extendable pipe inside a stormwater pipe for a temporary installation and (b) timber bolted to stormwater outlet wing-wall for a more permanent deployment location.

B2.2.4. Slow velocity waters

In areas where the stream or water flow is very slow, the DGTs could under-estimate water concentrations (as the diffusive boundary layer becomes thicker and no longer negligible). This can result in uncertainties of around 20% and for this reason, slow reaches of water should be avoided. For some purposes, such as initial screening, this level of additional uncertainty due to low flows may be acceptable. However for other purposes, a higher level of precision may be required. If there are no locations with faster flow, then this issue can be minimised by deploying DGTs with two different diffusive gel thicknesses. This provides information on the diffusive boundary layer thickness which can be used in a more sophisticated calculation of in-stream concentrations. We recommend consulting experts in DGTs if this is required.

B2.3. Equipment and field record forms

Equipment lists are provided in Sections B3.1 and B4.1, specific for deployment and retrieval, respectively. The equipment required differs depending on the location of deployment, either in a stormwater pipe / drain or in a constantly-flowing stream. Check that you have all the equipment needed prior to your field trip.

A standard field form should be used to record field visit metadata, including essential information on the timing of deployment. An example form is provided in Attachment 1. This form provides a record that verifies the location and timing under which deployment was carried out, along with other factors that may influence the data being collected. This record is also essential for later reconciliation with water quality results received from the laboratory. Waterproof paper is recommended for field forms.

A photograph of the DGT deployment site also provides a useful record.

B2.4. Health and safety

Collection of field measurements and water samples from rivers has some elements of danger that should be considered in a Health and Safety Plan, prepared in accordance with your own organisational processes. Safe access to routine monitoring sites in all weather conditions is particularly important. Special attention to safety is needed when sampling of rivers is conducted from the shore, a bridge, a boat or by wading during high, swift and/or turbid conditions. Only trained personnel shall be involved in fieldwork and suitable lone worker procedures are required if lone work is unavoidable. Appropriate personal protection equipment, such as hi-visibility clothing and floatation aids, should be provided to ensure safety. Gloves should be worn when sampling all river waters, from pristine to heavily contaminated. This is to protect samples from potential contamination and the sampler from potential harm. For further guidance on safety precautions when collecting discrete water samples refer to the NEMS Code of Practice Safe Acquisition of Field Data In and Around Fresh Water. http://www.nems.org.nz/assets/Documents/NEMS-12/Safe-Aquisition-of-Field-Data-in-and-Around-Fresh-Water-v11.pdf

When sampling for metals in summer, ensure that sunscreen being used is not a zinc-containing formula. The very high zinc content of these sunscreens has potential to easily contaminate samples.

B3. Field deployment

B3.1. Equipment list

For DGT deployment, you need to have a record of the water temperature, ideally throughout the deployment period. If there is a temperature recorder at or near the site of interest, this can be used, otherwise a temperature recorder should be deployed, for example an EXO Sonde or a Hobo Tidbit. If using DGTs for nitrate-N and there is doubt about the salinity of the waterbody, it should be checked prior to DGT deployment to ensure it is below 1 ppt.

Gear list for deployment	
DGTs in sealed plastic bags	
Chilly bin packed with frozen slicker pads	
Disposable, powder-free nitrile, latex or vinyl gloves	
Side-cutters or scissors for snipping cable ties	
Tidbit temperature logger (if no temperature sensor near site)	
Mobile phone or watch to note time (in NZST)	
Waterproof field sheets and pencils	
Stormwater application (above water during dry weather)	**Stream water application** (underwater during dry weather)
3-D printed trough & stainless screws*	Acrylic mounting plates (can be purchased from DGT Research*)
Screw-driver	Medium cable ties and long cable ties in a different colour if possible.
Small cable ties	Elbow length gloves
Chelex-cleaned DGT fluid *	Clean plastic bag or sheet, approx. 30 cm x 20 cm to place DGTs
Ruler to measure deployment depth	Waders (chest or thigh, depending on stream depth)
Waratah & waratah hammer if needed	Waratah & waratah hammer if needed

Note: * These items can be supplied by NIWA.

B3.2. Transport

DGTs should be transported to the site in their supplied zip-locked bags to ensure they are not contaminated and do not dry out. DGTs can be housed in a plastic container (such as a lunch box) to ensure they are not damaged by knocks during transport and placed within a chilly bin with slicker pads to ensure they remain cool.

B3.3. Deployment

B3.3.1. Stream deployment

If required, install waratah or other mounting structure in the stream.

Next insert the DGTs into the acrylic mounting plates:

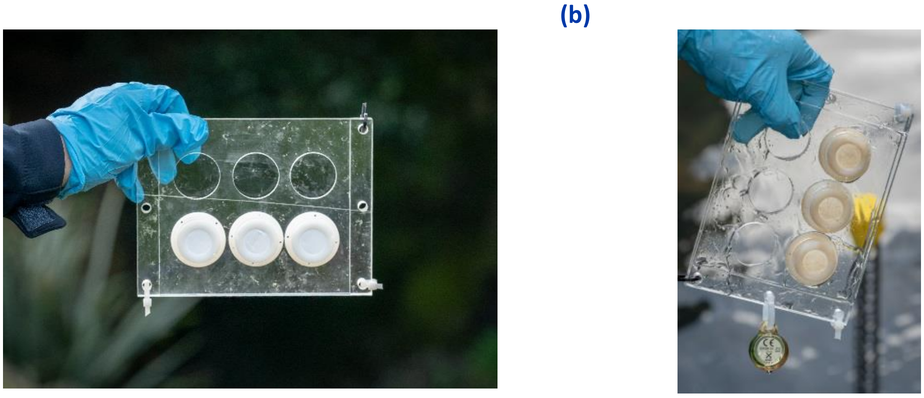
1. Place a clean sheet of plastic on the ground or on a chilly bin lid to use as a clean work surface.
2. Place acrylic mounting plate on plastic sheet and open up.
3. Put on disposable gloves (powder-free), to be worn at all times when handling the DGT devices.

4. Taking care not to touch the face of the DGT, remove one DGT from its zip-lock bag and place face-down in hole of acrylic plate. Close zip-lock bag and return to chilly bin (this will be used on sampler retrieval).
5. Repeat for second and third DGTs, placing all in a single line of the DGT holder.
6. Place the flat plate over the DGTs to squeeze into place.
7. Put cable ties through the plate holes to keep DGTs locked into the acrylic holder and pull all ties tight. Snip tails from cable ties to reduce collection of debris (Figure B-5a).
8. If using a Tidbit, attach this to the acrylic plate with small cable ties (Figure B-5b).

If the face of the DGT comes into contact with anything (e.g., is dropped on the ground) the device should be discarded and replaced with a clean device.

Next deploy the acrylic mounting plate containing DGTs in the stream. Enter stream from a location downstream of the sampling zone where possible. Carry DGTs in plate into stream taking care not to touch the DGTs (you could place the DGTs and mounting in a clean plastic bag while working in the stream). Place underwater and cable tie into position using the holes in the corners of the acrylic plate (Figure B-5c). If a different colour of cable tie is available, use this, to assist on retrieval. The holder can be oriented with DGTs in either top or bottom row depending on water depth, but when using triplicates, the plate should be oriented with three places across and two down so that all triplicates are at the same depth. Ensure that DGTs are not too close to the water surface (in case water level drops prior to the storm or prior to sampler retrieval) and not too close to the stream bed to avoid contaminants within the sediment influencing results. Snip tails from cable ties to reduce collection of debris. Note the time of deployment (in NZ Standard Time (NZST) for later cross referencing with hydrological records).

(a) (b)



(c)

Figure B-5: Deployment steps showing (a) DGTs contained within acrylic plate (b) with temperature recorder attached and (c) and plate attached to waratah.

B3.3.2. Stormwater deployment

There are two main steps to deployment: attaching the holder at the stormwater site and inserting DGTs into the holder. This can be done in either order, depending on the accessibility of the deployment location. If this is not very accessible, it may be easier to insert the DGTs into the trough first then carefully take to the deployment location. However, in cases where it may be fiddly to attach the trough, it may be easier to attach the trough first, then insert the DGTs, to ensure that DGTs are not contaminated (or dried) while attaching.

Step 1 (or 2): Insert the DGTs into the trough housing:

1. Put on disposable gloves (powder-free), to be worn at all times when handling the DGT devices.
2. Taking care not to touch the face of the DGT, remove one DGT from its zip-lock bag and place face-down in hole of trough insert plate. Close zip-lock bag and return to chilly bin (this will be used on sampler retrieval).
3. Repeat for second and third DGTs, keeping the plate flat so the devices don't fall out.
4. Carefully insert the plate into the sampler trough ensuring the plate is locked in behind the raised bump and trough tabs are through the slots.
5. Put cable ties through the holes in the trough tabs and pull tight to lock DGTs in place.
6. If using a Tidbit, attach this to the tabs with small cable ties.
7. Snip tails from all cable ties to reduce collection of debris.

Step 2 (or 1): Attach the DGT trough to the structure you have selected (see Section B2.1). Ensure the trough is horizontal (use a small level if you like). Measure and record the distance from the water surface (if any) or bed of pipe to the top of the trough (Figure B-6).

Step 3: Fill the trough with the clean DGT fluid.

If the face of the DGT comes into contact with anything (e.g., is dropped on the ground) the device should be discarded and replaced with a clean device.

Note the time of deployment (in NZST).

Figure B-6: Installing trough on an adjustable pipe and measuring deployment height.

B3.3.3. Quality assurance

Field blanks and laboratory blanks are used to assess potential contamination at each stage of the field study.

Field blanks are DGTs taken into the field, removed from their zip-lock bags and exposed to the air, then replaced into the bag. At least one field blank should be used with every batch of up to 10 samples. If deploying DGTs at multiple sites, expose the field blank at the site that has highest risk of contamination during DGT deployment. This could be a site near an industrial area with higher dust levels. For deployments in multiple catchments a field blank should be prepared for *each catchment*. For deployments on multiple days a field blank should be prepared for *each day* of field work.

Laboratory blanks consist of sampling devices that have not left the laboratory and are analysed alongside each batch of samples analysed.

B3.4. Water sampling

When using DGTs for metals, it is useful to have data on the Dissolved Organic Carbon (DOC) content of the water, particularly for comparing results between different streams. In locations where there is permanent flow (e.g., streams) a sample can be collected at the time of deployment or retrieval. Samples for DOC analysis should be collected in laboratory-supplied glass bottles for measurement of Dissolved Organic Carbon (analysed as DNPOC, dissolved non-purgeable organic carbon), with bottles filled and capped under water to remove any air gap. These samples should be sent to the laboratory as soon as possible as DOC is not stable until filtered. If there is no permanent flow, a sample could be collected at high flow with a Nalgene stormwater sampler with a glass sampling bottle.

When sampling is targeted to storm events, and DGTs are deployed and retrieved at baseflow, much of the time that they are accumulating contaminants will be during baseflow. To assist in understanding of the storm flow concentrations, it is useful to collect water samples at the time of deployment and retrieval. These are analysed for the same contaminants as the DGTs. These water samples provide information on the concentrations during baseflow and can be compared to the DGT concentrations integrated over the entire deployment period.

B3.5. Records

The field sheet attached in Attachment A, or similar, should be filled in. Record the time (in NZST) that the DGTs are deployed to the nearest 5-10 minutes.

B4. Field retrieval

B4.1. Equipment list

<table>
<tr><th colspan="2">Gear list for retrieval</th></tr>
<tr><td colspan="2">Plastic bags for DGTs</td></tr>
<tr><td colspan="2">Clean plastic bag or sheet, approx. 30 cm x 20 cm to place DGTs</td></tr>
<tr><td colspan="2">Chilly bin packed with frozen slicker pads</td></tr>
<tr><td colspan="2">Disposable, powder-free nitrile, latex or vinyl gloves</td></tr>
<tr><td colspan="2">Side-cutters or scissors for snipping cable ties</td></tr>
<tr><td colspan="2">Camera</td></tr>
<tr><td colspan="2">Mobile phone or watch to note time</td></tr>
<tr><td colspan="2">Field sheets and pencils</td></tr>
<tr><td colspan="2">Squirty bottle filled with ultra-pure water (Milli-Q or equivalent)</td></tr>
<tr><td>Stormwater application
(above water during dry weather)</td><td>Stream water application
(underwater during dry weather)</td></tr>
<tr><td>Screw-driver</td><td>Elbow length gloves</td></tr>
<tr><td></td><td>Waders</td></tr>
</table>

B4.2. Retrieval steps

B4.2.1. Stream retrieval

1. Prior to retrieval, the zip-lock plastic bags should be labelled with the site name and a number corresponding to each DGT replicate. Label from 1-3 from upstream to downstream to indicate the position the DGT was deployed in for future understanding.

2. Put on disposable gloves (elbow length if needed depending on water depth) for retrieval.

3. Wading into the stream, retrieve the DGT acrylic holder containing the DGTs by cutting the cable ties that attach it to the waratah or other permanent structure. Take care to only snip the cable ties that connect it, and not the cable ties that tie the plates together. Note that the DGT holder sinks so take care to grip the holder so that it and the cable ties are not lost. Return to the stream bank.

4. In a suitable location on the stream bank, lay out a clean plastic bag as a work surface and place the DGT holder onto it with the DGTs face up for inspection.

5. Document the extent of biofouling in each DGT (Figure B-7) both on the field form and by taking photographs. After noting biofouling, thoroughly rinse each DGT with Milli-q water to remove visible sediment and examine the integrity of each device. Note and photograph any damage, for example any scratches or ruptures in the membrane.

6. Snip the cable ties holding the acrylic plates together and carefully open the plates, ensuring that DGTs do not fall out onto the ground. Rinse back of DGTs if necessary to remove any trapped sediment. Place each DGT back into its labelled zip-lock bags and seal with minimum air space. Note on the field form which sampler is which.

7. Record the time of collection to the nearest 5 minutes.

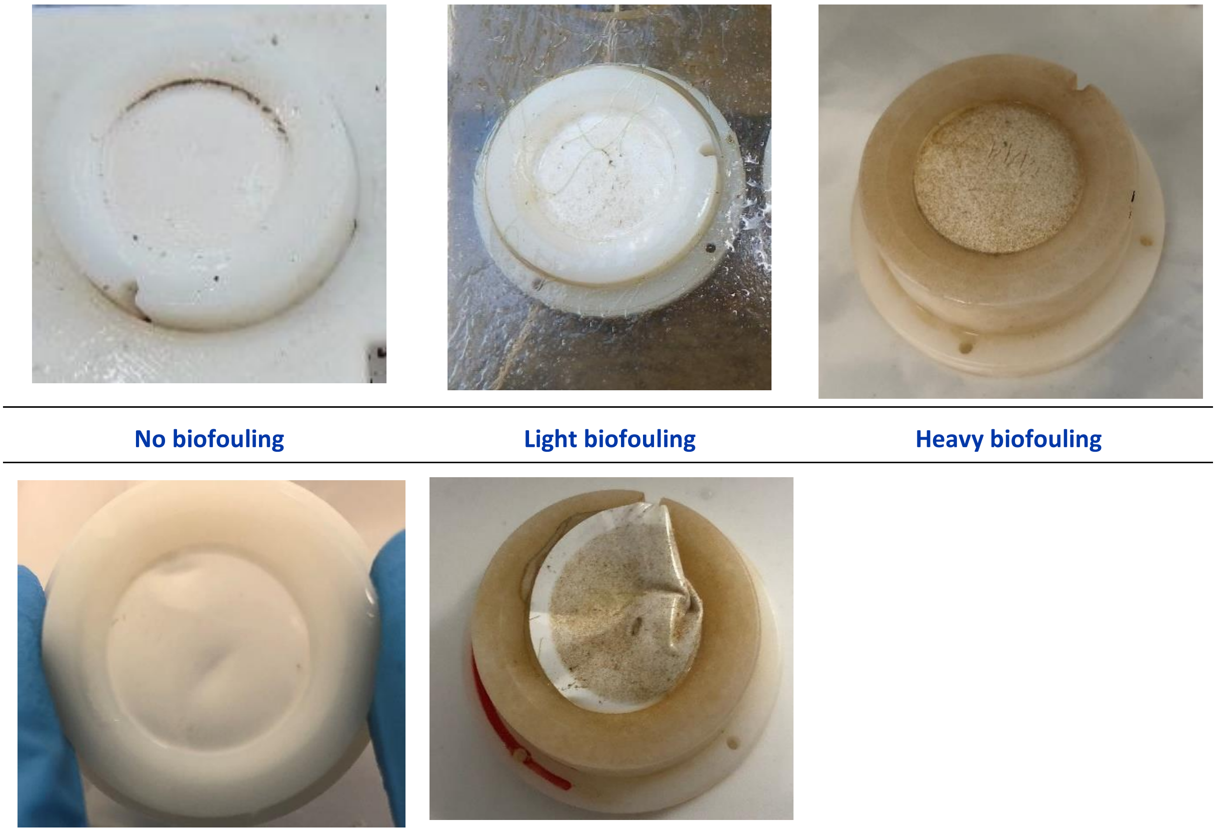


Figure B-7: Biofouling and damage of DGTs.

B4.2.2. Stormwater retrieval

1. Prior to retrieval, the zip-lock plastic bags should be labelled with the site name and a number corresponding to each DGT replicate. It may be easiest to label from 1-3 from upstream to downstream.

2. Put on disposable gloves for DGT retrieval.

3. Retrieve the DGT trough housing.

4. In a suitable location, lay out a clean plastic bag as a work surface. Snip the cable ties holding the DGTs in place and remove the holder insert keeping the DGTs on top / face down in order to not drop them.

5. Place DGTs in insert onto clean plastic bag with the DGTs face up for inspection.

6. Document the extent of biofouling in each DGT (as shown above in Figure B-7) both on the field form and by taking photographs. After noting biofouling, thoroughly rinse each DGT with Milli-q water to remove visible sediment and examine the integrity of each device. Note and photograph any damage, for example any scratches or ruptures in the membrane.

7. Rinse back of DGTs if necessary to remove any trapped sediment. Place each DGT back into its abelled zip-lock bags and seal with minimum air space. Note on the field form which sampler is which.

8. Record the time of collection to the nearest 5-10 minutes.

B4.3. Sample transport and handling

During transport to the laboratory, the DGTs should be stored in an insulated container with slicker pads or bagged ice. On return from the field, DGTs can be safely stored in a laboratory fridge for up to four weeks.

At present there are two laboratories in New Zealand that can analyse DGTs: Hill Hill Laboratories (Hamilton) and Lincoln University. DGTs, along with field and laboratory blanks, should be shipped with appropriate chain of custody documentation and laboratory request forms.

B4.4. Data and records

B4.4.1. Temperature

If a tidbit temperature logger has been used on site, download the data using the Hobo shuttle.

If temperature is continuously monitored on the site by some other means, download the data.

B5. Laboratory analysis

B5.1. Extraction

The laboratory will disassemble the DGT sampler by breaking the cap then peeling off the filter and diffusive gel layer to reveal the bottom resin-gel layer.

These resin-gel layer contains the contaminants and is extracted using methods specific to the type of contaminants. For metals (code LSNM-NP), the resin gel is immersed in 1 ml of 1M HNO_3 solution for 24 hours. Following this, an aliquot removed and diluted for metal analysis. For nitrate-N DGTs (code LSNN-AP), the resin gel is extracted with 5 ml of 5% NaCl (m/v) for 16 hours. For mixed resin gel DGTs (LSNX-NP), there are two extractions: first with 1mL of 1 M HNO_3 for 24 hours (for analysis of metals) then with 1 mL of 1M NaOH for 24 hours (for analysis of DRP).

B5.2. Analysis

Once extracted from the gel, the analysis is by standard laboratory methods. For metals, this is ICP-MS analysis at trace level. For nitrate-N, analysis is of total oxidised nitrogen by automated cadmium 61-80 reduction, Flow injection analyser.(APHA 4500-NO3- I modified).

The laboratory supplies the results as a concentration in the extraction fluid.

B6. Data analysis and use

This chapter describes how to convert the concentrations obtained from the laboratory to an in-water concentration; the sources of uncertainty in DGT measurements and potential uses of the data.

B6.1. Calculation of water concentration

Calculation of the in-stream concentration requires the following information:

1. The concentration of contaminants in the extraction fluid;
2. The length of time deployed; and
3. The average temperature during the deployment period.

Concentrations of each element in the blanks (specific to each batch) should be subtracted, then the mass of metal (or other contaminant) accumulated in the resin gel layer (M) calculated using Equation B-1:

$$M = Ce\frac{(V_{HNO_3} + V_{gel})}{fe} \quad \textbf{Equation B-1}$$

where Ce is the concentration of metals in the 1M HNO_3 elution solution (in µg/l), $VHNO_3$ is the volume of HNO_3 added to the resin gel, Vgel is the volume of the resin gel (0.15 ml), and fe is the elution factor for each metal.

The values of fe when eluted with 1 mL of 1M HNO_3 for 24 hours are 0.89 for copper and 0.9 for zinc.Next the metal concentration in the water column was calculated using Equation B-2:

$$C_{DGT} = \frac{(M\Delta g)}{(DtA)} \quad \textbf{Equation B-2}$$

where Δg is the thickness of the diffusive gel (0.078 cm) plus the thickness of the filter membrane (0.014 cm), D is the diffusion coefficient of metal in the gel, t is deployment time (in sec) and A is the exposure area (A=3.14 cm^2).

Diffusion coefficients were from the DGT research website and are reproduced in Table B-2.

Table B-2: Diffusion coefficients (D) of metal ions in DGT gel (open pore) at different temperatures from 12 to 25°C. (Units are E^{-6} cm^2/sec)

Temperature (°C)	Cd	Cu	Ni	Pb	Zn
12	4.16	4.26	3.94	5.49	4.15
13	4.30	4.39	4.07	5.67	4.29
14	4.43	4.53	4.20	5.85	4.42
15	4.57	4.68	4.33	6.03	4.56
16	4.72	4.82	4.47	6.21	4.70
17	4.86	4.97	4.60	6.40	4.85
18	5.01	5.12	4.74	6.60	4.99
19	5.15	5.27	4.88	6.79	5.14
20	5.30	5.42	5.02	6.99	5.29
21	5.46	5.58	5.17	7.19	5.44
22	5.61	5.74	5.32	7.40	5.60
23	5.77	5.90	5.47	7.61	5.76
24	5.93	6.06	5.62	7.82	5.92
25	6.09	6.23	5.77	8.03	6.08

B6.2. Uncertainty of measurement

As with any measurement, there are multiple sources of uncertainty associated with DGT measurements. The primary sources of uncertainty are reported to be related to the elution of the

DGT and issues in estimating the cross-sectional area of the DGT[22], neither of which can be controlled by users of DGTs.

We have found that contamination of the DGTs can be a major source of uncertainty, particularly in locations where low metal concentrations are found. Field blanks are highly recommended as described in Section B3.3.3. Ideally multiple field blanks are prepared, for each site or small number of sites. Concentrations in blank DGTs should ideally be below 10% of the concentration in sample DGTs. When field blanks contain metal concentrations above this, the results for samples in that batch should be viewed with caution. DGTs deployed for long periods of time (e.g., a week) accumulate metals to higher concentrations, which are more likely to be above the concentrations in field blanks, however this may not be compatible with a project objective that targets storm events (which typically have a short duration). Therefore, when deploying DGTs in locations where metal concentrations are expected to be at lower concentrations (e.g., in peri-urban streams or rural streams upstream of an urban area), extreme care should be taken when handling DGTs and multiple field blanks prepared.

Damage to the DGT membrane can affect the results by increasing the uptake of metals. If damage was noted on the field sheets during retrieval, results should be viewed with caution, particularly when higher than expected (for example, higher than replicates from the same location). Biofouling may decrease the uptake of metals by the DGTs and where there is extensive biofouling, the results should be considered as a lower estimate when comparing to guidelines or between sites.

Slow water velocity also affects the diffusion of metals into the DGTs and concentrations may be under-estimated in locations with slow velocities.

The water temperature during that deployment affects the calculation of the in-water concentrations as this influences the diffusion coefficient. Inaccuracies of > 2°C will give an error of more than 5%, and inaccuracies of 5°C will give an error of about 15%. Therefore, measuring water temperature at each site is recommended where high accuracy is required. On the other hand, accuracy in the time of deployment and retrieval is less important, with negligible differences in metal concentrations for discrepancies of even an hour, when deployed for at least 12 hours.

B6.3. Using the data

The information collected using DGTs is ideal for comparing between locations as it integrates over time. Where there are large differences in the water chemistry between sites, the concentrations may be less comparable, as some aspects of water chemistry affect metal speciation and therefore the concentrations measured by DGT. In particular, differences in DOC between sites will affect the concentrations of copper and to a lesser extent, zinc.

Concentrations calculated using DGTs are suitable for assessing metal toxicity as DGT concentrations more closely represent the bioavailable concentrations than total dissolved metal concentrations do[23]. Water quality guidelines, including the Australia New Zealand Guidelines for Water Quality, are almost all based on dissolved concentrations. However, a more advanced step in comparing water quality data to the guidelines includes considering the bioavailable fraction for toxicants. For metals,

[22] Knutsson, J.; Rauch, S.; Morrison, G.M. (2014). Estimation of Measurement Uncertainties for the DGT Passive Sampler Used for Determination of Copper in Water. International Journal of Analytical Chemistry 2014: 7.
Kreuzeder, A.; Santner, J.; Zhang, H.; Prohaska, T.; Wenzel, W.W. (2015). Uncertainty Evaluation of the Diffusive Gradients in Thin Films Technique. Environmental Science & Technology 49(3): 1594-1602.
[23] Degryse, F.; Smolders, E. (2016). DGT and bioavailablity. In: Davison, W. (ed.). Diffusive gradients in thin-films for environmental measurements, pp. 216-262. Cambridge University Press, Cambridge.

one of the methods recommended is to measure metal concentrations using DGTs[24], therefore the data obtained with DGTs can be directly compared to these guidelines.

[24] http://www.waterquality.gov.au/anz-guidelines/guideline-values/default/water-quality-toxicants/local-conditions#bioavailable-fraction

Attachment 1: Field Record Form

Water Quality Data Sheet – DGT Deployment & Retrieval

Site details

Site Location Code	Description

	Deployment	Retrieval
Date		
Person recording data		
Person deploying samplers		

DGTs details

Sample codes	Location	Deployment height	Time deployed (NZST)	Time retrieved (NZST)	Observations (e.g., biofilm, dents, holes)

Water samples collected for:

	Deployment		Retrieval	
	Water samples collected	Sample labels	Water samples collected	Sample labels
Dissolved metals (field filtered, <0.45 µm filters)				
DOC				

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