ADVANCING THE USE OF PASSIVE GRAVITY FLOW SAMPLERS FOR STORM EVENT POLLUTION CHARACTERISATION

Thesis Submitted by:
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Summary

A study was conducted to assess the feasibility of using multiple passive gravity flow samplers in a vertical configuration for stormwater pollutant characterisation on an event basis. Passive gravity flow samplers, or passive stormwater sampler bottles (PSSBs), have been used for a variety of stormwater analysis purposes, but common applications of such samplers use only a single sampler. By using PSSBs mounted at different heights, a larger part of a storm event can be sampled.

In Auckland, a field study was undertaken in an urban stream and at the stormwater outfall of a small drainage network. Baseline event data was collected using an autosampler and a flow-proportional sampling strategy, with flow data collected from a hydrologger combined with a weir at both sites. Eight PSSBs were used in various configurations, sampling a total of ten events which were analysed for suspended sediment concentration (SSC). For each event, the mean SSC of the PSSB samples was compared with the event mean concentration (EMC) established by the autosampler. SSC loads and concentration ranges were subsequently compared. One additional event was sampled in the urban stream and analysed for metals and nutrients.

The initial configuration trialled for the first three runoff events at the catchment outfall had the majority of the PSSBs mounted at relatively low water levels. Due to the event and site conditions, this resulted in a strong positive bias of the PSSBs' SSC compared to the autosamples. Over three events, the mean PSSB SSC deviated from the autosampler's EMC between 64% and 400%.

The two successive configurations had the PSSBs mounted relatively higher, using an equal PSSB mounting height increment (configuration 2) and a more complex configuration using a decreasing mounting height increment as a % of events captured (configuration 3). For configuration 2, the maximum deviation of the mean PSSB SSC from the autosampler EMC was 96%, with a mean of 35% measured over four events in an urban stream. The maximum deviation of the mean PSSB SSC of configuration 3 was 44%, with a mean deviation from the autosampler EMC of 24% measured over three events at a catchment outfall.

For some events, the PSSBs sampled the highest event SSC, along the rising limb of the event's hydrograph. For other events, the autosampler sampled the highest SSC, around peak discharge rate. Configuration 1 at a piped catchment's outfall picked up on high concentrations early on the hydrograph's rising limb, which the autosampler and configuration 3 did not observe. At the same location, configuration 3 missed the highest concentrations that were present further into the event during peak discharge. This resulted in a maximum PSSB SSC deviation of -66% and -47% from the autosamplers maximum SSC value. For three out of four events monitored in an urban stream, the PSSBs sampled the highest concentrations.

For the events sampled using configurations 2 and 3, an SSC site mean concentration (SMC) was established using the PSSB and the automatic sampler method. The PSSB method deviated from the autosampler SMC by 34% in the urban stream, and 26% at the outfall. An analysis of the mean concentration of several nutrients and metals for a single event showed that, though deviations of up to 60% were present, both the PSSB and the autosampler method painted a similar picture when compared to the ranges found regionally in urban streams.

For the assessed constituents, the developed configurations 2 and 3 were able to provide event mean concentrations that deviated within a factor of two from the autosampler's results. The developed PSSB method can provide a rough indication of an EMC, as well as maximum discharge concentrations, albeit limited to the rising limb of an event's hydrograph. The method sits between single manual grab sampling and an autosampler in terms of accuracy, and provides valuable data for intra-event and inter-event variation. The use of multiple passive gravity flow samplers in a vertical configuration has potential as an additional tool for stormwater scientists, which could prove preferable over other methods depending on the goal and conditions of the initiated study.

Though the results were promising, the limited number of sampled events, constituents, and locations mark the results a mere indication of the usability of the method. Further study is needed to assess uncertainty, and the optimal application and data interpretation for a variety of catchments under a variety circumstances, for a wider range of pollutants.

Contents

Preface

Since I started writing my Bachelor's Thesis, my academical interests have been centred around the management of urban freshwater, with stormwater in particular. The continuous change and expansion of the urban morphology, combined with ongoing climate change, have steered my interests from planning to engineering and research, trying to understand every aspect of it along the way.

I can stare into a stream like staring into a fire. A seemingly endlessness source of life, which became a cause of life inhibition through our anthropogenic influence. In Māori culture, water is seen as the foundation of all life, where streams hold an important spiritual status (*mana*) and a life force, called *mauri*. Each river has its own *mauri*, and should not be mixed with waters that hold human, animal, toxic, or industrial waste, as that would inhibit the strength of the *mauri*.

It has taken two centuries of industrialisation for the Western world to understand, through academic science, that there is a lot to be said for the way Māori value freshwater. It is through science, good urban planning and design that we can re-strengthen *mauri* (which I like to think of as water quality) and restore *mana* (which I like to think of as ecological state) in our receiving environments.

Writing a thesis in just four months has been immensely challenging, as well as rewarding. The pressing deadline from day one resulted in a steep learning curve. I am positive this has helped me in my personal development, such as decision making and maintaining a general overview of where a project is heading.

I want to thank Dr Jennifer Gadd, Jonathan Moores, and Dr Jes Vollertsen for their guidance and providing me with the opportunity to do my research in New Zealand. A big thank you to Pete Pattinson and Christian Hyde for helping me with the field work.

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1. Introduction

Contaminants in urban stormwater runoff contribute strongly to the degradation of water quality and ecology in the receiving freshwater bodies, estuaries, and coastal areas (Novotny and Olem, 1994; U.S. Environmental Protection Agency, 1996; Walsh, 2000). Therefore, urban stormwater managers are tasked with the analysis and quantification of key contaminants, their sources, and how they affect the receiving water bodies.

Stormwater sampling and analysis is a multi-faceted process, which varies according to the research goals, catchment type, sampling location, and available resources. Common methods of stormwater sampling involve manual grab sampling or using an autosampler setup. A flow-proportional grab sampling strategy is known to provide the most accurate storm event pollution data (Ma et al., 2009). This can be achieved by manual sampling or using an autosampler, combined with some form of continuous flow measurement.

Whereas autosamplers require a considerable initial investment for installation in terms of capital and labour, manual grab sampling is limited by the availability of field-workers during a storm event (Ma et al., 2009; Stenstrom and Kayhanian, 2005). The initial installation effort necessary for an autosampler setup makes them less suitable for temporary or short-term (but recurring) sampling needs or short-term research projects. As pollutant concentrations vary during and between runoff events (Butler and Davies, 2011), labour needs to be mobilised prior to storm events if important data is not to be missed. Additionally, rainfall does not follow the typical nine-to-five working schedule of most workers.

Passive forms of stormwater sampling have the potential to be the middle-ground solution to the limitations of manual sampling and autosampling. As with an autosampler, passive sampling can be prepared at a time of relative convenience to the field-worker, yet the necessary investment for short-term projects is likely to be smaller. Passive samplers come in many shapes and sizes, and often target a specific pollutant to analyse over multiple events (Klein, 2013).

Passive gravity flow samplers, or passive stormwater sampler bottles (PSSBs), on the other hand, are a potential alternative to other forms of grab sampling, as they provide a complete stormwater sample which can be analysed for the pollutants most commonly looked at, such as metals, nutrients, bacteria, and suspended sediment. PSSBs have been used for multiple purposes, such as the analysis of first flush pollutant concentrations from roads (Barrett, Kearfott, and Malina, 2006), and the assessment of phosphorus concentrations in shallow overland flows (Waschbusch, Selbig, and Bannerman, 1999). However, common applications of such samplers use only a single sampler. By using multiple PSSBs mounted at different heights, multiple phases of a storm event can be sampled.

2. Study objectives

2.1 Aim

The aim of this study was to assess whether and how gravity flow passive sampler bottles can substitute manual sampling or the use of autosamplers for stormwater grab sampling, for the purpose of characterising storm event pollutant concentrations or event loads.

2.2 Objectives

1. To assess the physical and chemical variation of runoff between storm events and catchments
2. To outline existing stormwater sampling methods
3. To assess how physical and chemical event variations will affect the initiated passive gravity flow sampling method
4. To develop a practical and effective setup configuration for passive gravity flow sampler bottles
5. To assess the functioning and complications of this sampling method by performing field experiments

2.3 Report outline

The literature review addresses objectives 1 and 2, after which the methods and results of the field study are presented. The discussion reviews the outcomes and their relation to objectives 3 to 5. The conclusion outlines the most important findings with the intent to conclude on the aim of the study.

3. Literature review

3.1 Urban stormwater contaminants and effects

There is clear evidence that contaminants in urban stormwater runoff are a leading cause of impaired water quality in freshwater bodies, estuaries, and coastal areas (e.g. Novotny and Olem, (1994) and Walsh, (2000)). Urban runoff pollution related to human activities is the single biggest source of pollutants causing water quality impairment in ocean shoreline waters, and the second leading cause in estuaries in the United States (U.S. Environmental Protection Agency, 1996).

The challenges of addressing the issue of water quality impairment, concerns both water quality, as well as quantity. The increase in impermeable surface area caused by urban development results in an increased peak runoff velocity and discharge, and decreases the lag time as water flows freely across impermeable surfaces and through pipes (Arnold and Gibbons, 1996; Ferguson, 1998; Leopold, 1968; U.S. Environmental Protection Agency, 1993). This effect has been studied extensively, and is incorporated in runoff models such as the HEC-HMS (U.S. Army Corps of Engineers, 2000) which can approximate the impact of a development on the runoff volume and velocity. Additionally, the channelled and piped discharge network causes the baseflows in streams to decline, where they receive reduced recharge from groundwater exfiltration (Ferguson and Suckling, 1990). The urban stream hydrograph is therefore characterised by sharp peaks shortly after rain events, with low baseflow in between. The difference between a pre-development hydrograph and a post-development hydrograph is presented in Figure 3.1.

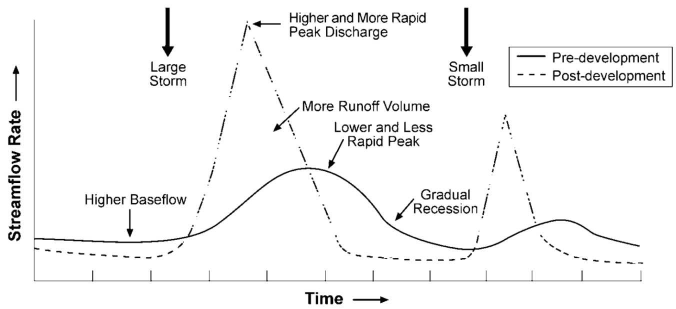


Figure 3.1: Pre-development and post-development hydrograph. From Ferrier and Jenkins (2009).

A wide range of sources contribute to stormwater pollution. Flowing over roofs, sidewalks and roads, urban stormwater runoff becomes polluted with solids, oxygen-consuming materials, hydrocarbons, nutrients, heavy metals, and bacteria (Butler and Davies, 2011). Construction activities, vehicular traffic, de-icing salts, animal urine and faeces, debris, spills and leaks of household cleaners and motor fluids, and wear and tear from roofing materials, gutters and roads, are some of the key sources of contributing pollutants (Förster, 1996; Shamseldin, 2011; Zanders, 2005). In areas where separated sewer systems are used, additional contamination of stormwater by wastewater is not uncommon. Cross-connections, illicit connections, overflows, and leakages of wastewater sewers are the main causes of this contamination type (Panasiuk et al., 2015).

The ecology of receiving water bodies is negatively impacted by stormwater in multiple ways. Suspended matter has an impact on the water ecology by reducing light penetration and water clarity. Non-degradable metals can reach toxic levels that have an instant effect, or accumulate over time affecting organisms through bioconcentration and bioaccumulation (Geffard et al., 2007; Moss, 2014). Accumulated hydrocarbons in sediments are prone to re-mobilisation during subsequent storm events and can have a chronic impact on bottom-dwelling organisms (Butler and Davies, 2011). Anthropogenic eutrophication from nutrients can lead to increased growth of aquatic plants and algae, dissolved oxygen depletion, and loss of biodiversity (Moss, 2014). An often overlooked factor affecting ecology is pollution in the form of thermal loading. Urban stormwater runoff comes with a thermal load that can affect the stream temperature (Hathaway et al., 2016; Herb et al., 2008). It is mainly within cold water ecosystems that a quick spike in temperature and reduction of dissolved oxygen can be harmful to the biota. The temperature spikes affect the persistence of fish by influencing their metabolism, egg development, resistance to disease and parasites, migration habits, and spawning habits (Armour, 1991; Beschta et al., 1987; Caissie, 2006; Hokanson, Kleiner, and Thorslund, 1977).

The effects of stormwater pollution on a water body can be distinguished between acute and accumulative effects (Hvitved-Jacobsen, Johansen, and Yousef, 1994). This time-based classification (Figure 3.2) indicates how a pollutant can be approached in terms of its effect and how one can remediate this effect. If the effect is acute, treatment and/or storage (buffering) of runoff can be established to reduce the shock effect of single (extreme) events. In the case of accumulative effect, efforts can be focused on reducing the total contributing pollutant load of a catchment over a specific period of time, without the need to consider single-event peak concentrations.

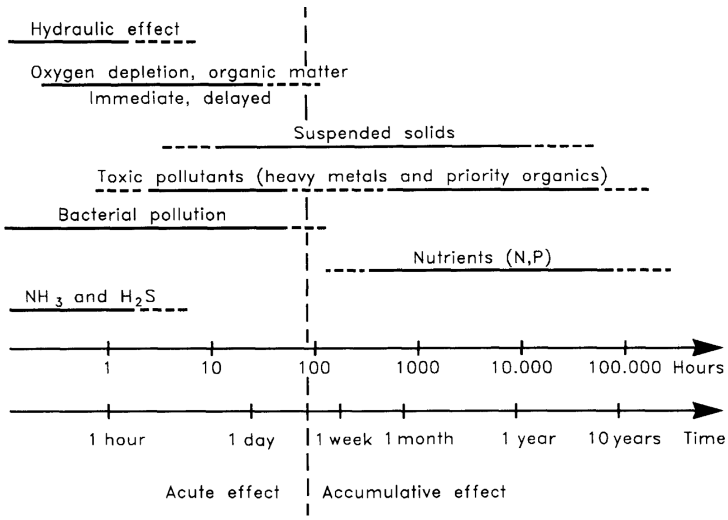


Figure 3.2: Time scale for effects related to stormwater runoff pollutants. From Hvitved-Jacobsen, Johansen, and Yousef (1994).

3.2 Urban stormwater characteristics

Accumulation, mobilisation, and pollutant load follow the patterns of rainfall events (Hvitved-Jacobsen, Vollertsen, and Nielsen, 2010). During inter-event dry periods, pollutants accumulate on the impermeable urban surfaces, after which they are mobilised by rainfall events. These dynamics result in inconsistent pollutant concentrations between catchments, but also variation between (inter) and within (intra) events at a single catchment. For a specific location, the standard deviation for pollutant concentrations measured over multiple runoff events is generally of the same order of magnitude as the average value (Hvitved-Jacobsen, Vollertsen, and Nielsen, 2010). To characterise pollutants in stormwater and to compare these with existing data and legislation, the terms event, event mean concentration, site mean concentration, first flush and (contributing) load must be introduced:

- Event: in urban hydrology, there is a distinction between a storm or rainfall event, and a runoff event. A storm event is defined by the minimum dry interval between periods of rainfall (Ignaccolo and Michele, 2009). A runoff event differs, as it depends on the catchment characteristics, and also the position of the point of interest in the larger catchment drainage system. A runoff event typically lasts longer than a rainfall event.
- Load: The mass of a substance conveyed from a source, usually defined per event, per unit of time, or per area per unit of time. The contributing load is the added mass of a substance from a defined (sub)catchment to the receiving environment.
- Event mean concentration (EMC): quantifies the average concentration of a substance in stormwater, established in the field by dividing the event load by the sampled volume (Ackerman et al., 2011) or establishing the mean of flow-proportional samples.
- Site mean concentration (SMC): is used to assess e.g. annual loads, and is established by dividing the total load measured over multiple events, by the total volume of these events (Francey, 2010).
- First flush: can be distinguished between concentration-based and mass-based first flush (Sansalone and Cristina, 2004). It refers to the presence of high initial concentration, or proportional load of a pollutant during a runoff event, after which a rapid decline follows.

In chapter 7 of the *Handbook of Catchment Management* (Ferrier and Jenkins, 2009), J.B. Ellis compiled eight papers and reports to set out the event mean concentrations (EMCs) and ranges for the most commonly analysed pollutants for two catchment types (Table 3.1). Pollutant concentrations in stormwater are most commonly expressed in the (equal) units of mg/L and g/m^3. A distinction is often made between catchment types, as certain land-use types, like highways or industrial areas, generally produce higher pollutant loads per area than, e.g., low density residential areas (Zhao and Li, 2013).

Pollutant parameter	Event mean concentration and range (mg L^{-1})	
	Residential and and commercial	Motorways and trunk roads
Total suspended solids	190 (1–4,582)	261 (110–5700)
BOD	11 (0.7–220)	24 (12.2–32.0)
NH_4-N	1.45 (0.2–4.6)	(0.02–2.1)
Total nitrogen	3.2 (0.4–20.0)	
Total phosphorus	0.34 (0.02–14.3)	
Total lead	0.21 (0.01–3.1)	0.96 (2.41–34.0)
Total zinc	0.30 (0.01–3.68)	0.41 (0.17–3.55)
Total hydrocarbons	1.9 (0.04–25.9)	28 (2.5–400)
Polyaromatic hydrocarbons	0.01	(0.03–6.0)
Faecal coliforms (*E. coli*)	6,430 (40–500,000) MPN 100 ml^{-1}	$10–10^3$ MPN 100 ml^{-1}

Table 3.1: Pollutant concentrations and loadings from urban stormwater runoff. BOD = biochemical oxygen demand, MPN = mean probable number. Altered from Ferrier and Jenkins (2009).

3.2.1 Inter-event variability

The stormwater quality from a given catchment varies between storm events. This is a result of pollutant accumulation, rainfall intensity, and, in some cases, seasonality (Butler and Davies, 2011). Accumulation of pollutants on impermeable surfaces depends on multiple factors, such as:

- land use,
- traffic intensity,
- street cleaning,
- season,
- street surface type and condition, and
- antecedent dry period.

Research has found that accumulation of pollutants has a decreasing rate over time (Sartor, Boyd, and Agardy, 1974), which can be linked to vehicle re-suspension and the presence of adjacent pollution traps, such as planted permeable areas (Ellis, 1986). Rainfall intensity affects the ability of stormwater runoff to convey certain pollutants. This will be further explained in Section 3.2.2. Seasons can have an effect on the mass of deposited organic material (e.g. deciduous tree leaves) and the presence of de-icing salts, but also correlate with the duration of inter-event dry periods and the survival and accumulation of pathogenic micro-organisms (Hathaway and Hunt, 2011; McCarthy et al., 2012). Build-up within the pipe network is an additional factor that impacts inter-event variability (Ashley and Crabtree, 1992). Having one or more small rainfall events may cause particles to build up within the piped system, generating a large release of sediment and associated pollutants during a subsequent larger storm.

3.2.2 Intra-event variability

Pollutant concentrations are also variable within a single storm event (Tiefenthaler, Schiff, and Leecaster, 2002). In some cases, pollutants in stormwater runoff exhibit a so-called first flush transport pattern. The presence of a first flush depends on a variety of factors such as pollutant type, storm size, rainfall intensity, watershed characteristics, and antecedent number of dry days (Deletic, 1998; Sansalone and Cristina, 2004). There is no agreement on a single quantifying definition of first flush. For example, some assessments evaluate the conveyed mass during the first 20% (MFF_{20}) of the total storm volume (Deletic, 1998; McCarthy et al., 2012; Sansalone and Cristina, 2004). MFF_{20} refers to the proportion of mass transported in the first 20% of the storm volume. First flush is present when the relative mass transported is higher than the relative volume it is conveyed in. In other studies, MFF_{25} and MFF_{30} have been assessed instead of MFF_{20} (Hathaway and Hunt, 2011).

Deletic (1998) concluded after a year-long study focusing on two catchments that first flush could not be predicted using a universal set of climate, rainfall, and runoff characteristics. The study measured suspended solids, pH, and temperature for FF_{20}. The occurrence of first flush was found to be site-specific and too complex for a general model. For event mean concentration and mass fluxes for suspended solids, however, engineers and researchers have a variety of models at hand (see e.g. Dembélé et al., 2011; Rossman and Huber, 2016).

Intra-event variability, including first flush, is dependent on many factors and is pollutant specific. Studies found that the size of the catchment influences pollutant characteristics, where larger catchments have more complex stormwater infrastructure and more variable pollutant sources (McCarthy et al., 2012). Rainfall intensity is known to have the strongest correlation with suspended solids concentration, as the kinetic energy of rainfall is the primary process in sediment transport (McCarthy et al., 2012; Shen and Julien, 1993; Vaze. J Francis H. S., 2003). Microbiological contaminants such as *Escherichia coli* show a strong correlation with antecedent weather conditions (McCarthy et al., 2012) and are generally equally discharged per volume throughout an event (Hathaway and Hunt, 2011). Polycyclic aromatic hydrocarbons are found to predominantly exhibit first flush patterns as they are promptly mobilised by rainfall (Stein, Tiefenthaler, and Schiff, 2006; Zhang and Sansalone, 2014).

3.2.3 Pollutant distribution in stormwater

Pollutants are present in stormwater in dissolved and particulate bound forms. A large share of the pollutants have a strong affinity with sediment particles (Butler and Davies, 2011), which can therefore be an effective surrogate parameter for pollutants that are associated with particles, such as numerous metals, ionic species and nutrients (Beck and Birch, 2012; Sansalone and Buchberger, 1997; Thomson et al., 1997; Zhang and Sansalone, 2014).

As suspended solids are receiving a lot of emphasis in stormwater quality assessments (e.g. Beck and Birch, 2012), it is useful to have an understanding of solid's behaviour in stormwater. Suspended particles are dispersed in water through hydrodynamic lift and drag forces. The dispersion of a particle is the net result of the upward velocity components (from turbulence), and the fall velocity, which depends on the particle's size, shape, density, and the density and viscosity of the water (Hicks and Fenwick, 1992). The coarse sediment fraction (sand) will therefore be generally more abundant towards the bottom of a water body as a result of their higher fall velocity. Fines (silt and clay) have a lower fall velocity and tend to have a vertical concentration profile that is relatively uniform. Hence, a vertical suspended solids concentration profile of e.g. an urban stream, stormwater channel or a storm sewer will show an increasing trend towards the bottom (Figure 3.3). Due to the vertical concentration profile of suspended solids, Martin, Smoot, and White (1992) found that in a non-urban stream there was a significant ($\alpha = 0.05$) difference in concentration between the top of the water column, and the vertically integrated average for suspended sediment, total phosphorus, and iron.

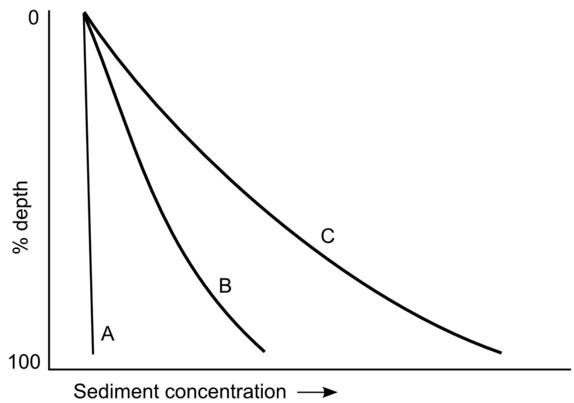


Figure 3.3: Vertical concentration profiles: A) Fine sediment fraction B) Coarse sediment fraction C) All size fractions. Altered from Hicks and Fenwick (1992).

Metals in stormwater are predominantly found in the particulate phase (Butler and Davies, 2011). The dissolved phase is relevant when looking at bioavailability and toxicity. A recent field study by Djukic et al. (2016) found that of the total metals mass (Fe, Zn, Cr, Cu, Ni, and Pb) in urban stormwater runoff, less than 3% was present in the dissolved phase. The study also found a strong correlation between total suspended solids (TSS) and the total content of metals. Beck and Birch (2012) found a significant correlation between TSS and Cu, Pb and Zn for all of the three tested catchments during rainfall events, and consequently advocated the use of TSS as a surrogate parameter for these pollutants once the relationship for a specific catchment is established.

Of the sediment fractions, silt and clay have the bulk of metal mass associated with them due to their binding capacity. A study looking at the runoff from a catchment in the Haidian District, Beijing, found that over 70% of the total metal mass (Cd, Cr, Cu, Ni, Pb, and Zn) was associated with particles smaller than 44 μm (silt and clay), with particles larger than 250 μm having the lowest metal mass associated with them (Zhao et al., 2010).

The presence of pathogenic micro-organisms is not usually measured directly, but through faecal indicator bacteria (FIB). McCarthy et al. (2008) found that for *E. coli*, spatial distribution was generally homogeneous throughout the water column at a given time, which is in line with the knowledge that FIB are associated with fine particulate matter (Davies and Bavor, 2000). Hydrocarbons, of which mainly petroleum-derived groups are found in stormwater, can be lighter than water and usually have a strong affinity for suspended particulate matter (Butler and Davies, 2011). Films and emulsions floating on top of runoff and water bodies reduce surface re-aeration of water at the water-air interface.

Of the nutrients, nitrogen and phosphorus are the main species that have associated water quality standards or other legislation. Nitrogen is present in four main forms: organic, ammonia, nitrite, and nitrate (Butler and Davies, 2011). Dissolved inorganic nitrogen in the form of ammonia, nitrite and nitrate have the greatest impact on water bodies as they are readily bioavailable. High nitrate concentrations are a result of general urban impact, whilst high ammonia concentrations may indicate organic pollution from sewers (Taylor et al., 2005). Nitrate is often the most common soluble form of N in urban stormwater (Galloway et al., 2003). A 2014 study by Zhang and Sansalone partitioned total nitrogen (TN) into dissolved, suspended, and settleable fractions. The study found that, taken over 14 storms, the dissolved fraction represented a mean of 51% of TN, and suspended particulate forms a mean of 17% of TN. Phosphorus in stormwater is found in particulate forms and dissolved forms, like the inorganic bioavailable orthophosphate. Waschbusch, Selbig, and Bannerman (1999) found that, for two catchments, the dissolved phosphorus constituted around 43% of the total phosphorus in runoff from a range of pollutant sources, such as lawns and parking lots. The partitioning of phosphorus between dissolved and particulate forms in stormwater is highly variable, between 20 and 90% (New York State, 2008). Therefore, dissolved and total phosphorus are usually both assessed.

3.3 Stormwater sampling

The three main methods of stormwater sampling are grab sampling, composite sampling, and continuous sampling. Grab samples are discrete samples of a specified volume that depict the local conditions of stormwater at a given time. When these samples are subsequently combined, a composite sample is created to represent an average value for a volume or time period. Continuous sampling differs slightly, as a small fraction of the stormwater is continuously diverted or taken in to represent an average pollutant value over a period of time. Continuous measurement is another method to obtain stormwater quality data, where monitoring equipment is used to obtain continuous data, e.g. for pH, temperature, flow rate, conductivity, and turbidity (Sun et al., 2015).

3.3.1 Sampling strategy

The strategy of sampling is subject to the goal of the study, the catchment, the location of sampling, time restrictions, and the availability of resources. For example, if the goal is to establish an event mean concentration of a specific pollutant, the ideal method would be to collect the whole runoff volume of the event and measure the concentration in the sample. However, this is unrealistic in most cases considering the physical implications and the burden on resources. Alternatively, continuous measurements throughout an event of both discharge volume and pollutant concentrations could provide a detailed EMC. This strategy may, however, be impractical or impossible. Initial investment, cost of maintenance, availability of power sources and the availability of automated analysers for certain pollutants could deem this approach infeasible (Ma et al., 2009).

Considering the above, it is for practical reasons that manual grab sampling and the use of autosamplers are the two most commonly used tools for stormwater quality assessment. The increasing interest in this form of pollution in the past decades translates into a demand for sampling strategies, equipment, and sample analysis methodologies (Lee et al., 2007). Sampling and analysing of stormwater runoff is mainly performed to assess the contributing pollutant load of a catchment, to identify high-risk discharges, or to compare the water quality with relevant standards, guidelines or consent conditions such as a total maximum daily load.

3.3.2 Autosampling

Autosamplers can be programmed to take multiple grab samples during a storm event, based on time or volume of water passed given a pre-determined interval. When set up correctly, autosamplers can provide a relatively accurate estimate of single storm event pollutant characteristics compared to most forms of manual grab sampling. Additionally, the autosampler can provide intra-event data by taking multiple samples over fixed intervals, which can e.g. help identifying the existence of first-flush patterns. There are downsides to the use of autosamplers, as the equipment requires a comparatively large initial financial investment. This limits the use to the purpose of specific research and monitoring efforts with an adequate budget. Additionally, autosamplers are complex to operate, and, due to the unpredictability of storm events, it can prove tricky to program the autosampler to catch the whole event.

3.3.3 Manual grab sampling

The manual grab sampling method is limited in the number of samples taken and relies on staff being available at the time of the storm event. The quality of the data is dependent on the followed procedure. There are known procedures which use a cross-sectionally (vertically) integrated sampling method which is accepted to be accurate, but resource intensive (Harmel, King, and Haggard, 2006). Fletcher and Deletic (2007) showed that if a single random sample is taken for multiple events (20 in the study), an accurate site mean concentration can be estimated with a similar certainty as when using an autosampler. The positive outcome found in this study demonstrated the Central Limit Theorem. Some storms will be under-estimated because the sample was taken when the concentration was at the low end of the pollutograph, and other storms are over-estimated as the sample was taken at the high end of the pollutograph. Apart from the large human resource investment needed to obtain reliable results (getting to the field site at unpredictable times, under harsh weather circumstances, for a multitude of events), the method does not obtain additional information that can be provided by an autosampler, such as intra-event variability and active volume measurements (Fletcher and Deletic, 2007).

3.3.4 Passive sampling

Passive sampling can be defined as a sampling technique based on free flow of analyte molecules from the sampled medium to a receiving phase in a sampling device (Vrana et al., 2005). Passive samplers are generally seen as an affordable alternative which can be installed without a power source on-site, and can be effective without the need of a person to operate it during an event. Passive forms of stormwater runoff sampling have been less explored, and could have the potential to be the middle-solution between grab sampling and autosampling. Passive samplers have been successfully used for groundwater, rivers/streams, wastewater monitoring, and air quality monitoring for some time. The use of multiple passive samplers within one setup can provide additional intra-event information that would not have been obtained using forms of manual grab sampling, which was seen as an important limitation by Fletcher and Deletic (2007).

There are a variety of passive samplers available, often targeting specific pollutants using principles such as diffusion and sorption (Klein, 2013). A common characteristic of this equipment is that it is generally applied in relatively stable sampling environments such as groundwater, wastewater flows, and air. These passive sampling devices are designed to quantify the presence of a target pollutant based on the chemical potential differences between the environmental media and the media used in the sampler.

Urban stormwater runoff, however, has an unpredictable, highly variable volumetric flow rate and variable pollutant concentrations throughout storm events. Some chemically-based passive sampler applications (e.g. the Sorbisense Sorbicell or DGT®s) can be effective for mean pollutant concentration assessments over a longer period of time. Nonetheless, they are unable to sample for suspended sediment, which, as mentioned in Section 3.2.3, is a primary water quality indicator. Nor do they provide data on intra-event variability. Unpredictable flow may introduce uncertainty in terms of (minimum and maximum) exposure time, and, unlike grab-sampling bottles, chemical-potential based passive samplers are single-use, which may prove costly and wasteful when used for extensive monitoring efforts.

Passive gravity flow samplers, or passive stormwater sampler bottles (PSSBs), are different to their chemical-potential based counterparts, as they have been purpose designed for collecting stormwater runoff samples. PSSBs collect whole stormwater samples, including suspended solids. The basic principle is the collection of stormwater flow as it passes through or over the sampler inlet. A variety of models have been developed and tested over time, with different study purposes in mind. One such development was the "street-runoff sampler" developed by Waschbusch, Selbig, and Bannerman

(1999). Figure 3.4 shows how the sampler was positioned in the road asphalt, collecting a small proportion of the road runoff flow at a time, slowly filling up the sampler bottle during an event.

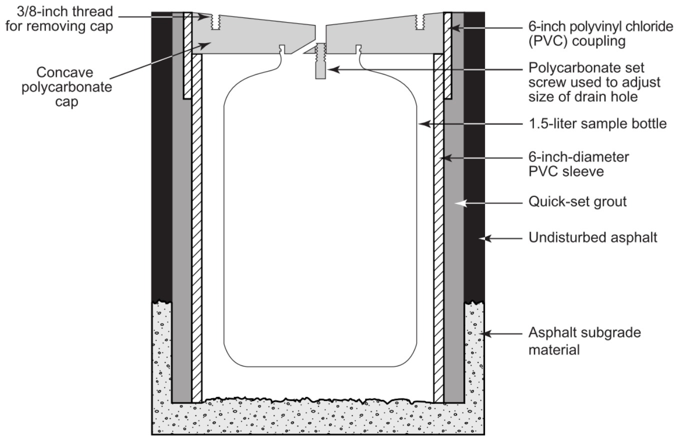


Figure 3.4: Street-runoff sampler by Waschbusch, Selbig, and Bannerman (1999).

A similar device has been developed by Young, Graziano, and Stein (1998), with an added valve which closes automatically once the sampler bottle has filled up. These setups have been used in several studies to assess pollutants in road runoff (e.g. Barrett and Stanard, 2008). The inlet can be adjusted and designed in such a way that first flush or a more extended portion of the event is being sampled. First flush sampling on large roads is often done with a similar sampler bottle, but with an additional perforated PVC tube positioned alongside the road catching the sheet flow (Figure 3.5).

Figure 3.5: Sheet flow sampler by Barrett, Kearfott, and Malina (2006).

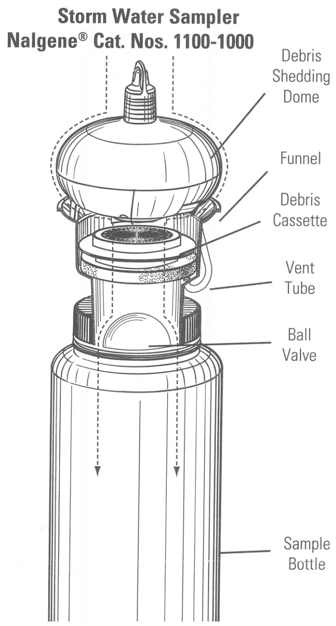


Figure 3.6: Nalgene Storm Water Sampler.

The Nalgene 1100-1000 HDPE Storm Water Sampler is another type of passive gravity flow sampler. This PSSB fills up when the water level overflows the rim to the inlet, after which it flows into a 1 litre HDPE bottle. Once filled, a ball valve closes the inlet on a seal, preventing any further water from mixing with the sample. The sampler was designed to be used in storm grates, ditches and storm streams. The sampler has been used in studies to assess site mean concentrations of pollutants (Jackson, 2005), in a pilot study of stormwater analysis tools for a lake catchment (2NDNATURE LLC, 2011), and is being used in municipal stormwater monitoring plans (City of Bend, 2013).

Although useful for obtaining a single grab sample without needing to be present during an event, it provides minimal information in terms of what part of a runoff event is sampled; hence, to what extent the sample is representative for the larger event. In its common application, the sampler is limited to capturing (part of) the first flush.

3.4 Sampling uncertainty

In terms of stormwater quality assessment, there is a difference between precision and accuracy (Butler and Davies, 2011). Precision refers to how well a procedure derives the same results when a test is repeated. Accuracy describes how well the procedure produces results that are representative. This is relevant for both the procedure of taking samples, as well as analysing them in the laboratory. Accuracy can be quantified by establishing the uncertainties for each individual step in a method. Uncertainties in water quality data are introduced in four stages (Harmel et al., 2006; McCarthy et al., 2008):

- discharge measurements,
- sampling,
- storage, and
- analytical uncertainties.

Uncertainty in discharge measurements is relatively well assessed. Harmel, King, and Haggard (2006) state that for well-designed weirs the uncertainty is around 10%, which is more accurate than discharge assessments of morphologically active channels, which have an uncertainty of around 20%.

Sampling uncertainty concerns the sampling strategy and equipment, and is related to the uneven distribution of pollutants throughout the water column and over time. For TSS, McCarthy et al. (2008) summarised a sampling uncertainty of 15-20%, though this was measured in streams. Concentrations of sediment-associated forms of pollutants, such as phosphorus, were found to be lower in surface samples than in cross-sectionally integrated samples (Martin, Smoot, and White, 1992), with a median difference, or bias, in the range of 20-25%. Assuming that piped runoff during an event will experience relatively large turbulence, the vertical gradient should be lower, potentially reducing this bias. Using standard autosampler intake tubes and positioning is found to significantly overestimate particles larger than 88 µm (Gettel et al., 2011), due to the intake tube commonly being positioned close to the bottom. Pollutants that are found in dissolved forms, or which have particulate forms that are mostly bound to the fine particle fractions, have a lower sampling error. For example, Martin, Smoot, and White (1992) found that the sampling error was close to 0 for most nitrogen species.

In terms of sampling strategy, grab samples collected at equal discharge volume intervals is regarded as the most accurate sampling strategy for stormwater quality assessment on an event-basis (Ma et al., 2009). Using sampling simulation and a large pre-existing set of data, Ma et al. (2009) established that the median sampling error for an equal discharge autosampling strategy to estimate an EMC was 23% using a series of 10 samples. The median error dropped to 17% when the number of samples was increased to 20.

A contributing load of a catchment can be assessed by establishing a site mean concentration. The characteristics of a catchment will determine the most suitable sampling strategy. Small events and large events have differing pollutant transport characteristics, and both should be accounted for. In an urban stream, baseflow and stormflow during events should be sampled. Not targeting events in small (urban) stream sampling could underestimate constituent loads by 40% (Haggard et al., 2003), whereas exclusively sampling during events has the opposite effect in smaller streams (Robertson and Roerish, 1999), i.e. overestimating the mean constituent concentration.

Often when sampling stormwater, samples will not be analysed immediately. In this storage time between sampling and analysing, the presence of pollutants can change. McCarthy et al. (2008) summarised that for suspended sediments this uncertainty is relatively low (around 10%), whereas for some nutrients species the uncertainty can be over 50% within just 6 hours. Though other authors have found significant changes in nutrient concentrations within 4 to 48 hours of refrigeration (Harmel et al., 2006), Kotlash and Chessman (2006) found that refrigeration was effective for up to two days for a range of sites under varying weather conditions. The material of the container used also has an influence. For example, dissolved phosphorus has a high affinity for adsorption to container walls (Jarvie, Withers, and Neal, 2002). With micro-organisms McCarthy et al. (2008) found an uncertainty of 30% for *E. Coli* for discrete samples, and an average uncertainty of 20% for EMC estimates. Moreover, there is a large error expected when samples are kept in unrefrigerated autosamplers.

Finally, there are analytical uncertainties relating to the lab procedures. Here, again, the uncertainty for suspended solids analysis is relatively lower (around 10%) than that of other pollutants such as micro-organisms which has an average analytical uncertainty of over 27% (McCarthy et al., 2008).

4. Methods

To assess how well, or accurately, a setup using multiple passive gravity flow samplers can characterise pollutant concentrations in the field, two sites with historical water level data available were selected. As suspended sediment is an important water quality indicator, the field study used suspended sediment concentration (SSC) for comparison between the Nalgene passive stormwater sampler bottles and the autosampler samples. Additionally, for one event, metals and nutrients were analysed.

4.1 Field study locations

Two sites were selected for field study (Figure 4.1), one within a stormwater network and one within an urban stream. These sites were selected for their position at the downstream part of a catchment, before discharging to the receiving environment. Therefore, there were no subsequent man-made structures that reduce pollutant loads, such as sediment traps or catchpits. The available space and water level data during events made it a suitable environment to test PSSBs in various configurations.

The **Pakuranga** site is located at the end of a drainage network. Here, a 1420 mm diameter pipe, which is the single discharge outlet pipe of a 0.3 km^2 catchment, drains into the Tamaki River tidal inlet. The **Blockhouse Bay** site, located immediately upstream of Blockhouse Bay Road, is located within a channelled urban stream in West Auckland called the Whau River, which drains into the Whau estuary.

The Pakuranga catchment has both commercial and residential land use. The catchment is bound in the north and south by two urban arterial roads, Pakuranga Road and Ti Rakau Drive. The commercial and residential area are approximately equally as large. The commercial area is situated in the western part of the catchment, dominated by the Westfield Pakuranga Plaza mall, and the eastern part is dominated by medium density residential land use. The baseflow is approximately 1 L/s.

The Blockhouse Bay catchment is larger and the stream has a larger baseflow. The bulk of the catchment constitutes of low to medium density residential area which are the suburbs of New Windsor and Avondale. The baseflow is approximately 10 L/s.

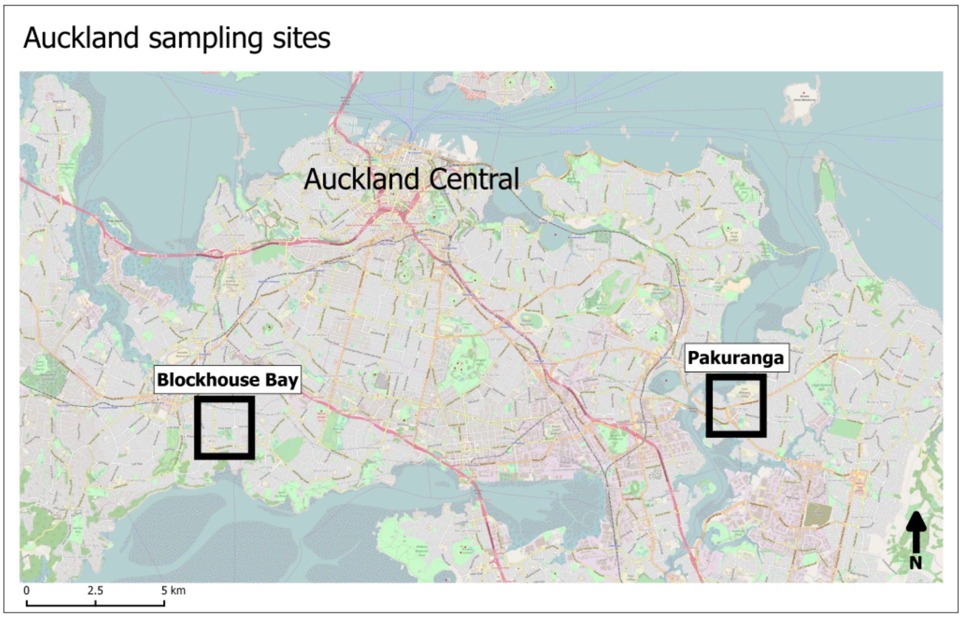


Figure 4.1: Field study sites in Auckland, New Zealand.

4.1.1 Climate conditions

Auckland has a subtropical climate with warm and humid summers and mild winters (NIWA, 2014). Rainfall is typically plentiful throughout the year, with sporadic heavy events. Dry spells can occur in the summer months, but they are rarely long-lived. Pakuranga and Blockhouse Bay have an average annual rainfall of about 1212 mm, with relatively wetter winters than summers (NIWA, 2014). At the start of this project, in February, little rain could be expected as this month generally only has 5% of total annual rainfall (Table 4.1). In March (8%), April (9%), and May (8%), the rainfall picks up again. Storm events are highly variable, from short and intense events to low-intensity rainfall that last for hours, and everything in between.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Ann
a	82	64	94	103	98	113	138	129	108	95	100	90	1212
b	7	5	8	9	8	9	11	11	9	8	8	7	
c	74	66	91	102	109	124	147	116	103	101	90	93	1213
d	6	5	7	8	9	10	12	10	8	8	7	8	

Table 4.1: Overview of monthly/annual rainfall normals (a,c; mm) and percentage of annual total for eacht month (b,d;%) at Pakuranga (a,b) and Blockhouse Bay (c,d). Modified from NIWA, (2014).

4.1.2 Historical flow and water quality data

Flow data for Pakuranga was available from June 12, 2015 until December 1, 2016. During this period, two sets of 9 storm events were analysed for pollutants. Samples were taken by an autosampler, using a flow-proportional sampling strategy. The samples of a single storm event were composited, and concentrations assessed for volatile suspended solids, total suspended solids (TSS), dissolved copper, total copper, dissolved lead, total lead, dissolved zinc, total zinc, and suspended-sediment (SSC). Bulking the samples meant that no intra-event data was generated.

For three additional events (07/10/2016, 25/11/2016, and 16/02/2017), intra-event variability of SSC was measured. Figure 4.2 shows the SSC variation and flow during the event, and a calculated correlation coefficient between the two parameters. As expected from literature (see Section 3.2.2), the SSC was strongly correlated with flow, which is related to rainfall intensity. The average MFF_{25} over the first two storms was 26%, indicating steady mass transport. First flush is likely to be present at e.g. catchpits within the catchment. Due to sampling at the outlet of the catchment, this effect is likely to be 'diluted' to a certain extent.

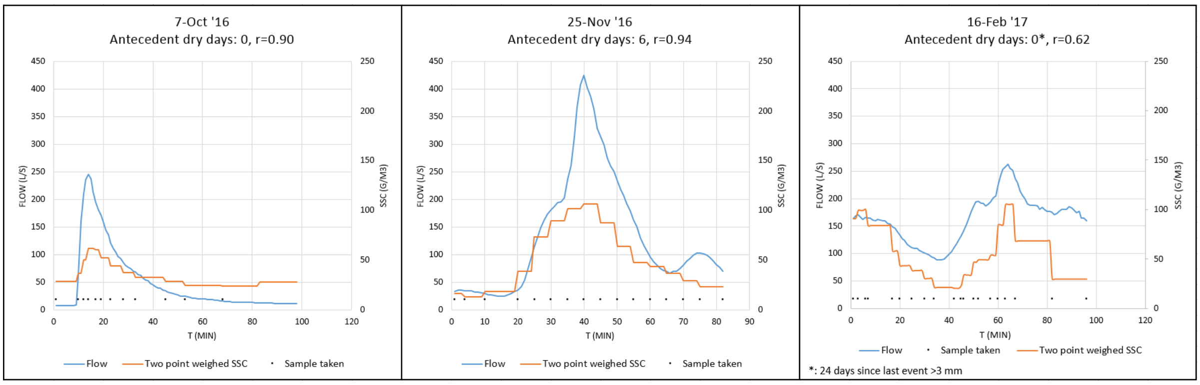
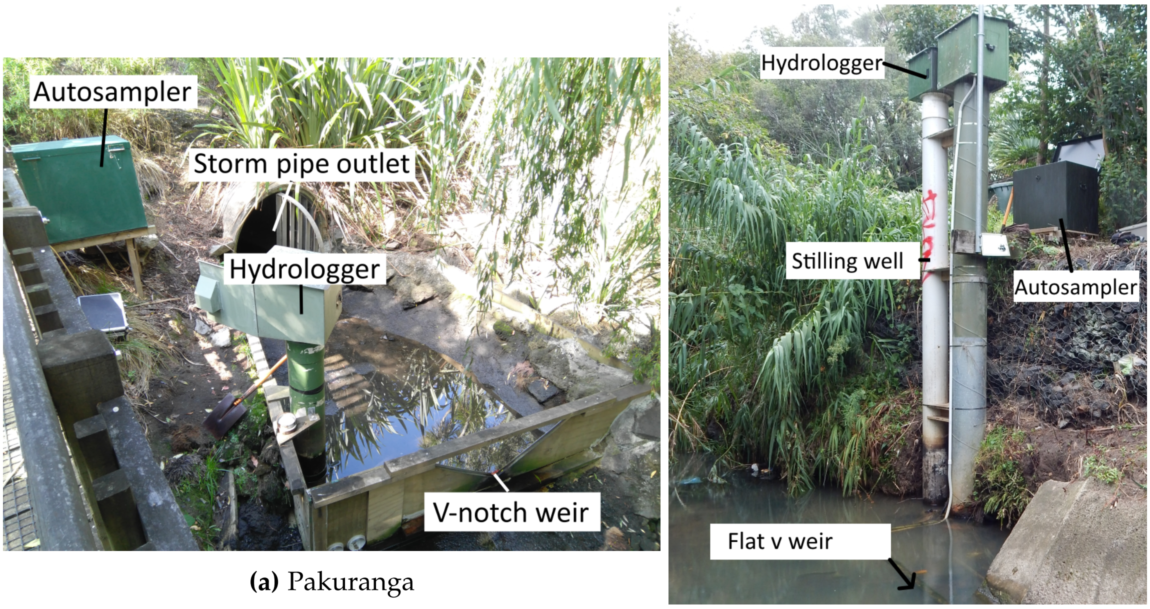


Figure 4.2: Inter-event variability of SSC and the flow. r = Pearson correlation coefficient between flow and SSC from analysed samples.

At Blockhouse Bay, in-house historical flow data was available from August 2005 through to September 2006. Though five events were analysed during this time period for TSS, particulate metals, dissolved metals, hydrocarbons, nutrients, and faecal indicator bacteria, no intra-event data was available for analysis.

4.1.3 Existing setup

At Pakuranga, a structure which controls water level directly at the outlet of the storm pipe was created in the form of a compound rectangular sharp-crested v-notch weir (Figure 4.3a). Design and flow rating was done as per ISO standards, using the Kindsvater-Shen equation (International Organization for Standardization, 1983). Stage height (water level above v-notch) was measured in a stilling well using a float and counterweight-based hydrologger, which was installed in a cabinet sitting on top of the well. The stage height value is the water depth from the lowest point of the v-notch to the water surface. The hydrologger determines flow from the rating, and was connected to an ISCO 3700 autosampler in order to take samples according to a programmed scheme. The intake hose of the autosampler was slightly elevated in the stormpipe, facing upstream under a 45 degree angle.



(a) Pakuranga

(b) Whau at Blockhouse Bay

Figure 4.3: Overview of the test sites, pointing out the autosampler, storm pipe outlet, hydrologger and the weir.

At Blockhouse Bay, a flat-v concrete weir was installed to determine the flow of the stream given a certain water level (ISO 4377:2012). The flat-v weir was approximately 4 meters downstream of Figure 4.3b. Gagings in the past have been done to calibrate the rating. A stilling well, hydrologger and ISCO 3700 autosampler were installed here as well. The intake hose of the autosampler was placed approximately 30 cm above the stream bed, with the opening perpendicular to the stream flow direction.

4.2 Autosampling

4.2.1 Strategy

Automatic sampling was used to provide baseline data for comparison with the PSSBs. The established EMCs and event loads from the autosampler were deemed as the 'true', or baseline values, as it provides the most accurate available data.

Weather forecasting was an important side-aspect of this study. A reliable forecast was needed to set up the sampling scheme in the hydrologger, which controls the autosampler. NIWA in-house forecasting, as well as freely online available forecasting from New Zealand's Metservice, was used to estimate rainfall depths. Small (<5 mm) rainfall events are not commonly sampled. Small events in Auckland are common and hard to predict in terms of geographical location, duration, and rainfall depth, meaning they are relatively difficult to sample. For practical reasons it was chosen to sample larger (>5mm) events during the course of this study. If an event of 5 mm or more was forecasted within one or two days of the event, the locations were set up to sample.

Autosampling was done using an ISCO 3700 automatic sampler loaded with 24 sampling bottles at Pakuranga, and 12 at Blockhouse Bay, which can hold a sample volume of approximately one litre each. For each individual rainfall event, an estimate was made of the expected flow volume based on historical flow-rainfall data, with the aim to obtain samples over the whole event. A flow-proportional sampling approach was used, where 24 samples are taken at a pre-determined volume interval. This sampling scheme was programmed to the hydrologger, which calculates flow based on the programmed stage height rating and sends a signal to the autosampler when the determined flow volume has passed. An initial trigger stage height was programmed, which is set to be directly above baseflow water level.

4.3 Passive sampling

4.3.1 Passive stormwater sampler bottles

Nalgene 1100-1000 HDPE Storm Water Samplers were used in this study. The passive gravity flow sampler bottles fill in under 90 seconds and the HDPE bottles hold a 1 litre sample each. Once fully filled, a ball valve closes the inlet on a seal, preventing any further water from mixing with the sample. An alternative mounting unit for the passive bottles was developed, where multiple bottles are mounted at increasing heights. Therefore, multiple samples are taken during a single event, with the number limited to the amount of bottles and the maximum water level reached during a storm event.

Using cable ties, the PSSBs were mounted onto the mounting unit at their designated heights. The debris cassettes were removed, as leaves and other suspended (organic) material could potentially clog the inlet. Though designated for single-use purposes, it was found that the PSSBs performed well over multiple events. All parts were thoroughly washed in between uses in a lab-grade dishwasher.

4.3.2 Number of passive stormwater sampler bottles

The larger the number of passive stormwater sampler bottles, the more samples and more accurate data can be obtained per storm. During a small or low intensity event, water levels only come up a little, whereas during a large or intense event, water levels rise relatively higher. The challenge was to sample with strategically placed PSSBs, without having to increase the number of bottles, and therefore the budget, too much. Within this study, eight bottles were used at both of the field sites, as this allowed for enough 'room to play' with different configurations, whilst staying within the designated budget. Analysis of configurations using fewer bottles was possible by leaving sample results out. Having a much larger number of PSSBs would decrease practical use and increase analysis costs, which would be contrary to the goal of developing a low-cost alternative to existing methods. At the same time, as samples can only be obtained during the rising limb of a storm event, adding more bottles between the lowest and highest water flow can only increase data accuracy for this limited part of the hydrograph.

4.3.3 Passive stormwater sampler bottle mounting unit

The objective of the PSSB mounting unit was to position and mount the PSSBs in a way that minimises the sampling error and sampled the most representative part of the flow, given the inherent constraints of the method. Positioning the PSSBs in the water column had to be done where there was no abnormal turbulence, to avoid sampling of e.g. locally re-suspended sediments or erosion from the stream bank. For each site a mounting unit was built that fit the local conditions (Figure 4.4), that was high enough to catch both high and low flows, and that was able to hold up to eight PSSBs. At Pakuranga the mounting unit was placed directly in line with the flow from the outlet pipe, towards the v-notch overflow. At Blockhouse Bay, the unit was mounted to a reinforced stream bank, in line with the flow direction.

(a) Pakuranga **(b)** Whau at Blockhouse Bay

Figure 4.4: The mounting units at Pakuranga and Blockhouse Bay. The Pakuranga mounting unit is secured in the concrete substratum, whereas the Blockhouse Bay mounting unit is mounted to a reinforced bank. Both units can hold eight bottles.

4.4 Determining sampler mounting heights

This aspect of the project was the most arbitrary, as there were no accepted basic procedures available that could be followed. The mounting height of the bottles determine what parts of the storm will be sampled. Mounting the bottles too high will result having no or too few samples, while mounting them too low means the PSSBs will only sample small storms or the initial stages of a larger one.

The PSSBs could be mounted using equal height increments, or increments that take into account how often events reach certain water levels. Based on available historical flow data, an initial configuration was trialled at Pakuranga for three events. Taking the SSC results from these events into consideration, a further assessment was done to improve on the initial configuration. A more simplified, third configuration was used at Blockhouse Bay, which used an equal mounting height increment between PSSBs.

Having extensive historical records available for stage height meant that a variety of analysis could be done. The data and its analysis contributed to making well-informed decisions about the mounting heights of the passive sampler bottles. A PSSB mounting configuration should achieve the following two aims:

1. Generate enough samples for an event of interest
2. Generate a combination of samples which provide a useful indication of event pollutant characteristics

In order to fulfil aim 1, it was necessary to establish what water levels are reached in the weir, and how often. In other words: for what % of runoff events does the water level reach *x* height? A dataset was extracted containing the stage height measurements at one minute intervals for both locations. As both sites have baseflow, this was first eliminated from the dataset. This leaves the runoff events. The return frequency of stage heights was then established as a percentage of the total number of storms. Using polynomial regression (Figure 4.5), a formula was generated which calculates the stage height for a given percentage of storms (Appendix A).

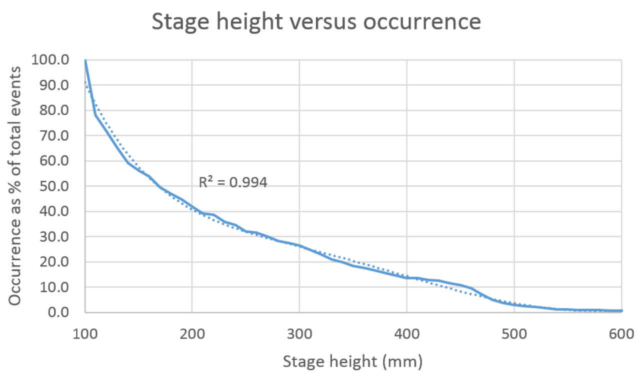


Figure 4.5: Stage height related to the occurrence as a percentage of the total number (393) of analysed storms at Pakuranga. Fifth order polynomial relationship (R^2=0.994) is established to calculate the relevant stage height for a corresponding storm occurrence. For Blockhouse Bay see Appendix A.

The initial setup, configuration 1, was developed to achieve Aim 1, and provide an insight into the SSC on the rising limb of an event. The bottles were mounted in such a way that at least three would fill up in 75% of storm events, and five in 50% of storm events. This means that in this setup, 25% of events would not generate a stage height high enough to fill the third bottle.

Two consecutive configurations were developed in an attempt to fulfil aim 2; to get a representative set of samples for event characterisation. Taking into account the results from configuration 1, configuration 2 was developed as a relatively simple approach, using equal mounting height increments between PSSBs. **This configuration was deployed in the field at Blockhouse Bay**.

Configuration 3 was based on a decreasing mounting height increment as a % of events captured. This was done so that, from the first to the second bottle, the mounting height increment is a decrease of *x*% of storms sampled. The third bottle is mounted at an increment of *x-1%* compared to the second bottle. So, if the difference between the first and second bottle is 9% fewer storms sampled, then the third bottle is mounted at 8% fewer storms sampled than bottle 2, the fourth bottle is mounted at 7% fewer storms sampled than bottle 3, and so on. The idea behind this approach was that it could deliver a higher mean of samples per event than when using an equal mounting height increment, like in configuration 2. **This configuration was deployed in the field at Pakuranga**.

For both sites, fifteen medium to large events were randomly selected from the dataset. The number of filled bottles (samples), the time between first and last sample, and the proportional volume of the storm sampled between the first and last sample were established to assess how the configuration would perform in the field. The following two Sections give an overview of the configuration analysis for the two sites.

4.4.1 Pakuranga

Configuration 1

Table 4.2 shows the initial configuration that was tested in the field for three events. Figure 4.6 shows that for most of the fifteen events seven PSSBs would be filled up, and that six events would have filled up the eighth bottle.

Bottle #	1	2	3	4	5	6	7	8
Mounting height (mm above v-notch)	100	110	120	140	168	203	265	353
Increment (mm)	-	10	10	20	28	35	62	88
% of storms captured at corresponding mounting height	100	82.5	75	62.5	50	40	30	20
Increment (%)	-	17.5	7.5	12.5	12.5	10	10	10

Table 4.2: Mounting configuration 1.

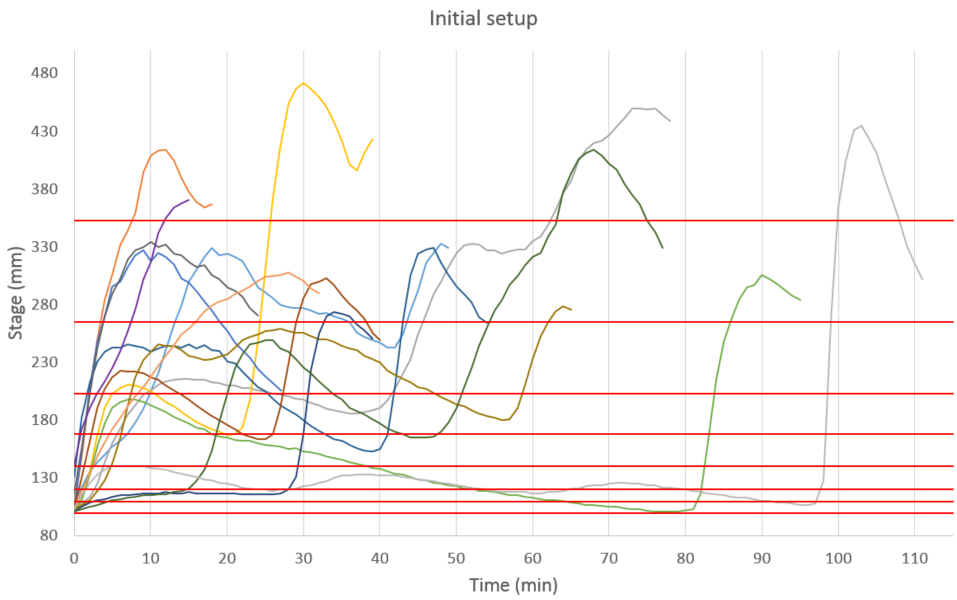


Figure 4.6: Fifteen events presented as water level over time. Using the initial setup, the horizontal red lines indicate the mounting heights of the PSSBs, and therefore a sampling point in time where it first crosses the stage level line of an event.

Configurations 2 and 3

In comparison to configuration 1, configurations 2 (Table 4.3) and 3 (Table 4.4) have the first and last bottle placed higher than the initial setup. This was as a result of the findings from the initial configuration.

Bottle #	1	2	3	4	5	6	7	8
Mounting height (mm above v-notch)	168	207	245	283	321	359	397	435
Increment (mm)	-	38	38	38	38	38	38	38
% of storms captured at corresponding mounting height	50	39	33	28	24	19	15	10
Increment (%)	-	11	7	5	4	4	5	5

Table 4.3: Configuration 2: equal mounting height increments.

Bottle #	1	2	3	4	5	6	7	8
Mounting height (mm above v-notch)	151	174	203	242	291	336	370	394
Increment (mm)	-	23	29	39	49	45	34	24
% of storms captured at corresponding mounting height	57	48	40	33	27	22	18	15
Increment (%)	-	9	8	7	6	5	4	3

Table 4.4: Configuration 3: decreasing mounting height increments as a % of events captured.

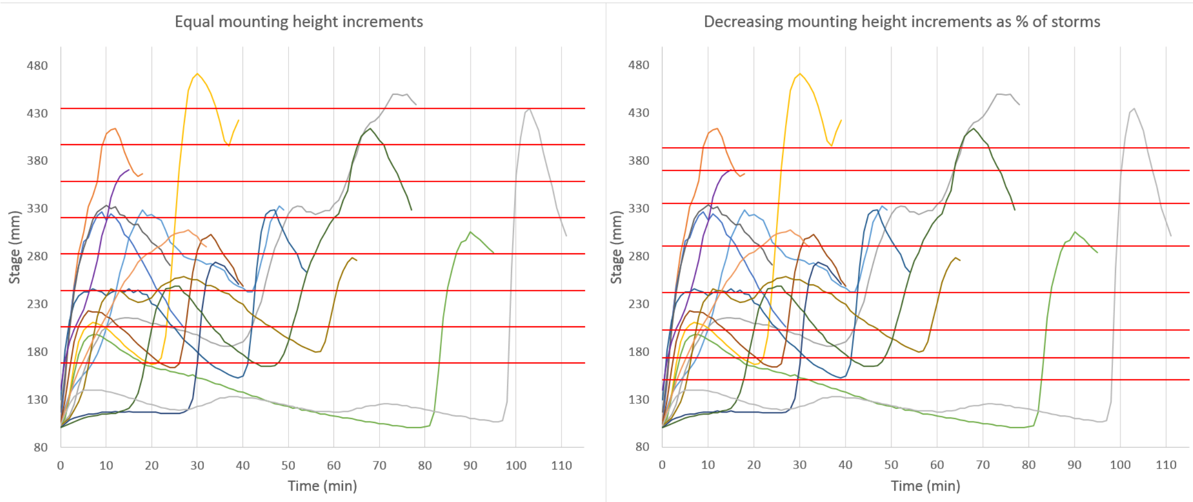


Figure 4.7: Configuration 2 (left) and configuration 3 (right). Fifteen events presented as water level over time. The horizontal red lines indicate the mounting heights of the PSSBs, and therefore a sampling point in time where it first crosses the stage level line of an event.

Table 4.5 and Figure 4.8 show that the time between the first and last sample taken per storm is longer on average when using configuration 1. Also, the number of samples per storm is the highest on average for configuration 1, whereas the volume passed between the first and last sample is about the same for all three configurations. Configuration 3 has a higher mean number of samples than configuration 2.

	Mean $t_{(\text{first-last})}$ PSSB (min)	Mean # PSSB filled	Mean % of total event volume between first-last PSSB
Configuration 1	38	7.3±0.5	24±15
Configuration 2	24	5.5±1.7	24±15
Configuration 3	24	6.0±1.5	22±15

Table 4.5: Configuration performance based on 15 events.

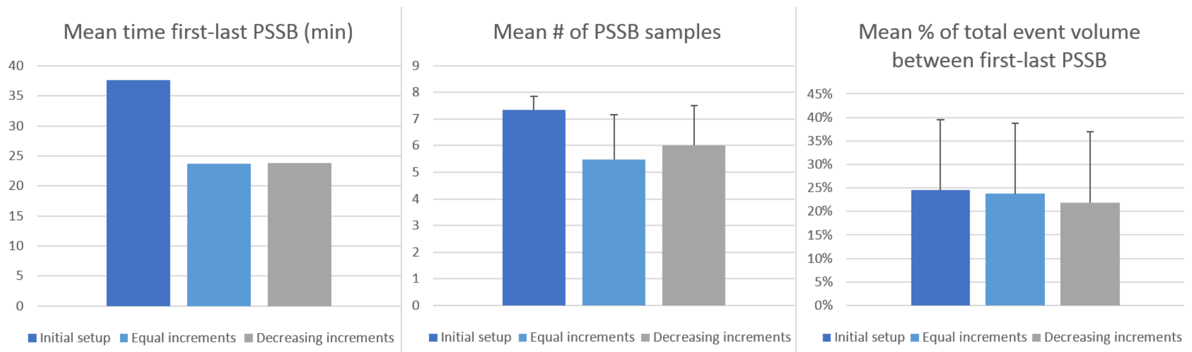


Figure 4.8: Time between first and last sample, number of samples, and relative volume between first and last sample, established over fifteen events at Pakuranga using three different PSSB mounting configurations. Error bars indicate standard deviation from the mean.

4.4.2 Blockhouse Bay

Due to site constraints, the lowest PSSB could not be placed lower than a stage height corresponding with 40 % of runoff events, or 276 mm above the v-notch. In other words, the lowest PSSB would be filled up in only 40% of events. This was assessed for configuration 2, which was tested in the field, but not for configuration 3.

Bottle #	1	2	3	4	5	6	7	8
Mounting height (mm above v-notch)	276	334	392	450	508	566	624	682
Increment (mm)	-	58	58	58	58	58	58	58
% of storms captured at corresponding mounting height	40	29	23	19	17	15	13	11
Increment (%)	-	11	6	4	2	2	2	2

Table 4.6: Configuration 2: Mounting configuration using equal height increments.

Bottle #	1	2	3	4	5	6	7	8
Mounting height (mm above v-notch)	224	251	283	320	368	438	541	632
Increment (mm)	-	27	32	37	48	70	103	91
% of storms captured at corresponding mounting height	55	46	38	31	25	20	16	13
Increment (%)	-	9	8	7	6	5	4	3

Table 4.7: Configuration 3: Mounting configuration using decreasing increments as a % of events captured.

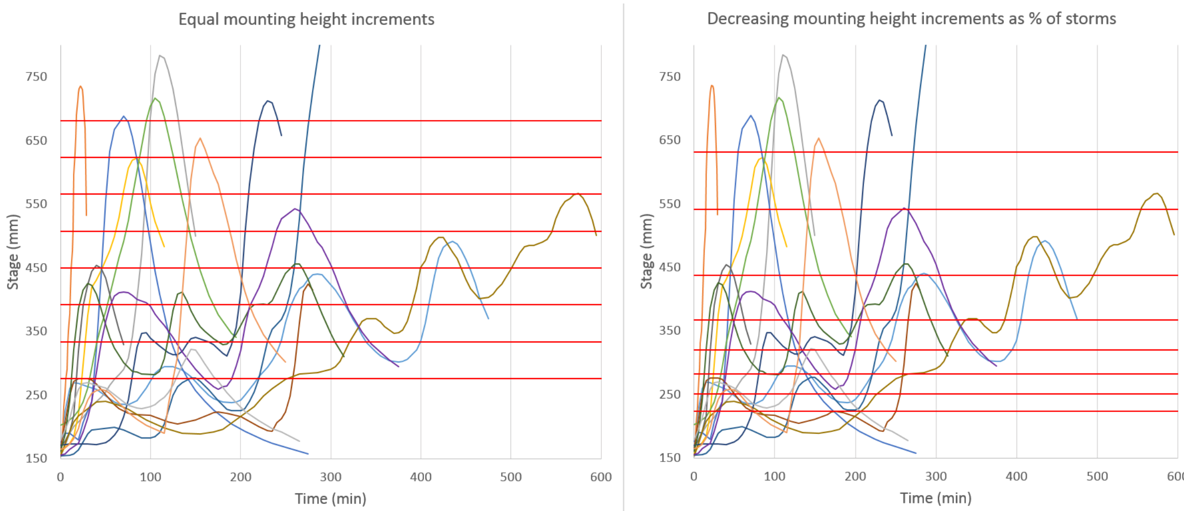


Figure 4.9: Fifteen events presented as water level over time, using configuration 2 (left) and configuration 3 (right). The horizontal red lines indicate the mounting heights of the PSSBs, and therefore a sampling point in time where it first crosses the stage level line of an event.

Table 4.8 and Figure 4.10 show that the mean time between the first and last PSSB is higher for configuration 3, due to the lower mounting of the first bottle. The mean percentage of the total event volume passed between the first and last bottle is about equal for both configurations, with configuration 3 having a higher number of samples on average.

	Mean $t_{(first-last)}$ PSSB (min)	Mean # PSSB filled	Mean % of total event volume between first-last PSSB
Configuration 2	112	5.8±2.2	29±21
Configuration 3	152	6.9±1.2	32±19

Table 4.8: Configuration performance based on 15 events.

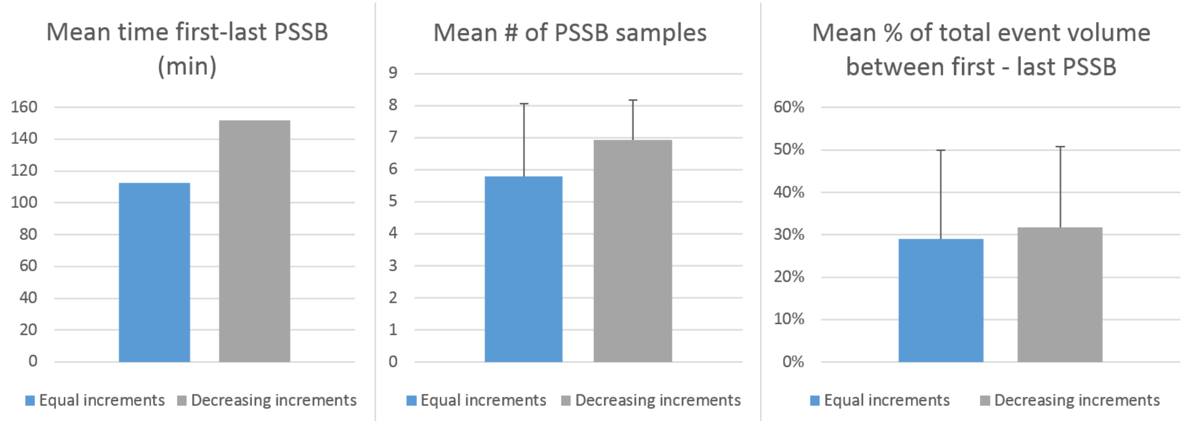


Figure 4.10: Side-to-side comparison of the sampling performance of the two configurations at blockhouse bay. Error bars indicate standard deviation from the mean.

4.5 Analytical methods

4.5.1 Suspended sediment concentration

Suspended sediment concentration (SSC) was analysed as a method for suspended solids concentration measurement. Total suspended solids (TSS) analysis was not used, as literature suggests the SSC method is more accurate (Galloway, Evans, and Green, 2005; Kayhanian et al., 2008). This is because the SSC method uses the whole sample, where TSS introduces uncertainty with the subsampling procedure. For the SSC analysis, the full sample was filtered through a pre-weighed, 0.4 µm membrane filter, using vacuum filtration equipment (Figure 4.11). The volume was measured and the filter subsequently dried at 60 degrees Celsius for 48 hours. After drying, the filters were placed in a desiccator to cool down, and subsequently re-weighed using a Mettler Toledo AX26 scale. The SSC concentration was determined using the following formula:

$$SSC = \frac{W_f - W_i}{V} \times 1000 \tag{4.1}$$

Where:

SSC: is the suspended sediment concentration [g/m^3]

W_f: is the final weight of the filter after drying [mg]

W_i: is the initial weight of the filter before filtration [mg]

V: is the volume of the sample filtered [mL]

Figure 4.11: SSC analysis setup using vacuum filtration equipment.

4.5.2 Event mean concentration and loads

To assess the performance of the developed PSSB methods, SSC results were compared in a variety of ways. For each event, the mean SSC of the PSSB samples was established to represent an event mean concentration, which was compared with the autosampler's EMC. Maximum concentrations were compared on an event basis, to identify whether the PSSB method could identify high risk discharges. Loads between the first and last sample of the autosampler and the PSSBs were established, to assess whether the relative load of the PSSBs was a steady indicator of the baseline load.

Baseline data for loads were determined for each sampled event by using the automatic samples that were analysed for SSC, and the rated discharge from the hydrologger at one minute intervals. The load was calculated using a two-point weighted suspended sediment concentration, multiplied by the discharge volume between the two sampling points. The sum of the calculated loads between points is the baseline event load.

The EMC was calculated by dividing the total load of an event by the total discharge volume of an event.

As flow and stage height data was available, a load between the first and last PSSB sample could be determined. This was done the same way as the autosamples, where a two-point weighted mean between two bottles was established, and the load calculated from the volume that passed between the time of sampling.

4.5.3 Mass first flush analysis

Analysing mass first flush (MFF) could add an additional layer in the understanding of the results from the field work. If there was a strong first flush presence, a higher pollutant concentration during the initial stage of an event can be expected. Intuitively, one would expect concentrations on the rising limb to be relatively high, and therefore result in a high mean SSC found in the PSSBs relative to the automatic sampler's EMC.

MFF_{25} was established by taking the total volume between the first and last autosample, and by establishing the point in time at which 25% of the total event volume has passed. Next, the sum of the load up to this time point is calculated, after which the relative percentage to the total load is established. A MFF_{25} is noted when this percentage is larger than 25.

4.5.4 Metals and nutrients

For one event at Blockhouse Bay, the samples were analysed for metals (Cu, Pb, and Zn) and nutrients (P and N). This was done in order to assess whether the dissolved, bioavailable fractions were distributed evenly throughout the water column, and to assess the difference of the particulate fraction between the PSSBs and the autosampler. The samples were collected the day of the event, and subsequently sent to an International Accreditation New Zealand accredited lab, recognised by the International Laboratory Accreditation Cooperation (ILAC). The results and used methods can be found in Appendix C.

5. Results

5.1 Baseline data

5.1.1 Sampled events

A total of 10 events were sampled, six at Pakuranga (Table 5.1) and four at Blockhouse Bay (Table 5.2). Three additional events experienced issues with the autosampler, meaning that no baseline data was available. Therefore, these events were not analysed further.

Pakuranga

Antecedent dry days varied from 1.5 days on 28/3 to 13 days on 26/03. The first two events sampled using the initial setup at Pakuranga were events leading up to two major (average recurrence interval (ARI) = 5 yr and ARI = 10 yr) rainfall events (NIWA, 2017a). The event on 12/04 was of relative high rainfall depth measured over two hours, having an ARI of 1.58. In terms of rainfall intensity, the 26/03 event was steady with low intensity, where 12/04 saw the highest intensity.

	10/03	26/03	28/03	12/04	29/04	04/05
Antecedent dry days	2	13	1.5	4.5	8	3
Rainfall depth (mm) and (event duration (hr))	8 (3)	12 (2)	41 (12)	38.5 (6)	22 (12)	6.5 (6)
Maximum 5-minute rainfall intensity (mm/hr)	30	9	30	78	36	24

Table 5.1: Sampled events at Pakuranga. Rainfall depth is the total event rainfall depth, duration is rounded for ARI comparison. Rainfall depth and intensity extracted from the Auckland Council website (Auckland Council, 2017b)

Blockhouse Bay

The first event sampled at Blockhouse Bay was a large rainfall event, with an ARI between 2-5 yr (NIWA, 2017a). The events on 05/04 and 11/05 were relatively normal with 7.5 and 7 mm of rainfall depth respectively.

	04/04	05/04	12/04	11/05
Antecedent dry days	0	0	4	6
Rainfall depth (mm) and (event duration (hr))	56.5 (6)	7.5 (6)	29.5 (6)	7 (6)
Maximum 5-minute rainfall intensity (mm/hr)	42	12	36	15

Table 5.2: Sampled events at Blockhouse Bay. Rainfall depth is the total event rainfall depth, duration is rounded for ARI comparison. Rainfall depth and intensity extracted from the Auckland Council website (Auckland Council, 2017a)

5.1.2 SSC, EMC and loads

Pakuranga

For the first two events the autosampler was programmed, based on forecasted rainfall, for bigger events than occurred and therefore only five autosamples were taken during the first event and 13 during the second. On 28/03 the autosampler was set up for a smaller volume than occurred, resulting in that only part of the whole event was sampled. Table 5.3 shows that the inter-event EMC varies considerably, from 21 g/m^3 to 92 g/m^3. The intra-event variability shows that within a single storm the variability is generally larger than between storm variability.

	10/03	26/03	28/03	12/04	29/04	04/05
# of autosamples	5	13	19	23	12	14
Volume between first-last sample (= baseline volume) (m^3)	790	1371	2042	4379	2517	801
Suspended Sediment EMC (g/m^3)	54	36	27	92	64	21
SSC range (g/m^3)	9-100	16-133	2-96	43-163	15-162	7-53
Suspended Sediment event load (kg)	43	49	56	402	161	17
MFF_{25} (%)	28	51	11	32	17	49

Table 5.3: Established baseline data from the autosampler for six events at Pakuranga.

Figure 5.1 shows the SSC and discharge over time. During a flashy rainfall event, such as 29/04 and 04/05, the SSC seems strongly correlated with the discharge, whereas on 26/03 the opposite seems to be true.

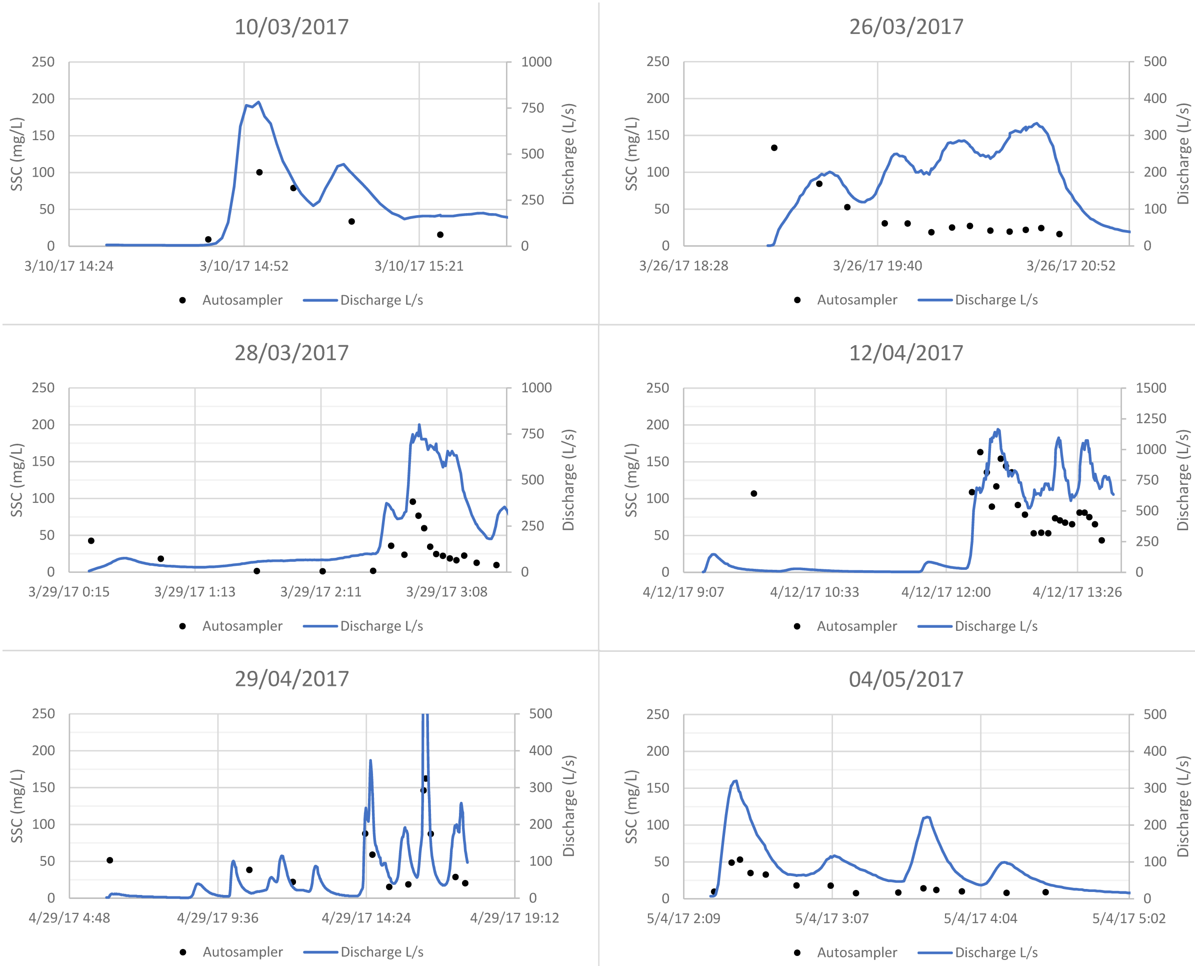


Figure 5.1: This figure shows the discharge over time, the time at which autosamples were taken (black dots) and the SSC of these samples.

Blockhouse Bay

The observed inter-event range (Table 5.4) is from 63 g/m^3 on 05/04 up to 486 g/m^3 on 11/05 respectively, which is a relatively similar variability as at Pakuranga. The intra-event variability is not as large as at Pakuranga, with observed concentrations not going below 7 g/m^3.

	04/04	05/04	12/04	11/05
# of autosamples	12	9	11	9
Volume between first-last sample (= baseline volume) (m^3)	23977	15418	24471	6201
Suspended Sediment EMC (g/m^3)	303	63	367	486
SSC range (g/m^3)	125-642	49-78	33-484	193-874
Suspended Sediment event load (kg)	7266	977	8983	3014
MFF_{25} (%)	37	28	27	36

Table 5.4: Established baseline data from the autosampler for four events at Blockhouse Bay.

After initial increase, the SSC shows a decrease over time in all events. The hydrographs of Figure 5.2 clearly show how the events on 04/04 and 12/04 were only partially sampled. On 11/05 the hydrologger triggered the first sample well before the actual event due to a small water level rise. This meant that no sample was obtained in the first minutes of the actual event. A second sample was taken four hours before the event, after the programmed water volume had passed. The concentration of this sample is used for the two-point-weighted SSC from the start of the event several hours later.

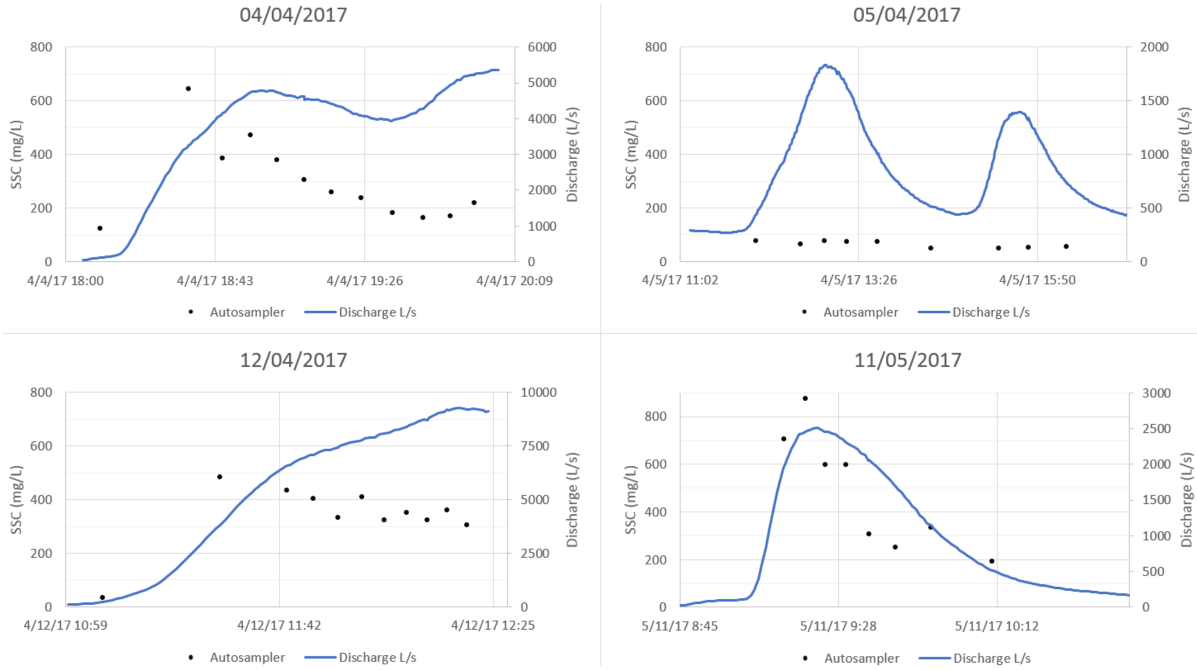


Figure 5.2: This figure shows the discharge over time, the time at which autosamples were taken (black dots) and the SSC of these samples.

5.1.3 Mass first flush

Figure 5.3 plots the normalised cumulative loads against the normalised cumulative volume for all events. Two events at Pakuranga had no mass first flush pattern, but rather the opposite (Table 5.3). Two events had a relatively strong MFF_{25} of around 50%, and two events were relatively close to flow-proportional discharge at just above 25%. The four sampled events at Blockhouse Bay show an MFF_{25} of over 35% for two events, and just above 25% for two others (Table 5.4).

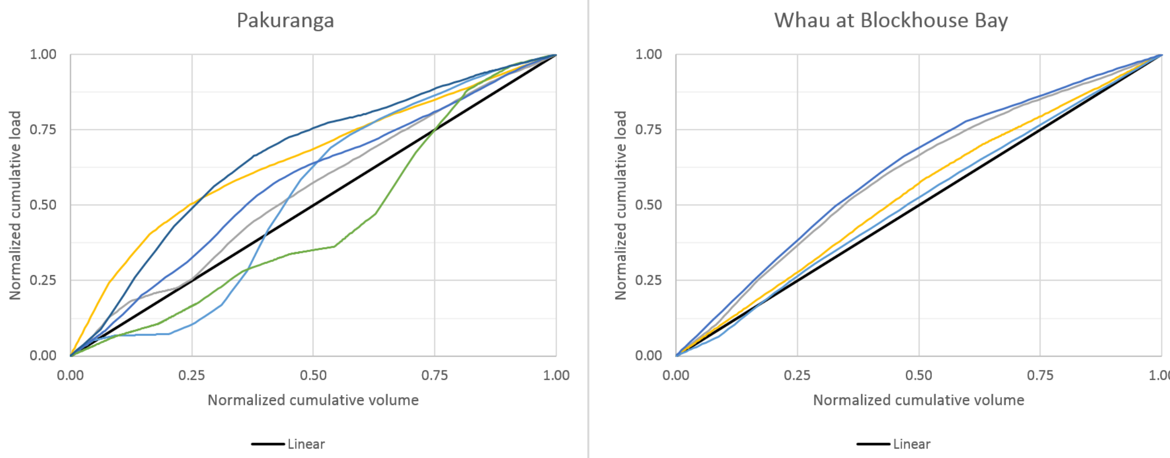


Figure 5.3: Normalised cumulative volume versus load, where the black line indicates steady mass transport, and the coloured lines represent the measured events.

5.2 Passive stormwater sampler bottles

5.2.1 Pakuranga

Figure 5.4 and 5.5 plot the PSSBs analysis in a similar fashion as the autosamples. It can be observed how the samples are distributed over time, the representativeness of the samples in relation to the whole event, and the differences between the autosamples. In the three events using the initial setup, it is clearly visible that the mean concentration of all PSSBs will be higher than that of the autosampler's 'true' EMC. The majority of the bottles in these events filled up within minutes, leaving the rest of the event without passive samples. The PSSB SSC generally follows the pattern of the discharge rate for the last two sampled events.

Configuration 1: initial setup

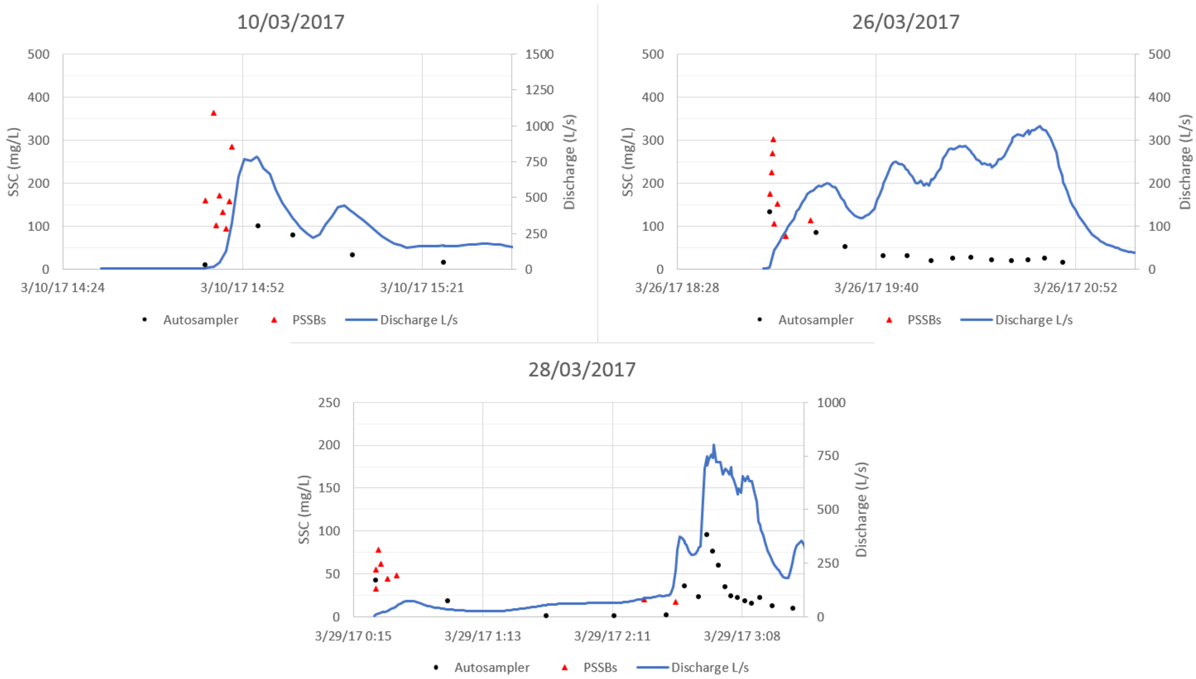


Figure 5.4: Three sampled events using the initial setup. Red triangles represent the SSC and time of sampling of the PSSBs, the black dots that of the autosampler, and the blue line represents the discharge in litres per second during the course of the event.

Configuration 3: decreasing increments as % of events captured

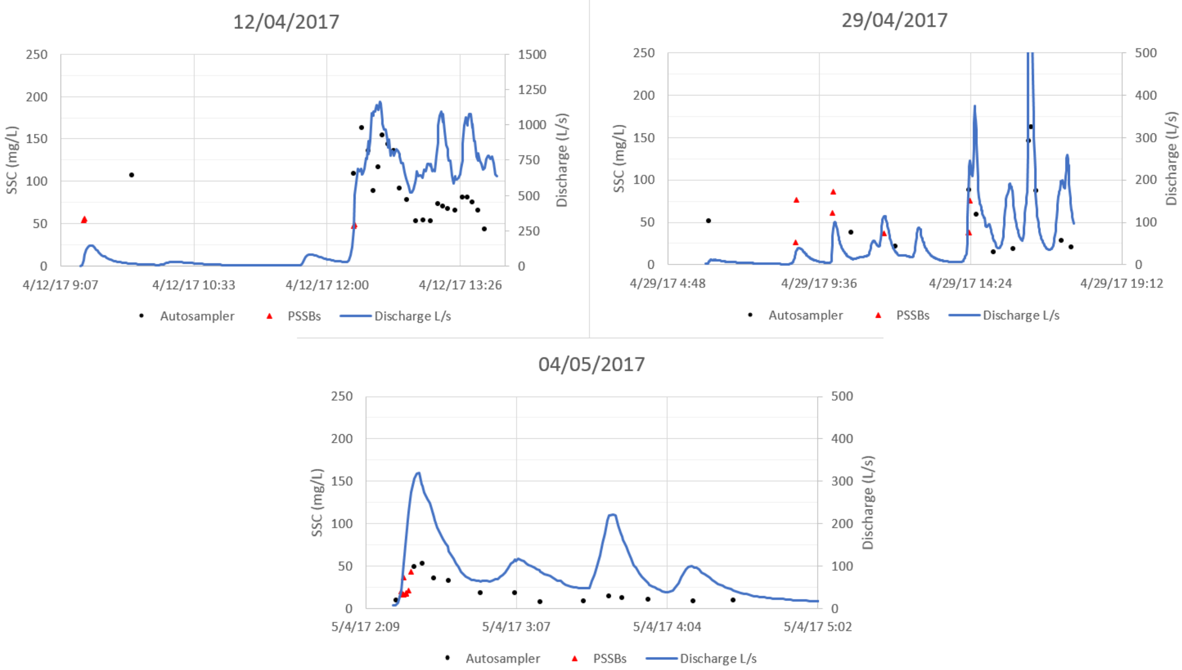


Figure 5.5: Three sampled events using configuration 3. Red triangles represent the SSC and time of sampling of the PSSBs, the black dots that of the autosampler, and the blue line represents the discharge in litres per second during the course of the event.

Table 5.5 gives a summary of the PSSB samples. On 12/04 only four bottles were mounted using the second configuration. The second configuration seemed to have performed markedly better than the initial setup. The first two events using this configuration are spaced well over time, where the last sampled event had a short time between samples due to the high initial discharge peak. The % of baseline volume between first and last PSSB seems to be at a similar level for both configurations, which is in line with the findings in Table 4.5.

	Initial setup			Configuration 3		
	10/03	**26/03**	**28/03**	**12/04**	**29/04**	**4/05**
# of PSSB samples	8	8	8	4	8	8
$t_{(first\text{-}last)}$ PSSB and (autosampler) (min)	4 (38)	12 (106)	133 (191)	176 (229)	332 (689)	4 (128)
% of baseline volume between first and last PSSB	4	7	23	8	26	6
Mean PSSB SSC (g/m^3)	184	177	45	51	55	23
SSC range (g/m^3)	95-363	77-302	17-79	47-56	27-86	16-44
Load between first and last PSSB (kg)	6	10	15	17	34	1

Table 5.5: The PSSB data obtained per event at Pakuranga. On 12/04 only four bottles were mounted using the third configuration.

5.2.2 Blockhouse Bay

Figure 5.6 shows that for two events, 04/04 and 12/04, the actual event had a higher rainfall depth and discharge than forecasted. Therefore, only part of the event was caught by the autosampler. Nevertheless, all PSSB samples were taken between the first and second autosample during these events. The 05/04 and 11/05 events saw PSSB samples better spaced over time in relation to the whole event.

Configuration 2: equal mounting height increments

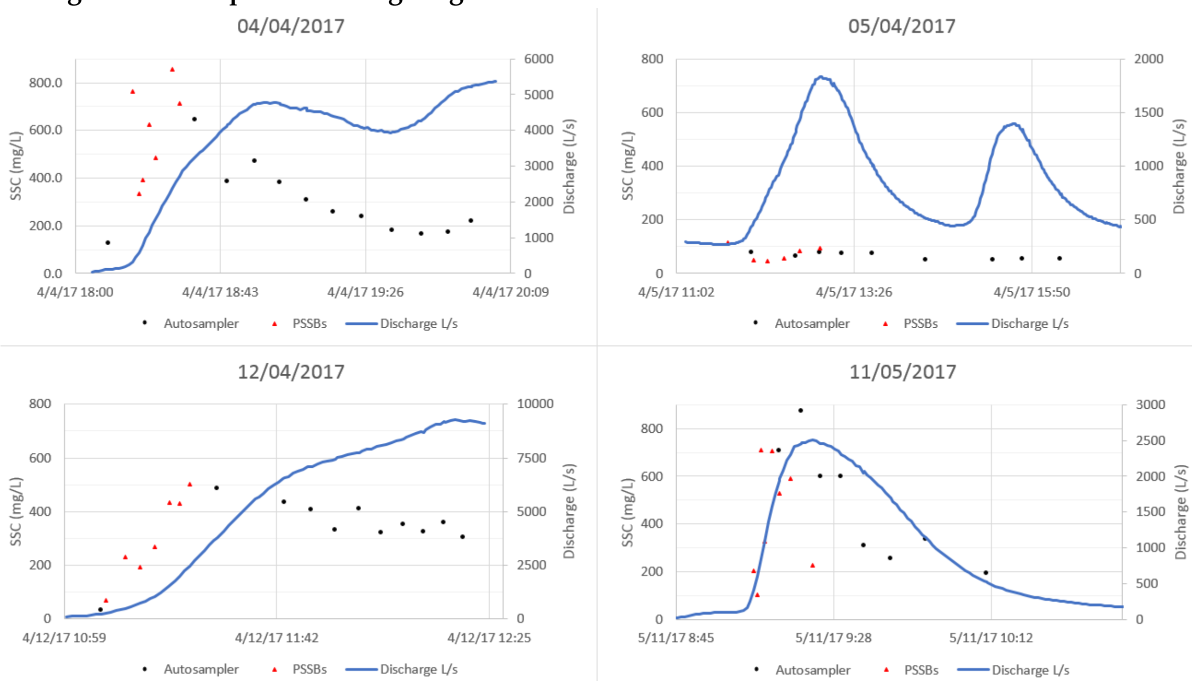


Figure 5.6: Four sampled events using equal mounting height increments at Whau stream. Red triangles represent the SSC and time of sampling of the PSSBs, the black dots that of the autosampler, and the blue line represents the discharge in litres per second during the course of the event.

The 05/04 event shows relatively little change in SSC over time, with only a small response to the discharge peak. For the other events, the PSSB SSC follows the trend of rising concentrations with increasing discharge rates. Table 5.6 summarises the outcomes for Blockhouse bay PSSB samples per event.

	04/04	05/04	12/04	11/05
# of PSSB samples	7*	6	7*	8
$t_{(first\text{-}last)}$ PSSB and (autosampler) (min)	14 (108)	75 (250)	18 (74)	16 (57)
% of baseline volume between first and last PSSB	6	27	5	30
Mean PSSB SSC (g/m^3)	595	73	304	421
SSC range (g/m^3)	335-855	45-113	71-502	102-711
Load between first and last PSSB (kg)	1123	302	418	873

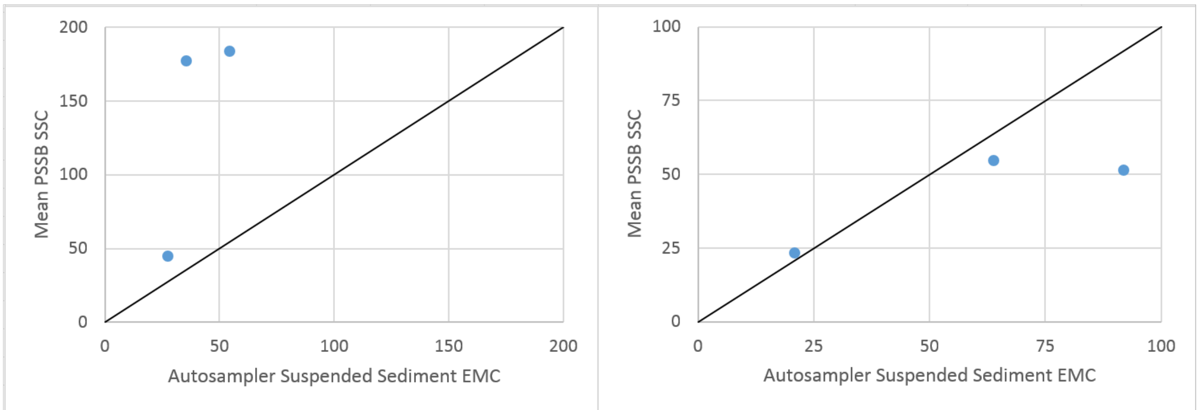
Table 5.6: The PSSB data obtained per event at Blockhouse Bay. *= excluding 1 outlier, due to faulty valve.

5.3 Comparison between baseline data and passive stormwater sampler bottles

5.3.1 EMC and PSSB mean SSC

Pakuranga

Figure 5.7 shows a plot of the mean SSC of the PSSBs and the autosampler EMC for the sampled events. The initial setup had an absolute mean difference of the PSSBs from the autosampler of 234%, whereas the decreasing increment configuration had an absolute mean difference from the autosampler's EMC of 24%.



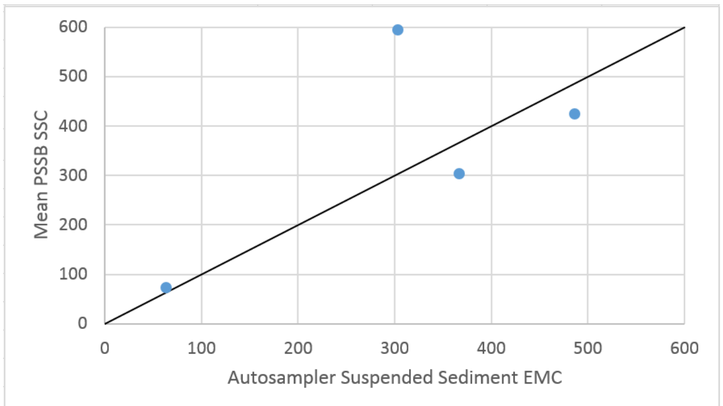
Initial setup	10/03/2017	26/03/2017	28/03/2017
Autosampler SS EMC (g/m3)	54	36	27
Mean PSSBs SSC (g/m3)	184	177	45
Difference (%)	238%	400%	64%

Decreasing increments	12/04/2017	29/04/2017	4/05/2017
Autosampler SS EMC (g/m3)	92	64	21
Mean PSSBs SSC (g/m3)	51	55	23
Difference (%)	-44%	-14%	12%

Figure 5.7: Mean PSSB SSC vs Autosampler SS EMC. The black line represents a 1:1 linear relationship.

Blockhouse Bay

Figure 5.8 shows a plot of the mean SSC of the PSSBs and the autosampler EMC for the sampled events. In three out of four events the mean PSSB SSC deviated less than 20% from the autosampler EMC, whereas the first event had the largest difference from the autosampler's EMC with a 96% difference. The mean absolute deviation of the PSSB mean from the autosampler EMC over four events was 35%.



Equal increments				
	4/04/2017	5/04/2017	12/04/2017	11/05/2017
Autosampler SS EMC (g/m3)	303	63	367	486
Mean PSSBs SSC (g/m3)	595	73	304	424
Difference (%)	96%	15%	-17%	-13%

Figure 5.8: Mean PSSB SSC vs Autosampler SS EMC. The black line represents a 1:1 linear relationship.

5.3.2 Maximum sampled concentration

Table 5.7 shows the maximum observed concentrations per method and event. The PSSB botlle # with the highest concentration is given. The results show that configuration 1 at Pakuranga picked up on concentration spikes at low discharge, which the autosampler missed (see Figure 5.4). Using configuration 3 however, these spikes were either not present or not sampled, and the highest concentrations were measured by the autosampler at peak discharge rates (Figure 5.5). PSSB configuration 2 at Blockhouse Bay sampled the highest concentration in three out of four time. On the 11/05 event the autosampler caught the peak concentration at the maximum discharge rate (see Figure 5.6).

	Pakuranga						Blockhouse Bay			
	Configuration 1			Configuration 3			Configuration 2			
Event	10/03	26/03	28/03	12/04	29/04	4/05	04/04	05/04	12/04	11/05
Max. autosampler SSC (g/m^3)	100	133	96	163	162	53	642	78	484	874
Max. PSSB SSC (g/m^3)	363	302	79	56	86	44	855	113	502	711
PSSB botlle #	2	4	3	4	4	8	7	1	7	3
PSSB deviation from autosampler (%)	263	127	-18	-66	-47	-17	33	45	4	-19

Table 5.7: Maximum SSC concentrations found in the samples for the PSSB and autosampler method on an event basis, and the deviation of the maximum PSSB value from the autosampler's maximum value. A red cell indicates the maximum measured per event.

5.3.3 SSC loads

Figure 5.9 shows the load between the first and last PSSB sample per event, as a % of the baseline load per event. For Pakuranga, this varied between 4 and 21% for configuration 3. At Blockhouse Bay, a wide range was found as well, between 8 and 31% respectively. Configuration 1 had less variation over its three sampled events than the other two configurations. The baseline load during the 10/03 event, however, missed most of the peak concentrations due to the autosampler being set up for a larger event. The same applies to the 26/03 event, where the autosampler missed the peak initial concentrations, likely underestimating the load. On 28/03 the passive samples were spread out over a long time, which explains the large share of the load between the first and last PSSB.

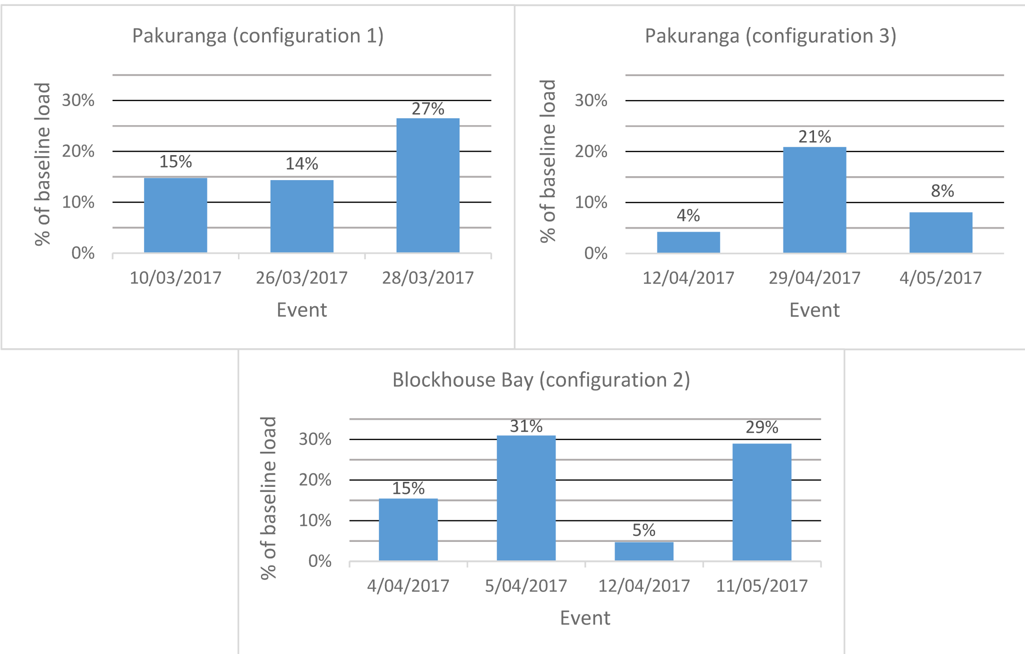


Figure 5.9: The suspended sediment load between the first and last PSSB sample, calculated from PSSB samples and measured discharged, as a % of the baseline load measured with the autosampler.

At both sites, the load between the first and last sample was relatively larger for small events than for larger events. For example, the events on 04/04 and 12/04 at Blockhouse Bay were not fully sampled by the autosampler, and the load between the first and last PSSB was relatively lower than at the other two, fully sampled events.

5.4 Metals and nutrients

On 16/05/2017, one event at Blockhouse Bay was sampled and analysed for metals and nutrients. The event had a rainfall depth of 11 mm over approximately 6 hours (Auckland Council, 2017a). Figure 5.10 shows the progression of the event in discharge over time, and the time at which passive and autosamples were taken. Eleven autosamples and seven PSSB samples were taken during the event.

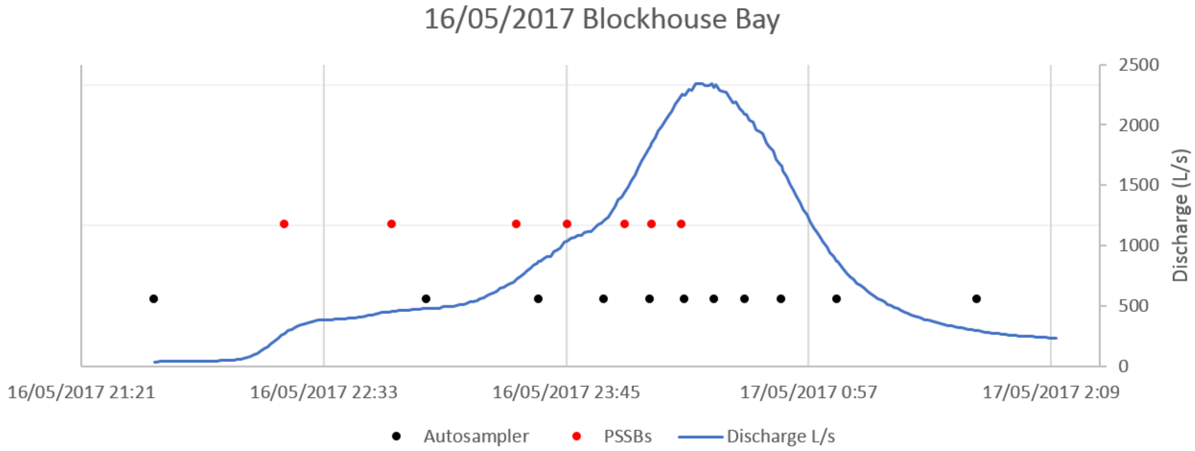


Figure 5.10: Discharge and sampling over time. Red dots indicate a PSSB sample, black dots indicate an autosample. The blue line represents the discharge in the stream over time.

Table 5.8 shows that the mean PSSB concentrations deviated from the autosampler's EMCs within a factor of two, ranging from -56 % for TP to +60% for dissolved zinc. Nitrate and nitrite nitrogen had the lowest deviation between the two methods, with a difference of only 3%. In total, for four out of the five constituents, the total fraction was lower in the PSSB mean concentration than for the autosampler EMC. Additionally, for three out of four of the constituents' dissolved fractions, the mean PSSB concentration was lower than the autosampler's EMC.

	DCu	TCu	DPb	TPb	DZn	TZn	DRP	TP	NO3-N + NO2-N	TN
PSSB range (g/m^3)	0.0008-0.0024	0.0033-0.0107	0.00023-0.00042	0.0022-0.0145	0.024-0.058	0.088-0.135	0.006-0.016	0.056-0.164	0.184-0.48	0.77-1.18
PSSB mean concentration (g/m^3)	0.0019	0.0072	0.00032	0.0075	0.041	0.108	0.0110	0.131	0.290	0.94
Autosampler range (g/m^3)	0.0021-0.0052	0.0078-0.0146	0.00022-0.00094	0.0065-0.017	0.0169-0.067	0.069-0.134	0.0035-0.062	0.162-0.52	0.162-0.41	1.08-2.3
Autosampler EMC (g/m^3)	0.0037	0.0112	0.00047	0.0111	0.0254	0.093	0.0157	0.301	0.281	1.68
Deviation of mean PSSB concentration from EMC(%)	-49	-36	-31	-33	60	17	-30	-56	3	-44

Table 5.8: Mean concentrations per constituent of the samples taken on 16/05/2017, and the deviation of the mean PSSB concentration from the autosampler EMC. DCu = dissolved copper, TCu = total copper, DPb = dissolved lead, TPb = total lead, DZn = dissolved zinc, TZn = total zinc, DRP = dissolved reactive phosphorus, TP = total phosphorus, TN = total nitrogen.

Figure 5.11 shows that, in general, the PSSB samples follow the autosample concentrations relatively closely. For total copper, the initial deviation between the two methods is rather large, but decreases after the discharge increases. The dissolved fraction of lead was much smaller than the particulate fraction, comprising less than 5% of the measured total lead concentration on average. Total copper and total zinc show small concentration variations between the autosamples during the event, where the copper concentration increases by around 50% from the first sample to the highest measured concentration, and zinc decreases around 25% from the first sample to the lowest measured concentration.

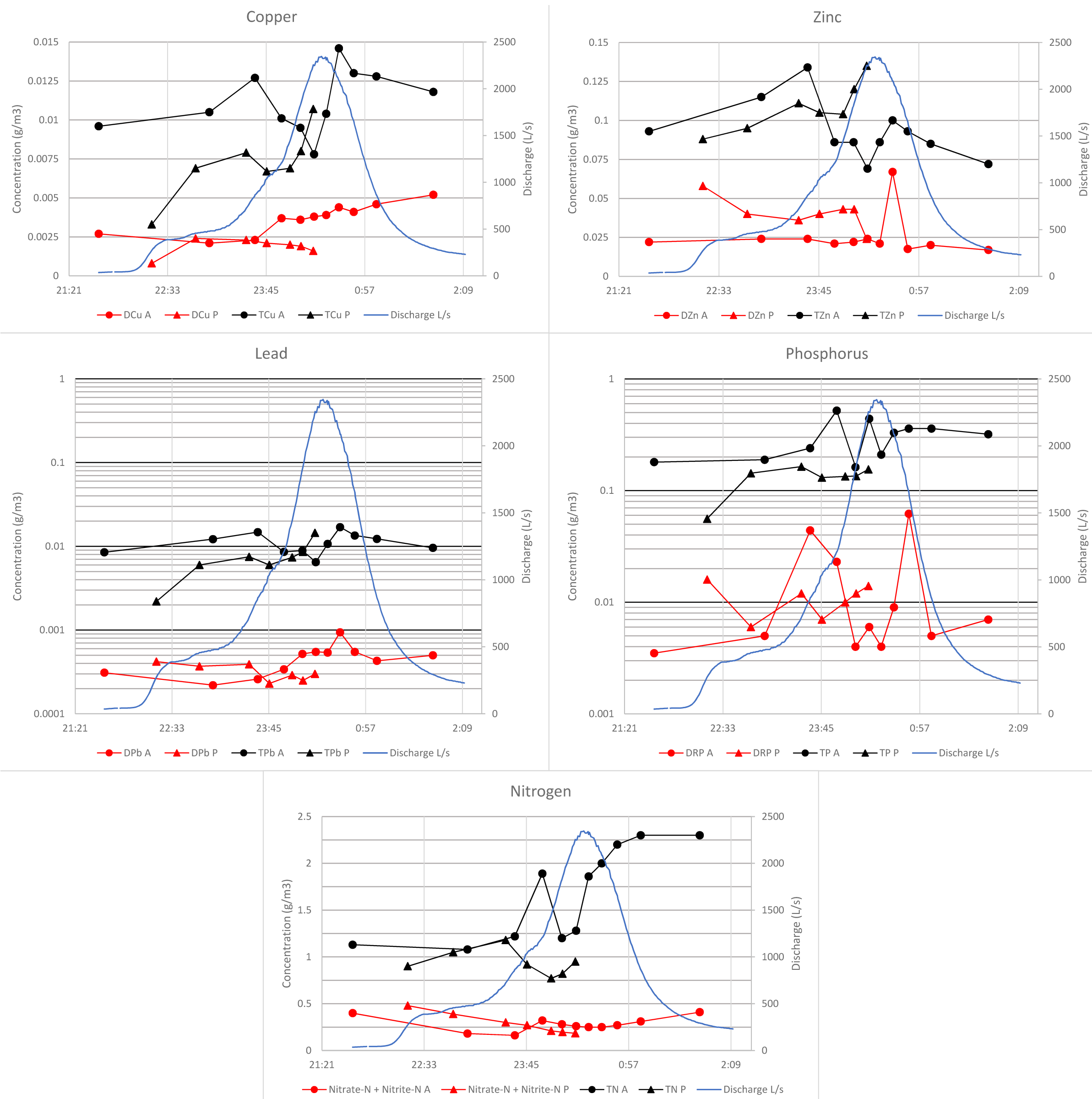


Figure 5.11: Metal and nutrient concentrations from the autosamples and the passive samples over time. P and A refer to the passive and autosamples respectively. DCu = dissolved copper, TCu = total copper, DPb = dissolved lead, TPb = total lead, DZn = dissolved zinc, TZn = total zinc, DRP = dissolved reactive phosphorus, TP = total phosphorus, TN = total nitrogen.

6. Discussion

6.1 Field results

The initial setup at Pakuranga worked well in terms of better understanding the pollutograph at this particular catchment. In the first two events the bottles to filled up in 4 and 12 minutes respectively (Figure 5.4). In terms of time, all PSSB samples were taken between the first and second autosample in these two events. The autosampler missed the peak concentration in the first event and a similar situation occurred in the second sampled event. This resulted in PSSB SSCs that were considerably higher than the autosampler's event mean SSC. Besides exposing a weakness of this PSSB configuration, it also exposed the limitations of the autosampling method, which depends on accurate forecasting and an accurately established rainfall-discharge relationship. For these particular three storms, the SSC during the first minutes of the event was considerably higher than the concentrations found further into the event, with the average SSC of PSSB #1-4 being higher than PSSB #5-8. This had a marked influence on the mean PSSB SSC assessment. It was found that sampling at the lower end of the hydrograph (at this location) may not be useful when trying to assess a mean concentration. However, if maximum concentrations are of interest, one might want to consider positioning a PSSB so that it samples the early discharge.

The initial setup was designed to have most bottles filled up in half of the events (Section 4.4), not realising that the events sampled generally had a considerably higher discharge rates (read: water levels) than 'most events'. As high water levels represent high discharge and high volume, it was an unsatisfactory decision to place most PSSBs at low stage heights as in configuration 1. As a result, in the consecutive field configurations, the lowest PSSBs were mounted at water levels which are reached in 57% of events (Pakuranga) and 40% (Blockhouse Bay) respectively.

Contrary to the initial setup, configuration 3 at Pakuranga showcased results that more closely matched the autosampler's for the three sampled events (Figure 5.5). The events on 29/04 and 04/05 were fully sampled by the autosampler, and the mean PSSB SSC deviated from the autosampler EMC by 14% and 12% respectively. The first event using this configuration, on 12/04, was a large event which was not fully sampled by the autosampler. There, the mean PSSB SSC was 44% lower than the autosampler's EMC. However, if the declining part of the event was sampled, this deviation would likely be smaller. Considering the autosampler results from the 26/03 event, where high initial SSCs declined sharply throughout the first hour of the event (Figure 5.4), it is likely that deviations higher than 44% will occur.

Using configuration 2 at Blockhouse Bay, only two events were fully sampled by the autosampler. The first event on 04/04 was a heavy rainfall event, with a maximum rainfall intensity measured over five minutes of 36 mm/hr (Auckland Council, 2017a). In this event, all PSSB samples were taken between the time of the first and second autosample (Figure 5.6). Though the PSSBs represented the rising limb of the hydrograph seemingly well, the sharp SSC decrease measured by the autosampler meant that the mean SSC from the PSSBs was a factor of two (96%) higher than the autosampler's EMC. A similar situation occurred on 12/04, but in this case the sharp decline in SSC was not observed in the autosamples. The deviation of the mean PSSB SSC deviation from the EMC, averaged over the four events, was 35%, with the other three events ranging between -17% and 15% deviation respectively.

The analysis of 15 events found that, between configuration 2 (equal mounting height increments) and configuration 3 (decreasing mounting height increments as a % of events captured), the most samples on average would be obtained from using configuration 3 (Figure 4.8 and 4.10). Using equal mounting height increments between PSSBs is, however, a more straightforward method, especially when no or limited historical flow data is available. The time and volume between the first and last PSSB sample for a given event depends on the height at which the lowest PSSB is mounted, and at what height the uppermost sample is taken. Using eight PSSBs provided a high resolution of data on the rising limb of the event's hydrograph. Configurations 2 and 3 were developed with the idea that one setup could successfully sample most events of interest, providing multiple samples during medium-sized events as well. However, an additional analysis of rainfall depth versus water level could have added more perspective in terms of understanding what water levels would be reached during the events the study aimed to sample (>5 mm rainfall depth).

A configuration using fewer (1-3) PSSBs could have provided similar performance in terms of estimating an EMC for a given event. For example, only using bottles #1,2,5 at Blockhouse Bay's 04/04 event would improve the deviation of the mean PSSB SSC from the autosampler EMC from 96% to 74%. However, this configuration would increase the deviation from the autosampler EMC for the three other events by 15, 16, and 17% respectively. With every PSSB taken out of the configuration, the results become more susceptible to outliers. The PSSB SSC scatter plots in Section 5.2 show that even though clear trends can be observed, strong deviations from the trend were not uncommon. This seems to be the nature of stormwater, which is never fully homogeneous in the field. Sampling at the water surface might increase the number of outliers compared to autosamplers because of floating material entering the sample. Additionally, the maximum concentrations observed in the PSSBs do not relate to a specific stage height (discussed below). Reducing the number of PSSBs would decrease the chance of obtaining a representative maximum value, as well as obtaining a sample near peak discharge for most events.

The SSC ranges observed using configurations 2 and 3 (Figure 5.5 and 5.6) are not as wide as the ranges observed with the autosampler. This is due to the PSSBs limitation to sampling the rising limb. The overall SSC range measured with the autosampler for Pakuranga was 1.7 - 163 g/m^3, which is roughly a factor of 100 difference, and 33 - 874 g/m^3, roughly a factor of 25 difference, at Blockhouse Bay. The inter-event range of the suspended sediment EMC is 21 - 92 g/m^3 for Pakuranga, a factor 4 difference. Blockhouse Bay's range is larger: between 63 and 486 g/m^3, which is nearly a factor 8 difference. The relatively larger variation at Pakuranga can be explained by the size of the catchment, which was comparatively small and fully developed. Therefore, the build-up of sediment to wash out during an event was limited, and relatively low concentrations were reached, down to 1.7 g/m^3. The larger catchment of Whau at Blockhouse Bay, however, had extended and complex sources of SSC. This meant that measured SSC concentrations did not go as low as observed at Pakuranga.

The results of the maximum observed SSC concentrations (Section 5.3.2) show no clear indication of which method is best for identifying maximum SSC concentrations. For some events, the PSSBs found the highest concentration along the rising limb. For other events, the autosampler found the highest concentration around peak discharge rate. The determining factors are the event or catchment characteristics. Configuration 1 at Pakuranga picked up on high concentrations early in the hydrograph's rising limb, which the autosampler and configuration 3 did not observe. Configuration 3 missed peak concentrations that were present further into the event during two out of three events. This resulted in a maximum PSSB SSC deviation of -66% and -47% from the autosamplers maximum SSC value. For three out of four events at Blockhouse Bay, configuration 2 found the highest concentrations. The maximum deviation from the autosampler was 45%. Taken over several events, the PSSB method is likely to give a good estimate of the maximum discharge concentrations, under the condition that samples close to peak discharge are obtained. Configuration 3 at Pakuranga could be improved by increasing the upper mounting heights further. This method could be relevant where outfall concentration limitations are in place.

An additional element that could be extracted from the results was the site mean concentration (SMC). To compare the PSSBs with the autosampler, the PSSB loads were determined by multiplying the event mean PSSB SSC with the baseline event volume, after which the event loads were summed up and divided by the total volume of the events. The outcome is presented in Table 6.1.

	Autosampler SMC (g/m^3)	**PSSB SSC SMC (g/m^3)**	**Difference from autosampler (%)**
Pakuranga	75	50	-34
Blockhouse Bay	289	363	26

Table 6.1: Event-based site mean concentration for Pakuranga and Blockhouse bay, measured over three (Pakuranga) and four (Blockhouse Bay) events.

It should be noted that in field situations where there is baseflow, such as at the two sampled sites, an additional assessment should be made of the baseflow in order to obtain an accurate SMC. The SMC difference of -34% at Pakuranga measured over three events, and +26% at Blockhouse Bay measured over four events, show that the PSSB method has potential for cost-friendly annual load assessments.

Table 6.2 shows the mean and quartiles for SSC found in urban streams and urban stormwater runoff during events, for mixed urban land use in New Zealand. A comparison of the values from Table 6.1 with Table 6.2 shows that both the PSSB and autosampler method depict a similar condition when put into context. For Pakuranga, the event-based suspended sediment SMC falls in the interquartile range, or the middle 50% of data values. This means that, based on three events, the mean SSC at Pakuranga is within the common range of SSC measured in urban stormwater in the region. At Blockhouse Bay, the urban stream Whau is found in the upper quartile of above 250 g/m^3 SSC, based on four events. This means the mean event SSC at Blockhouse Bay is higher than in most (>75%) urban streams.

Water type	Mean	Lower quartile	Upper quartile	N
Urban stormwater runoff SSC (g/m^3)	67	12	83	150
Urban streams SSC (g/m^3)	150	42	250	37

Table 6.2: Event-based data for suspended sediment concentrations. Mean and quartiles for stormwater runoff and urban streams, from mixed urban land-use sources. N = number of datasets included. Obtained from NIWA (2017b).

The loads established by the PSSBs presented in Figure 5.9 show a variation of 5 to 31% of the baseline load. This variation is a result of the differences in sampling time and the size of an event. The longer an event lasts after all PSSB samples have filled, the lower the relative load is going to be. The load calculated using this method is not a useful indicator of the total event load due to this high variation. A similar observation could be made in the Methods, where Table 4.5 and 4.8 already indicate that the volume between the first and last PSSB was highly variable. If an assessment of the event volume can be done, loads calculated using the mean PSSB SSC and the event volume will provide a better general indication of the total event load.

Of the events that were fully captured by the autosampler, mass first flush was evidently present on the 26/03 and 04/05 events (around 50% of mass transported in the first 25% volume) at Pakuranga, and the 11/05 event (36% of mass transported in the first 25% volume) at Blockhouse Bay. The hypothesis was that the mean PSSB SSC would be higher than the autosampler's EMC when mass first flush is present. The 26/03 event had a mean PSSB SSC that was four times higher than the EMC, but this was due to the mounting heights and site conditions (see discussion on initial setup). On 04/05, using configuration 3, the mean PSSB SSC was 12% higher than the autosampler's EMC. At Blockhouse Bay the mean PSSB SSC was 13% lower than the EMC on 11/05. The results were therefore inconclusive, and, furthermore, the mean PSSB SSC deviations from the autosampler's EMC for configuration 2 and 3 for these two first flush events were relatively small compared to the other, non-first flush events.

The 16/05 event at Blockhouse Bay that was analysed for copper, lead, zinc, phosphorus and nitrogen showed that the PSSBs performed differently for every analysed constituent. Interestingly, for copper and zinc, the mean dissolved concentration found in the PSSBs deviate more from the EMC than the mean concentration of total copper and zinc (Table 5.8). The opposite was to be expected, with dissolved concentrations being fairly homogeneous throughout the water column. For zinc, particulate-dissolved interactions of the metal between the water phase and the particles may have caused the dissolved fraction to increase in the automatic samples to a larger extent than in the PSSBs. For copper, the deviation can be explained by the increase in concentration measured by the automatic sampler further into the event, where no PSSB samples were taken (Figure 5.11).

The analysed nutrients showed a deviation range of -56% for total phosphorus to +3% for nitrite and nitrate nitrogen (Table 5.8). There was large uncertainty for most constituents coming from the sample preservation method of both the automatic samples and the PSSB samples, as the samples were refrigerated but not analysed directly. For TP, this uncertainty ranges somewhere from -64% to +92% (Harmel et al., 2006). The mean PSSB deviation of -56% from the autosampler EMC could therefore be within the deviations expected due to the sampling error and analytical uncertainty.

More sampled events are needed to assess the performance of the PSSB method for these other commonly assessed pollutants.

Table 6.3 shows the quartiles of the metal and nutrient concentrations found in urban streams in New Zealand (NIWA, 2017b). Comparing the field results of Blockhouse Bay (Table 5.8) with the common ranges found in the region, the mean concentrations from the two different methods mostly draw a similar conclusion (green colour). For total copper, total lead, dissolved zinc, and total zinc, both methods indicate mean values that were in the interquartile range of New Zealand urban streams. Both methods found that for TP and DRP the mean concentration was in the upper quartile of urban streams in New Zealand, whereas NO_3+NO_2-N is positioned around the lower quartile. For dissolved copper, the mean PSSB concentration was in the lower quartile, whereas the autosampler EMC was well within the interquartile range. The mean dissolved lead concentrations were within the interquartile range for the PSSBs, where the autosampler found a value in the upper quartile. In short, both methods found relatively high phosphorus concentrations compared to other sites, but the PSSB method did not indicate the relatively high dissolved lead values, which the autosampler picked up on as the event progressed. For the other assessed constituents, both methods draw a similar conclusion when put in a larger context, based on one event.

Constituent	Lower quartile	Interquartile range	Upper quartile	N
DCu (g/m^3)	0.0024	>0.0024 <0.0048	0.0048	803
TCu (g/m^3)	0.0052	>0.0052 <0.016	0.016	658
DPb (g/m^3)	0.0002	>0.0002 <0.0004	0.0004	89
TPb (g/m^3)	0.0026	>0.0026 <0.015	0.015	102
DZn (g/m^3)	0.011	>0.011 <0.060	0.060	690
TZn (g/m^3)	0.032	>0.032 <0.02	0.2	652
TN (g/m^3)	N/A		N/A	N/A
NO_3+NO_2-N (g/m^3)	0.28	>0.25 <0.94	0.94	259
TP (g/m^3)	0.018	>0.018 <0.092	0.092	132
DRP (g/m^3)	0.0076	>0.0076 <0.034	0.034	723

Table 6.3: Event-based data for pollutant concentrations in urban streams from mixed urban land-use sources. N = number of datasets included. Obtained from NIWA (2017b). The colours represent where the mean values sit from the two methods. Blue = PSSB, red = autosampler, green = both methods in same range.

6.2 Implications of the use of passive gravity flow samplers for storm event pollutant characterisation

The first two objectives of this study were to assess the physical and chemical variation of runoff between storm events and catchments, and to assess how these variations affect the initiated passive gravity flow sampling method.

An understanding of the chemical and physical stormwater variation, both inter-event and intra-event, is important in formulating a relevant sampling strategy as well as for selecting the right tools to execute the research. Understanding the differences in pollutant concentrations between various land-use types, as well as first flush patterns, is relevant for governing bodies when they formulate their pollutant-reduction strategies. First flush has been a debated topic for some time, and will remain relevant as policies are commonly developing towards some form of treating first flush. For this study, the intra-event variation was most relevant, as the passive samplers were primarily tested for their ability to characterise single events.

Figure 6.1 shows how using passive gravity flow in this setup affects the sampling strategy compared to autosampler strategies. PSSB samples are only obtained on the rising limb of the hydrograph. As a result, a large volume of the typical hydrograph cannot be sampled. This is the main limitation of using passive gravity flow sampler bottles.

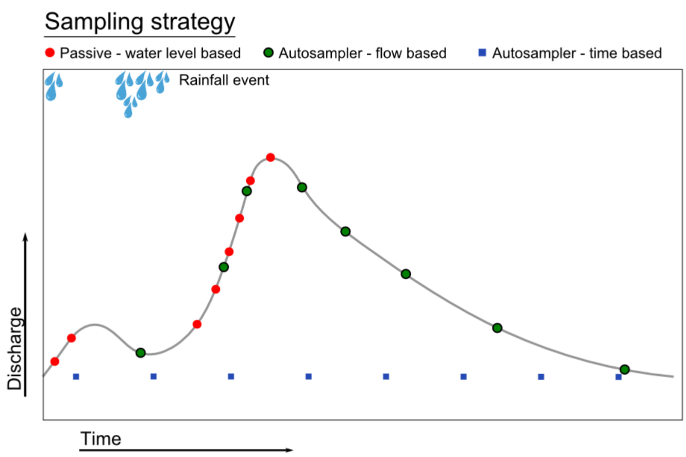


Figure 6.1: Illustration of sampling methods and strategies. The line represents the discharge hydrograph during a rain event, and the red, green, and blue dots indicate when a sample would approximately be taken over time.

The number of PSSBs and their mounting height will determine the sampled reach within the rising limb of the hydrograph of an event. It is important to sample high flows as they represent high discharge rates, and thus large volumes of discharge. If the PSSBs are mounted too high, important parts of an event will not be sampled, or an event might not be sampled altogether. Mount the majority of PSSBs too low, and low flows will be over-represented in the analysis. The representativeness of a PSSB configuration for a single event depends on:

- the number of samples and their corresponding mounting heights,
- the duration of an event,
- the first flush characteristics, and
- the intensity of an event over time.

Using an autosampler coupled with flow measurement, it is straightforward to connect a sample with a discharge volume. On the other hand, when using PSSBs, the relation of a sample to a specific volume of an event is harder to theorise. The representativeness of a single bottle in relation to the larger event, regardless of the mounting height, varies per event. Any mounting height might be equally accurate when considering multiple years of stormwater data. This makes a case that when assessing stormwater quality on an event basis using the method explored in this paper, more samplers and hence, samples, is indeed better. This also means, following the Central Limit Theorem, the right conditions and enough sampled events, that a more limited number of PSSBs could provide a good estimate of a site mean concentration, as mentioned by Fletcher and Deletic (2007). For future research, the inter-event variety brings forth the idea of using discharge-rate-weighted samples, depending on the event's hydrograph. Assuming a concentration-discharge correlation, a volume could be linked to a discharge rate range, and the discharge rate to a corresponding PSSB sample. Therefore, weighting the samples could, depending on the catchment, improve the event mean concentration estimate.

An additional potential limitation to the use of PSSBs is that sampling is limited to the upper part of the water column. As mentioned in Section 3.2.3, sampling from the upper part of the water column could have reduced accuracy for the coarse particulate fraction. It is therefore important to choose the right location for sampling, that being where the water column is vertically mixed as much as possible. For dissolved pollutants and the fine sediment fraction, the PSSBs should generate more accurate samples. Figure 6.2 shows a scatter plot of PSSB and autosamples taken within approximately five minutes of each other. The mean absolute difference of the PSSB SSC from the related autosample was 45% ($\pm$27) for Pakuranga, and 31% ($\pm$35) for Blockhouse Bay respectively. At both sites there were PSSBs with lower SSC than their autosample counterpart, as well as the other way around. Compared to the autosampler, sampling from the surface using PSSBs did not seem to result in a bias towards lower suspended sediment concentration at either Pakuranga or Blockhouse Bay. The trendlines indicate a very slight bias towards higher SSC in the PSSBs for both sites. Potential explanations are seasonality, having higher VSS at the water surface, or a build-up of sediment in the valve mechanism which is released to the sample when unscrewing it from the sampler bottle.

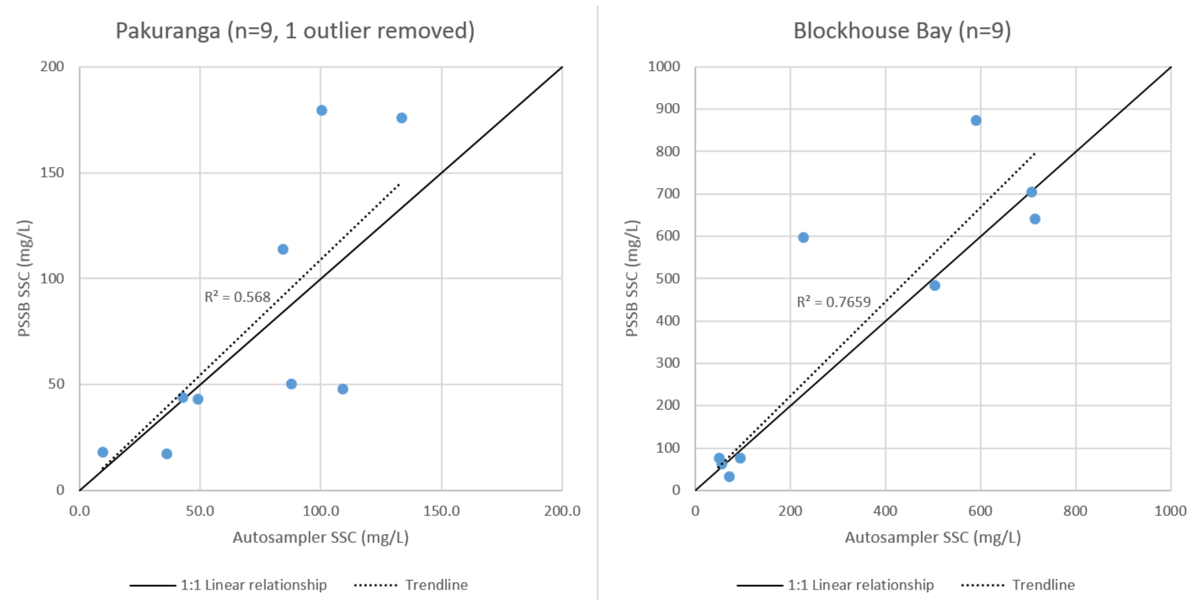


Figure 6.2: SSC scatter plot of PSSB samples and autosamples taken within 5 minutes of another. The black line represents a 1:1 linear relationship and the dashed line the trendline.

The appeal of the developed method over the use of an autosampler is the ease with which it can be set up and the relatively low cost. The benefits of this method over manual grab sampling are the convenience of installation when it best suits the field-worker, and the generation of higher resolution of data for single events than when using a single grab sample method at a random point in time during the event. The passive nature of the method makes it accessible to sample a single event at multiple sites simultaneously, at a relatively low cost. The main advantage of this method over other passive sampling methods is that the passive gravity flow sampler bottle provides a full grab sample which can be analysed for numerous substances of interest. An important additional difference is that intra-event concentration variability can be sampled, whereas other passive sampling methods generally provide a mean concentration over a longer period of time.

7. Conclusion

The initial setup, configuration 1, that was trialled at the Pakuranga catchment outfall showed that the discharge had high initial suspended sediment concentrations at the lower end of the hydrograph's rising limb for the first three sampled events. This resulted in a deviation of the mean PSSB SSC from the autosampler's EMC as high as 400%. As a result, the consequent configurations 2 and 3 had the PSSBs mounted relatively higher. This should also improve the representativeness of the samples for a larger discharge volume.

The subsequent field results showed that when sampling larger (>5 mm rainfall depth) events, using a well-informed PSSB mounting configuration, the mean PSSB suspended sediment concentration was within a factor of two from the autosampler's suspended sediment event mean concentration for the same event. Using equal mounting height increments (configuration 2), the PSSB method resulted in a deviation range from the EMC of -17% to +96%, with a mean of 35% in an urban stream measured over four events at Blockhouse Bay. When using decreasing mounting height increments as a % of events captured (configuration 3), the PSSB method's deviation from the autosampler's EMC ranged from -44% to +12%, with a mean of 24% at a storm pipe outlet measured over three events at Pakuranga.

To address maximum discharge concentrations, the developed PSSB method's samples were compared with the autosamples on an event basis. Configuration 2 at Blockhouse Bay found the highest SSC concentrations in three out of four events. At Pakuranga, the maximum negative deviation of the PSSB method was -66% from the maximum concentration found by the autosampler. Maximum concentrations were found on the rising limb (by the PSSBs) and during peak discharge (usually by the autosampler). Taken over four events in an urban stream at Blockhouse Bay, the PSSB method showed promising results for assessing maximum discharge concentrations, albeit limited to the rising limb of the event's hydrograph. Configuration 3 at Pakuranga could have been improved further by mounting PSSBs higher, to capture samples at peak discharge rates.

The assessed SSC load between the first and last PSSB sample was not found to be a useful method for the indication of the total event load, due to the extent of event variability. Given the presence of flow measurement, loads calculated using the mean PSSB SSC and the event volume will likely provide a better general indication of the total event load.

It was hypothesised that if mass first flush was present, the mean PSSB SSC would exhibit a positive bias when compared to the autosampler's EMC. The first three events at Pakuranga using the initial setup showed that high initial concentrations at low discharge rates, combined with relatively low mounted PSSBs, resulted in a strong positive SSC bias compared to the autosampler's EMC. When using configuration approaches 2 and 3, the two events (that were fully sampled by the autosampler) that had mass first flush, showed no evident positive bias of the PSSB mean SSC.

An analysis of the mean concentration of several nutrients and metals for a single event at Blockhouse Bay showed that, though deviations between of up to 60% were present, both the PSSB and autosampler method have a similar outcome when compared to the ranges found regionally in urban streams, for 7 out of 9 measured constituents.

The main limitation of using passive gravity flow samplers is that sampling is limited to the rising limb of an event's hydrograph. Therefore, important discharge information can be missed after the samplers have filled up. An additional limitation that was identified in literature, was that sampling at the water surface could result in a negative bias towards the concentration of solids and their associated pollutants. However, a comparison between autosamples and PSSB samples taken at approximately the same time showed no indication of a negative bias of the PSSBs towards SSC during runoff events in these two catchments.

The accuracy of a PSSB configuration for assessing a single storm event depends on the number of samplers used, their relative mounting heights, the catchment and event characteristics, and the assessed pollutant. Using the mounting approach of configuration 3 should result in a higher average number of samples per event. Apart from providing more samples, there is no indication that configuration 3 will provide more accurate results than configuration 2. Additionally, configuration 2, using equal mounting height increments, is more straightforward and requires little analysis compared to configuration 3.

The aim of this study was to assess whether and how passive gravity flow samplers can substitute manual sampling or the use of autosamplers for stormwater grab sampling, for the purpose of characterising storm event pollutant concentrations or event loads. Though considerable deviations of the passive gravity flow samplers from the autosampler were observed, the established mean suspended sediment concentrations of both methods depict a similar condition when viewed in a larger context. The method is able to provide a rough estimate of an suspended sediment EMC, as well as maximum discharge concentrations, albeit limited to the rising limb of an event's hydrograph. The method sits somewhere between single manual grab samples and an autosampler in terms of accuracy. Rather than substitute, the use of multiple passive gravity flow samplers in a vertical configuration can be seen as an additional tool along with existing methods. It is an extra method which could prove preferable over other methods depending on the goal and conditions of the initiated study.

The findings of this paper demonstrate that passive gravity flow samplers can be used in more ways than solely a single-sampler application. However, the study is limited to the small number of events and constituents that were assessed. Only one event in an urban stream was analysed for metals and nutrients. Besides the small number, this leaves a gap concerning different catchment types and pollutants which are known to exhibit first flush patterns more strongly than SSC, metals and nutrients. This study had accurate water level and flow monitoring equipment available. In situations where this equipment is not available, assumptions in regards to discharge have to be made in order to establish a constituent's contributing load. Additionally, historical water level data was available, which may not be the case for many other real-world sites.

The developed configurations 2 and 3 found deviations within a factor of two from the autosampler's EMC for SSC. This is based on two catchments, ten events, and two types of stormwater (piped stormwater drainage outfall and an urban stream). The results are a mere indication. More knowledge is needed to address the sampling error and uncertainty, and to develop practical guidelines for applying the method. If this method was to be developed further, future research could focus on the deviation ranges from the true event EMC by using existing datasets and/or build-up/wash-off modelling. Other pollutants could be assessed, such as bacteria and hydrocarbons. Using existing datasets and/or modelling, configurations could be optimized further and the effect of using fewer samplers assessed. Finally, an approach could be developed for sites where no water level history is available, e.g. by establishing mounting heights in relation to the minimum and maximum assumed water level.

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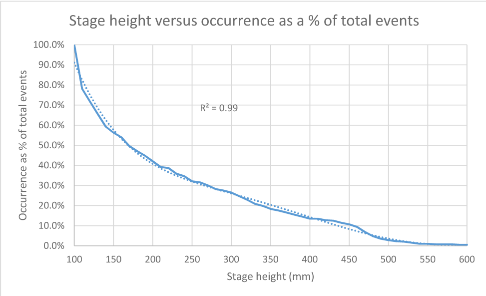
A. Site configurations

Pakuranga

Reg: $y = -1.83555090540873E\text{-}13x^5 + 4.02973485109460E\text{-}10x^4 - 3.38056363384899E\text{-}07x^3 + 1.36433541185504E\text{-}04x^2 - 2.77788807933102E\text{-}02x + 2.62411548133912E{+}00$



Events	
N	393
Start	12/06/2015
End	21/02/2017

Configuration 1: initial setup

Bottle	Mounting height (mm)	% of storms captured	% difference
1	100	91.1%	
2	110	82.5%	17.5%
3	120	75.0%	7.5%
4	140	62.5%	12.5%
5	168	50.0%	12.5%
6	203	40.0%	10.0%
7	265	30.0%	10.0%
8	353	20.0%	10.0%

Configuration 2: equal mounting height increments

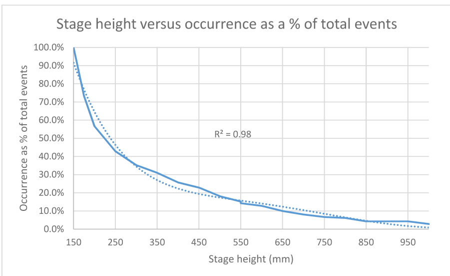
Bottle	Mounting height (mm)	% of storms captured	% difference	Increment (mm)
1	168	50%		
2	207	39%	11%	38
3	245	33%	7%	38
4	283	28%	5%	38
5	321	24%	4%	38
6	359	19%	4%	38
7	397	15%	5%	38
8	435	10%	5%	38

Configuration 3: decreasing mounting height increments as a % of events captured

Bottle	Mounting height (mm)	% of storms captured	% difference	Increment (mm)
1	151	57%		
2	174	48%	9	23
3	203	40%	8	29
4	242	33%	7	39
5	291	27%	6	49
6	336	22%	5	45
7	370	18%	4	34
8	394	15%	3	24

Blockhouse Bay

Reg: $y = 4.06284242998405E\text{-}18x^6 - 2.53226302977992E\text{-}14x^5 + 6.22849458530378E\text{-}11x^4 - 7.70593050809657E\text{-}08x^3 + 5.07105832622798E\text{-}05x^2 - 1.72615191247480E\text{-}02x + 2.59416125047644E{+}00$



Events	
N	210
Start	9/09/2005
End	21/09/2006

Configuration 2: equal mounting height increments

Bottle	mounting h (mm)	% of storms		% decrease	Increment (mm)
1	276	**40%**			
2	334	**29%**		11%	58
3	392	**23%**		6%	58
4	450	**19%**		4%	58
5	508	**17%**		2%	58
6	566	**15%**		2%	58
7	624	**13%**		2%	58
8	682	**11%**		2%	58

Configuration 3: decreasing mounting height increments as a % of events captured

Bottle	mounting h (mm)	% of storms		% decrease	Increment (mm)
1	224	**55%**			
2	251	**46%**		9%	27
3	283	**38%**		8%	32
4	320	**31%**		7%	37
5	368	**25%**		6%	48
6	438	**20%**		5%	70
7	541	**16%**		4%	103
8	632	**13%**		3%	91

B. Suspended sediment concentrations

B.1 Pakuranga

Pakuranga - Autosampler SSC (g/m3)												
	10-Mar		26-Mar		28-Mar		12-Apr		29-Apr		4-May	
Bottle	Time	SSC (mg/L)	Time	SSC (mg/L)	Time	SSC (mg/L)	Time	SSC (mg/L)	Time	SSC (mg/L)	Time	SSC (mg/L)
1	14:46	9.270	19:02	133.229	0:26	42.585	-	-	6:06	51.431	2:21	9.612
2	14:55	100.328	19:19	84.288	0:57	18.121	9:53	106.899	10:37	38.393	2:28	48.976
3	15:00	79.012	19:29	52.620	1:41	1.431	12:17	108.786	12:01	22.036	2:31	53.066
4	15:10	33.507	19:43	30.633	2:11	1.156	12:22	163.082	14:21	87.603	2:35	34.898
5	15:25	15.640	19:52	30.479	2:34	1.752	12:26	135.696	14:35	58.991	2:41	32.789
6	-	-	20:00	18.557	2:43	35.830	12:30	89.037	15:08	15.237	2:53	18.019
7	-	-	20:08	24.960	2:49	23.642	12:33	116.512	15:45	18.734	3:06	17.733
8	-	-	20:15	27.132	2:53	95.554	12:35	154.207	16:15	146.136	3:16	7.548
9	-	-	20:22	20.861	2:55	76.552	12:39	144.202	16:19	162.341	3:32	8.364
10	-	-	20:29	19.416	2:58	59.620	12:43	135.631	16:29	87.223	3:42	14.137
11	-	-	20:35	21.807	3:01	34.489	12:47	91.329	17:17	28.742	3:47	11.949
12	-	-	20:41	24.211	3:03	24.519	12:51	78.244	17:35	20.294	3:57	9.925
13	-	-	20:48	16.099	3:06	22.142	12:57	52.870	-	-	4:14	7.970
14	-	-	-	-	3:10	18.642	13:02	53.728	-	-	4:30	8.901
15	-	-	-	-	3:13	16.087	13:07	53.048	-	-	-	-
16	-	-	-	-	3:16	22.391	13:11	73.308	-	-	-	-
17	-	-	-	-	3:22	12.656	13:14	70.396	-	-	-	-
18	-	-	-	-	3:31	9.616	13:18	67.361	-	-	-	-
19	-	-	-	-	3:37	13.301	13:22	65.266	-	-	-	-
20	-	-	-	-	-	-	13:27	80.988	-	-	-	-
21	-	-	-	-	-	-	13:31	80.882	-	-	-	-
22	-	-	-	-	-	-	13:34	74.912	-	-	-	-
23	-	-	-	-	-	-	13:37	65.187	-	-	-	-
24	-	-	-	-	-	-	13:42	43.395	-	-	-	-

Pakuranga - PSSB SSC (g/m3)												
	10-Mar		26-Mar		28-Mar		12-Apr		29-Apr		4-May	
Bottle	Time	SSC (mg/L)	Time	SSC (mg/L)	Time	SSC (mg/L)	Time	SSC (mg/L)	Time	SSC (mg/L)	Time	SSC (mg/L)
1	14:46	160.063	19:02	176.006	0:26	55.062	-	-	8:51	26.665	2:23	16.196
2	14:48	362.989	19:03	225.064	0:26	33.485	9:22	53.762	8:53	76.934	2:23	20.335
3	14:48	102.695	19:03	268.793	0:27	78.559	-	-	10:01	60.916	2:24	36.134
4	14:49	171.432	19:03	301.862	0:28	62.107	9:23	55.688	10:03	85.712	2:24	15.991
5	14:49	133.566	19:04	104.980	0:31	45.054	-	-	11:39	36.770	2:25	16.924
6	14:50	94.725	19:05	152.369	0:35	47.961	12:17	47.041	14:20	37.583	2:25	17.615
7	14:50	158.317	19:08	76.554	2:25	20.934	-	-	14:21	38.072	2:26	21.057
8	14:51	285.633	19:17	114.050	2:39	17.383	12:17	48.914	14:23	75.718	2:27	43.500

B.2 Blockhouse Bay SSC

Blockhouse Bay - Autosampler SSC								
	4-Apr		5-Apr		12-Apr		11-May	
Bottle	Time	SSC (mg/L)	Time	SSC (mg/L)	Time	SSC (mg/L)	Time	SSC (mg/L)
1	18:10	124.713	12:03	77.830	11:07	33.138	-	-
2	18:35	642.373	12:39	62.976	11:30	484.091	8:40	193.101
3	18:45	384.615	12:59	77.817	-	-	9:13	705.406
4	18:53	471.534	13:17	74.811	11:44	433.366	9:19	873.736
5	19:01	380.367	13:41	72.293	11:49	404.463	9:25	598.371
6	19:08	306.426	14:24	49.667	11:54	331.131	9:31	409.148
7	19:16	258.508	15:19	49.344	11:59	409.639	9:37	307.771
8	19:25	236.165	15:42	53.126	12:04	321.690	9:44	252.347
9	19:34	180.365	16:13	53.989	12:08	350.398	9:54	334.371
10	19:43	162.395	-	-	12:12	322.548	10:10	193.101
11	19:51	170.549	-	-	12:16	359.539	-	-
12	19:58	217.182	-	-	12:20	303.501	-	-

Blockhouse Bay - PSSB SSC								
	4-Apr		5-Apr		12-Apr		11-May	
Bottle	Time	SSC (mg/L)	Time	SSC (mg/L)	Time	SSC (mg/L)	Time	SSC (mg/L)
1	18:17	764.831	11:44	113.271	11:08	70.682	9:07	203.125
2	18:19	334.968	12:05	48.754	11:12	231.935	9:08	101.770
3	18:20	390.531	12:16	44.757	11:15	193.075	9:09	711.235
4	18:22	624.138	12:30	54.970	11:18	267.486	9:10	327.118
5	18:24	484.423	12:42	83.413	11:21	432.882	9:12	706.924
6	18:26	1359.316	12:59	92.703	11:23	428.757	9:13	527.192
7	18:29	854.526	-	-	11:25	502.005	9:17	589.054
8	18:31	712.857	-	-	11:26	1255.905	9:23	226.670

(pink shading) = Faulty seal likely / observed in field

C. Lab results metals and nutrients

C.1 Autosampler

Hill Laboratories
TRIED, TESTED AND TRUSTED

R J Hill Laboratories Limited
1 Clyde Street Hamilton 3216
Private Bag 3205
Hamilton 3240 New Zealand

T 0508 HILL LAB (44 555 22)
T +64 7 858 2000
E mail@hill-labs.co.nz
W www.hill-laboratories.com

ANALYSIS REPORT Page 1 of 3

Client:	NIWA Head Office	**Lab No:**	1777511 SPv1
Contact:	Dr J Gadd	**Date Received:**	18-May-2017
	C/- NIWA Head Office	**Date Reported:**	29-May-2017
	Private Bag 99940	**Quote No:**	84576
	Newmarket	**Order No:**	U254330
	Auckland 1149	**Client Reference:**	
		Submitted By:	Dr J Gadd

Sample Type: Aqueous

Sample Name:		BB160517-1	BB160517-2	BB160517-3	BB160517-4	BB160517-5
Lab Number:		1777511.1	1777511.2	1777511.3	1777511.4	1777511.5
Individual Tests						
Volatile Suspended Solids	g/m³	12	19	30	17	16
Total Suspended Solids	g/m³	79	129	197	151	109
Dissolved Copper	g/m³	0.0027	0.0021	0.0023	0.0037	0.0036
Total Copper	g/m³	0.0096	0.0105	0.0127	0.0101	0.0095
Dissolved Lead	g/m³	0.00031	0.00022	0.00026	0.00034	0.00052
Total Lead	g/m³	0.0085	0.0122	0.0148	0.0086	0.0089
Dissolved Zinc	g/m³	0.022	0.024	0.024	0.021	0.022
Total Zinc	g/m³	0.093	0.115	0.134	0.086	0.086
Total Nitrogen	g/m³	1.13	1.08	1.22	1.89	1.20
Total Kjeldahl Nitrogen (TKN)	g/m³	0.73	0.90	1.06	1.57	0.92
Total Phosphorus	g/m³	0.180	0.189	0.24	0.52	0.162
Nutrient Profile						
Total Ammoniacal-N	g/m³	0.015	< 0.010	< 0.010	< 0.010	< 0.010
Nitrite-N	g/m³	0.007	0.003	0.004	0.004	0.003
Nitrate-N	g/m³	0.39	0.178	0.159	0.32	0.28
Nitrate-N + Nitrite-N	g/m³	0.40	0.181	0.162	0.32	0.28
Dissolved Reactive Phosphorus	g/m³	0.036	0.008	0.026	0.36	0.026

Sample Name:		BB160517-6	BB160517-7	BB160517-8	BB160517-9	BB160517-10
Lab Number:		1777511.6	1777511.7	1777511.8	1777511.9	1777511.10
Individual Tests						
Volatile Suspended Solids	g/m³	15	25	35	46	41
Total Suspended Solids	g/m³	110	172	260	260	290
Dissolved Copper	g/m³	0.0038	0.0039	0.0044	0.0041	0.0046
Total Copper	g/m³	0.0078	0.0104	0.0146	0.0130	0.0128
Dissolved Lead	g/m³	0.00055	0.00054	0.00094	0.00055	0.00043
Total Lead	g/m³	0.0065	0.0107	0.0170	0.0135	0.0123
Dissolved Zinc	g/m³	0.024	0.021	0.067	0.0175	0.020
Total Zinc	g/m³	0.069	0.086	0.100	0.093	0.085
Total Nitrogen	g/m³	1.28	1.86	2.0	2.2	2.3
Total Kjeldahl Nitrogen (TKN)	g/m³	1.02	1.61	1.77	1.92	2.0
Total Phosphorus	g/m³	0.44	0.21	0.33	0.36	1.33
Nutrient Profile						
Total Ammoniacal-N	g/m³	< 0.010	< 0.010	< 0.010	< 0.010	0.011
Nitrite-N	g/m³	0.003	0.003	0.003	0.003	0.004
Nitrate-N	g/m³	0.26	0.25	0.25	0.27	0.30
Nitrate-N + Nitrite-N	g/m³	0.26	0.25	0.25	0.27	0.31
Dissolved Reactive Phosphorus	g/m³	0.29	0.034	0.038	0.076	1.04

Sample Type: Aqueous						
Sample Name:		BB160517-11	BB160517-12			
Lab Number:		1777511.11	1777511.12			
Individual Tests						
Volatile Suspended Solids	g/m^3	34	17	-	-	-
Total Suspended Solids	g/m^3	280	152	-	-	-
Dissolved Copper	g/m^3	0.0052	0.0062	-	-	-
Total Copper	g/m^3	0.0118	0.0170	-	-	-
Dissolved Lead	g/m^3	0.00050	0.00067	-	-	-
Total Lead	g/m^3	0.0096	0.0067	-	-	-
Dissolved Zinc	g/m^3	0.0169	0.020	-	-	-
Total Zinc	g/m^3	0.072	0.067	-	-	-
Total Nitrogen	g/m^3	2.3	1.82	-	-	-
Total Kjeldahl Nitrogen (TKN)	g/m^3	1.86	1.27	-	-	-
Total Phosphorus	g/m^3	0.32	0.20	-	-	-
Nutrient Profile						
Total Ammoniacal-N	g/m^3	0.021	0.016	-	-	-
Nitrite-N	g/m^3	0.006	0.005	-	-	-
Nitrate-N	g/m^3	0.40	0.54	-	-	-
Nitrate-N + Nitrite-N	g/m^3	0.41	0.54	-	-	-
Dissolved Reactive Phosphorus	g/m^3	0.056	0.044	-	-	-

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Aqueous

Test	Method Description	Default Detection Limit	Sample No
Nutrient Profile		0.0010 - 0.010 g/m^3	1-12
Filtration, Unpreserved	Sample filtration through 0.45µm membrane filter.	-	1-12
Total Digestion	Nitric acid digestion. APHA 3030 E 22nd ed. 2012 (modified).	-	1-12
Total Kjeldahl Digestion	Sulphuric acid digestion with copper sulphate catalyst.	-	1-12
Total Phosphorus Digestion	Acid persulphate digestion.	-	1-12
Volatile Suspended Solids	Filtration (GF/C, 1.2 µm). Ashing 550°C, 30 min. Gravimetric. APHA 2540 E 22nd ed. 2012.	3 g/m^3	1-12
Total Suspended Solids	Filtration using Whatman 934 AH, Advantec GC-50 or equivalent filters (nominal pore size 1.2 - 1.5µm), gravimetric determination. APHA 2540 D 22nd ed. 2012.	3 g/m^3	1-12
Filtration for dissolved metals analysis	Sample filtration through 0.45µm membrane filter and preservation with nitric acid. APHA 3030 B 22nd ed. 2012.	-	1-12
Dissolved Copper	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m^3	1-12
Total Copper	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m^3	1-12
Dissolved Lead	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.00010 g/m^3	1-12
Total Lead	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00011 g/m^3	1-12
Dissolved Zinc	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0010 g/m^3	1-12
Total Zinc	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0011 g/m^3	1-12
Total Nitrogen	Calculation: TKN + Nitrate-N + Nitrite-N. Please note: The Default Detection Limit of 0.05 g/m^3 is only attainable when the TKN has been determined using a trace method utilising duplicate analyses. In cases where the Detection Limit for TKN is 0.10 g/m^3, the Default Detection Limit for Total Nitrogen will be 0.11 g/m^3.	0.05 g/m^3	1-12
Total Ammoniacal-N	Filtered sample. Phenol/hypochlorite colorimetry. Discrete Analyser. (NH_4-N = NH_4+-N + NH_3-N). APHA 4500-NH_3 F (modified from manual analysis) 22nd ed. 2012.	0.010 g/m^3	1-12
Nitrite-N	Automated Azo dye colorimetry, Flow injection analyser. APHA 4500-NO_3^- I 22nd ed. 2012 (modified).	0.002 g/m^3	1-12
Nitrate-N	Calculation: (Nitrate-N + Nitrite-N) - NO2N. In-House.	0.0010 g/m^3	1-12
Nitrate-N + Nitrite-N	Total oxidised nitrogen. Automated cadmium reduction, flow injection analyser. APHA 4500-NO_3^- I 22nd ed. 2012 (modified).	0.002 g/m^3	1-12

Sample Type: Aqueous			
Test	**Method Description**	**Default Detection Limit**	**Sample No**
Total Kjeldahl Nitrogen (TKN)	Total Kjeldahl digestion, phenol/hypochlorite colorimetry. Discrete Analyser. APHA 4500-N_{org} D. (modified) 4500 NH_3 F (modified) 22nd ed. 2012.	0.10 g/m^3	1-12
Dissolved Reactive Phosphorus	Filtered sample. Molybdenum blue colorimetry. Discrete Analyser. APHA 4500-P E (modified from manual analysis) 22nd ed. 2012.	0.004 g/m^3	1-12
Total Phosphorus	Total phosphorus digestion, ascorbic acid colorimetry. Discrete Analyser. APHA 4500-P B & E (modified from manual analysis) 22nd ed. 2012. Also modified to include the use of a reductant to eliminate interference from arsenic present in the sample. NWASCA, Water & soil Miscellaneous Publication No. 38, 1982.	0.004 g/m^3	1-12

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

Ara Heron BSc (Tech)
Client Services Manager - Environmental

C.2 PSSBs

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ANALYSIS REPORT **Page 1 of 2**

Client:	NIWA Head Office	**Lab No:**	1777513 SPv1
Contact:	Dr J Gadd	**Date Received:**	18-May-2017
	C/- NIWA Head Office	**Date Reported:**	29-May-2017
	Private Bag 99940	**Quote No:**	84576
	Newmarket	**Order No:**	U254330
	Auckland 1149	**Client Reference:**	Stormwater Samples
		Submitted By:	Dr J Gadd

Sample Type: Aqueous

Sample Name:		FFB160517-1 16-May-2017	FFB160517-2 16-May-2017	FFB160517-3 16-May-2017	FFB160517-4 16-May-2017	FFB160517-5 16-May-2017
Lab Number:		1777513.1	1777513.2	1777513.3	1777513.4	1777513.5
Individual Tests						
Dissolved Copper	g/m³	0.0008	0.0024	0.0023	0.0021	0.0020
Total Copper	g/m³	0.0033	0.0069	0.0079	0.0067	0.0069
Dissolved Lead	g/m³	0.00042	0.00037	0.00039	0.00023	0.00029
Total Lead	g/m³	0.0022	0.0060	0.0075	0.0060	0.0074
Dissolved Zinc	g/m³	0.058	0.040	0.036	0.040	0.043
Total Zinc	g/m³	0.088	0.095	0.111	0.105	0.104
Total Nitrogen	g/m³	0.90	1.05	1.18	0.92	0.77
Total Kjeldahl Nitrogen (TKN)	g/m³	0.42	0.66	0.88	0.65	0.56
Total Phosphorus	g/m³	0.056	0.143	0.164	0.131	0.134
Nutrient Profile						
Total Ammoniacal-N	g/m³	0.022	0.019	0.026	0.027	< 0.010
Nitrite-N	g/m³	0.006	0.008	0.007	0.006	0.004
Nitrate-N	g/m³	0.47	0.38	0.30	0.27	0.20
Nitrate-N + Nitrite-N	g/m³	0.48	0.39	0.30	0.27	0.21
Dissolved Reactive Phosphorus	g/m³	0.016	0.006	0.012	0.007	0.010

Sample Name:		FFB160517-6 16-May-2017	FFB160517-7 16-May-2017			
Lab Number:		1777513.6	1777513.7			
Individual Tests						
Dissolved Copper	g/m³	0.0019	0.0016	-	-	-
Total Copper	g/m³	0.0080	0.0107	-	-	-
Dissolved Lead	g/m³	0.00025	0.00030	-	-	-
Total Lead	g/m³	0.0086	0.0145	-	-	-
Dissolved Zinc	g/m³	0.043	0.024	-	-	-
Total Zinc	g/m³	0.120	0.135	-	-	-
Total Nitrogen	g/m³	0.82	0.95	-	-	-
Total Kjeldahl Nitrogen (TKN)	g/m³	0.62	0.77	-	-	-
Total Phosphorus	g/m³	0.135	0.155	-	-	-
Nutrient Profile						
Total Ammoniacal-N	g/m³	< 0.010	< 0.010	-	-	-
Nitrite-N	g/m³	0.003	0.003	-	-	-
Nitrate-N	g/m³	0.193	0.181	-	-	-
Nitrate-N + Nitrite-N	g/m³	0.196	0.184	-	-	-
Dissolved Reactive Phosphorus	g/m³	0.012	0.014	-	-	-

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Aqueous

Test	Method Description	Default Detection Limit	Sample No
Nutrient Profile		0.0010 - 0.010 g/m^3	1-7
Filtration, Unpreserved	Sample filtration through 0.45µm membrane filter.	-	1-7
Total Digestion	Nitric acid digestion. APHA 3030 E 22nd ed. 2012 (modified).	-	1-7
Total Kjeldahl Digestion	Sulphuric acid digestion with copper sulphate catalyst.	-	1-7
Total Phosphorus Digestion	Acid persulphate digestion.	-	1-7
Filtration for dissolved metals analysis	Sample filtration through 0.45µm membrane filter and preservation with nitric acid. APHA 3030 B 22nd ed. 2012.	-	1-7
Dissolved Copper	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0005 g/m^3	1-7
Total Copper	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00053 g/m^3	1-7
Dissolved Lead	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.00010 g/m^3	1-7
Total Lead	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.00011 g/m^3	1-7
Dissolved Zinc	Filtered sample, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012.	0.0010 g/m^3	1-7
Total Zinc	Nitric acid digestion, ICP-MS, trace level. APHA 3125 B 22nd ed. 2012 / US EPA 200.8.	0.0011 g/m^3	1-7
Total Nitrogen	Calculation: TKN + Nitrate-N + Nitrite-N. Please note: The Default Detection Limit of 0.05 g/m^3 is only attainable when the TKN has been determined using a trace method utilising duplicate analyses. In cases where the Detection Limit for TKN is 0.10 g/m^3, the Default Detection Limit for Total Nitrogen will be 0.11 g/m^3.	0.05 g/m^3	1-7
Total Ammoniacal-N	Filtered sample. Phenol/hypochlorite colorimetry. Discrete Analyser. (NH_4-N = NH_4+-N + NH_3-N). APHA 4500-NH_3 F (modified from manual analysis) 22nd ed. 2012.	0.010 g/m^3	1-7
Nitrite-N	Automated Azo dye colorimetry, Flow injection analyser. APHA 4500-NO_3^- I 22nd ed. 2012 (modified).	0.002 g/m^3	1-7
Nitrate-N	Calculation: (Nitrate-N + Nitrite-N) - NO2N. In-House.	0.0010 g/m^3	1-7
Nitrate-N + Nitrite-N	Total oxidised nitrogen. Automated cadmium reduction, flow injection analyser. APHA 4500-NO_3^- I 22nd ed. 2012 (modified).	0.002 g/m^3	1-7
Total Kjeldahl Nitrogen (TKN)	Total Kjeldahl digestion, phenol/hypochlorite colorimetry. Discrete Analyser. APHA 4500-N_{org} D. (modified) 4500 NH_3 F (modified) 22nd ed. 2012.	0.10 g/m^3	1-7
Dissolved Reactive Phosphorus	Filtered sample. Molybdenum blue colorimetry. Discrete Analyser. APHA 4500-P E (modified from manual analysis) 22nd ed. 2012.	0.004 g/m^3	1-7
Total Phosphorus	Total phosphorus digestion, ascorbic acid colorimetry. Discrete Analyser. APHA 4500-P B & E (modified from manual analysis) 22nd ed. 2012. Also modified to include the use of a reductant to eliminate interference from arsenic present in the sample. NWASCA, Water & soil Miscellaneous Publication No. 38, 1982.	0.004 g/m^3	1-7

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

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