Targeted wet weather monitoring of Curlett and Haytons Streams 2021

Report on results and recommendations for future monitoring

Prepared for Christchurch City Council

July 2022

Climate, Freshwater & Ocean Science

Prepared by:
Karine Borne
Jennifer Gadd

For any information regarding this report please contact:

Jennifer Gadd
Aquatic Chemist
Urban Aquatic Environments
+64-9-375 2058
jennifer.gadd@niwa.co.nz

National Institute of Water & Atmospheric Research Ltd
Private Bag 99940
Viaduct Harbour
Auckland 1010

Phone +64 9 375 2050

NIWA CLIENT REPORT No: 2022041AK
Report date: July 2022
NIWA Project: CCC22102

Revision	Description	Date
Version 1.0		Day Month Year
Version 1.1	Amendments to …	Day Month Year

Quality Assurance Statement		
J. P. Moores	Reviewed by:	Jonathan Moores
	Formatting checked by:	Emma Hope-Ede
J. P. Moores	Approved for release by:	Jonathan Moores

Contents

Tables

Figures

Executive summary

In accordance with the conditions of the Comprehensive Stormwater Network Discharge Consent granted to Christchurch City Council by Environmental Canterbury, targeted wet weather monitoring (TWWM) is to be performed to improve knowledge of the state of the receiving environment, contaminant inputs and treatment efficiency, and to inform mitigation options. Haytons and Curlett Streams were identified as the priority catchments to investigate, due to having the poorest water quality within Christchurch City. This report presents the results of the first year of monitoring (2021) in these catchments. The specific long-term objectives of this project were to (1) map hotspots or localised discharges of contaminants along the length of the streams during base flows and storm flows, (2) investigate whether there are also hotspots of other currently unknown emerging or unusual contaminants, and (3) to establish what discharges from individual sites are contributing to the identified hotspots of contaminants.

This phase of the TWWM project incorporated sampling at 15 different locations throughout the Haytons and Curletts Stream catchments, and upstream and downstream within the Ōpāwaho/Heathcote River (Figure 1-1). Sampling was primarily conducted using autosamplers to collect water samples throughout the duration of a storm event (time weighted composite samples), supplemented with Nalgene Stormwater Sampler bottles to collect “grab” samples during high flow events at additional sites. Sites were monitored collaboratively with Environment Canterbury, University of Canterbury and NIWA each running sites, with sampling by all agencies during the same rain events to allow comparisons across the catchments. Four events were sampled between May and December 2021 at 7 to 9 sites simultaneously with technical issues or flooding preventing sampling at the remaining sites.

Overall, the water quality data indicate that the Curlett Stream had the highest concentrations of metals (copper and zinc), total suspended solids (TSS), Biochemical Oxygen Demand (BOD_5) and *Escherichia coli* (*E. coli*), although some high concentrations were occasionally observed at HS1 (upper Haytons Stream, Figure 1-1) for TSS and dissolved copper (DCu). However, some uncertainties persist regarding the locations presenting the highest concentrations for each event due to either the variability between samples and events or the possible overestimation of pollutants (especially particulate forms) in samples collected by Nalgene bottles at some sites. Key areas of uncertainty include the following: (1) Although high concentrations of both DCu and dissolved zinc (DZn) were identified at the Curlett Stream site “CSAuto1” , it was not possible to identify which upstream subcatchment was the highest contributor of metals, as no upstream monitoring station was installed on the eastern branch; and (2) for some pollutants such as DCu, no decrease in concentration was observed until after the Curlett wetland suggesting that copper is released in several locations along the upper part of the Curlett Stream and precise source identification is therefore not realistic.

Overall, nutrient water quality data suggest that both Haytons (upstream HS2) and Curlett (upstream CSAuto2 and/or CSNal1) streams received dissolved reactive phosphorus, ammoniacal nitrogen and nitrate input, sometimes simultaneously with *E. coli* and BOD_5 (especially at CSAuto2). Observations of nutrients in combination with sulphate and fluoride suggest potential input associated with the fertiliser manufacturing and storage site in the Haytons Stream catchment but the lack of data at sites further downstream limits the identification of any additional potential contributions. High nitrate concentrations were observed at the downstream site on Ōpāwaho/Heathcote River for Event 3 and 4, however as the upstream site (HR1) was not sampled on these occasions it is unclear where the source came from.

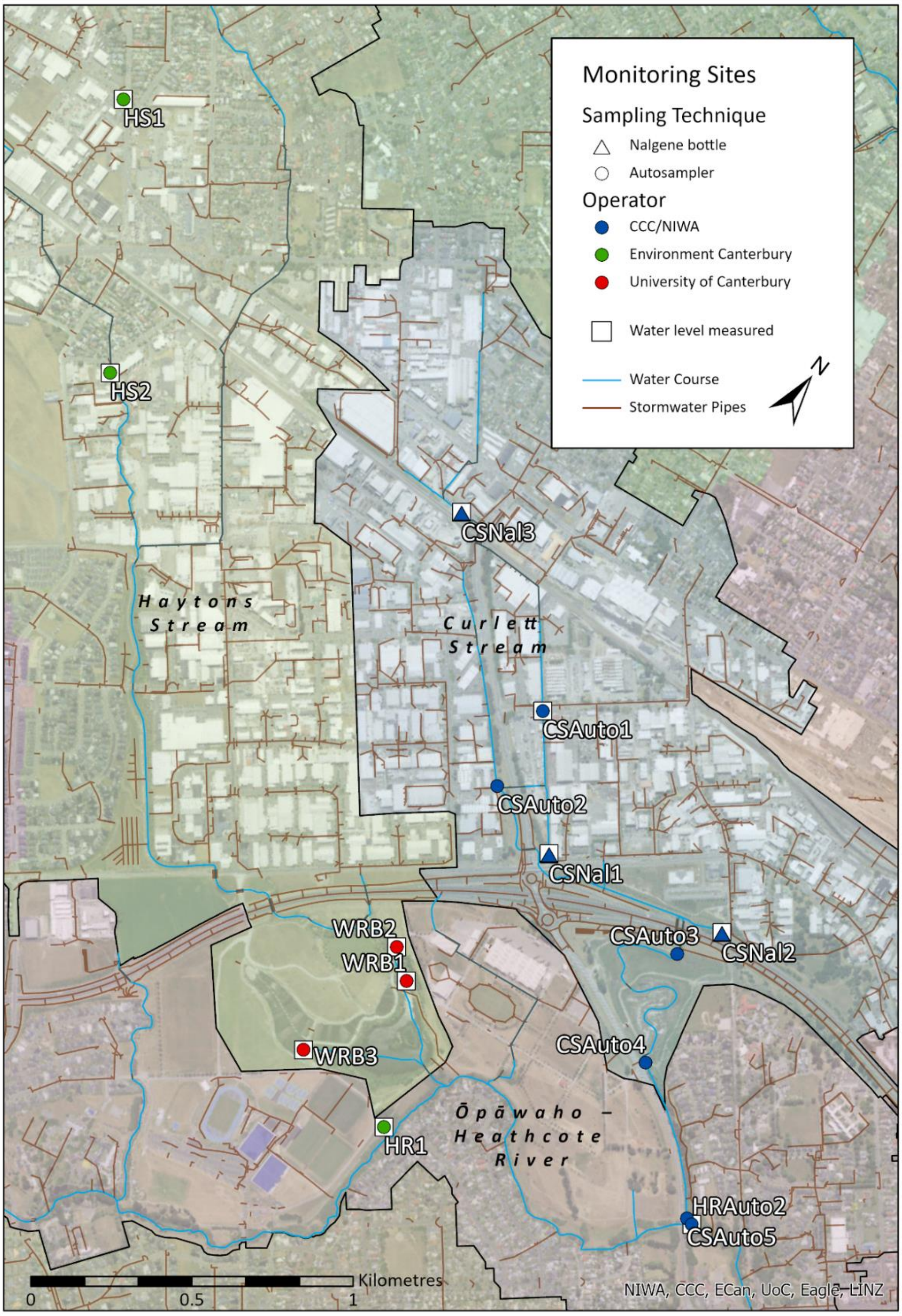

Figure 1-1: Location of water quality monitoring sites in the Hayton and Curlett Stream catchments. Black border and shading indicates stormwater catchment areas.

Finally, it is clear that the current land use of the Curlett Stream subcatchment comprises many potential pollutant sources (various industrial sites, scrap metal yards, railway, machinery manufacturing sites). It will be difficult to achieve the third objective of the wet weather monitoring project (i.e. identification of individual sites contributing to hot spots) without putting in place a widespread monitoring programme to collect samples at the scale of individual potential contributing sites. We recognise that this may not be technically nor economically feasible, particularly within the specified timeframe.

Reflecting the various areas of uncertainty encountered in sampling to date, in order to gain a better understanding of the main contributing sources to the Haytons and Curlett streams, the following actions are recommended:

- The autosamplers at HR1, HRAuto2 and CSAuto5 can be removed. Upstream and downstream sites on Ōpāwaho/Heathcote River showed relatively lower and less variable concentrations than the Curlett and Haytons streams (except for nitrate-N) and therefore would appear as stations of lower interest from a hotspot identification perspective (except for nitrate hotspot identification). CSAuto5 showed usually lower concentrations than CSAuto4 suggesting no additions between these sites and CSAuto5 could therefore be removed, relying on CSAuto4 as an indication of the output from the Curlett Stream catchment.
- Replace the single autosampler located at CSAuto1 with two autosamplers located just upstream, on each of the western and eastern branches. This would enable us to identify which of these two branches contributes the majority of contaminants to the current CSAuto1 site.
- Coordinate sampling with University of Canterbury in order to collect water quality data at the inlet and outlet of the Wigram Retention Basin. This would improve understanding of whether additional sources to Haytons Stream exist downstream of HS2.
- Replace the liquid level actuators on ISCOs with a more reliable triggering system (such as connecting to a pressure transducer and logger) as these systems seemed prone to issues including: a) not triggering sampling at all (event 1, CSAuto3); b) collecting multiple samples straight away, possibly due to the trigger turning on and off; and c) the variable sample pacing not working as intended. If pressure transducers are included at all sites to measure water level (and flow, see below) there would be no additional cost or equipment required for this.
- Autosamplers from HR1, HRAuto5 and CSAuto5 could be moved to the Nalgene sites (CSNal3, CSNal1 and CSNal2) to provide more reliable estimates of contaminant concentrations.
- Where variable sample pacing is used to target first-flush, ensure the sample pacing is different downstream of the wetlands where flows are attenuated and remain high for a longer duration. Although this approach was attempted in some storm events, it should be used in all events.
- Measure the flow at each site: this would allow for flow-weighted composite sampling and estimation of the actual mass of pollutants at each site as opposed to concentrations. Flows could be monitored either through use of continuous water level measurement combined with a series of gaugings at different flows; or through the combination of water level and velocity instruments to provide flow. Although this would require additional equipment and resource, it would provide greater confidence in the water quality information obtained in

the monitoring programme. Comparison of pollutant concentrations solely between sites and /or branches of stream does not allow for hot spot identification as inputs to the streams are diluted to different degrees depending on stream flows. In particular, flow measurement is crucial to precisely identify which branch of the Curlett Stream actually receives (and delivers) most of the pollutant loads.

- If flow weighted sampling is performed at each site (implying flow measurement at each site) then only one sample (flow weighted composite sample) could be analysed at each site (as opposed to 3 or 4 as in 2021). These measures would reduce analytical costs.
- Ideally sample up to eight additional storm events to better account for the variability of pollutant export between events, with a review of the results and information obtained after four additional events.
- Due to low lead concentrations observed at all sites, remove this parameter from the monitoring programme.
- Reconsider how hardness-adjusted guidelines for zinc are used for the Ōpāwaho/Heathcote catchment as hardness was lower than 30 mg $CaCO_3$/L within the Haytons and Curlett streams.
- Investigate the use of nitrate isotopes (δ15N and δ18O of NO3) in assessing the contribution of nitrogen from the fertiliser manufacturing and storage site to Haytons Stream. Isotopic methods should be able to distinguish between nitrogen sources that enter the stream from fertiliser via surface or subsurface flows (close to the sampling sites) and those from deeper Canterbury aquifers with greater distance between nitrogen sources and the Haytons Stream sampling sites.
- In order to map hot spots during base flow conditions (one of the objectives of the “wet weather monitoring”), some dry weather investigations need to be performed over 2022-2023. This could include dry weather sampling at the current and/or proposed wet weather monitoring stations and where resource permits, additional sites in between. Alternatively, instrumentation could be installed to measure water level, and water quality indicators such as pH, conductivity and turbidity. These approaches have been used in the Haytons Stream catchment previously, identifying the presence of dry weather discharges and with some success in identifying possible sources of contamination.

1 Introduction

1.1 Background

Christchurch City Council (CCC) was granted consent by Environment Canterbury to discharge water and contaminants to land and water from the stormwater network in December 2019, under what is known as the Comprehensive Stormwater Network Discharge Consent (CSNDC; CRC214226). This consent includes a stormwater quality investigation programme (Schedule 3) with multiple actions, one of which (Schedule 3, item k) is to “carry out a targeted wet weather monitoring of surface water in selected receiving environments to improve knowledge of the state of the receiving environment, contaminant inputs and treatment efficiency, and to inform mitigation options under the Stormwater Management Plans (SMPs). Selected areas may include new stormwater developments and retrofits and known existing hotspots of contaminants. Sampling shall focus on detailed methods to characterise inputs, such as the use of auto-sampling, rather than grab sampling.” This action was set to commence within 6 months of the consent commencement and is ongoing over the 25-year term of the consent.

This document reports on the first year of monitoring undertaken for this consent condition. It contains the following information:

- the overall project aims and objectives, and the specific objectives for this year of monitoring
- the sampling sites and rationale for their selection
- the methods used to collect wet weather stormwater and stream samples, and the laboratory analytical methods used.
- a description of rainfall during the wet weather events sampled.
- the results of the water sampling, including comparison to CSNDC targets and guidelines
- an assessment of the results against project objectives
- recommendations on the next steps to achieve the overall project objectives.

1.2 Why focus on Curlett and Haytons streams?

CCC monitors surface water quality within the five major river catchments of the City: Ōtākaro/Avon, Ōpāwaho/Heathcote, Huritini/Halswell, Pūharakekenui/Styx and Ōtūkaikino rivers (Margetts & Marshall, 2020). Information from this monitoring has demonstrated that the Ōpāwaho/Heathcote River catchment records the poorest water quality, and the worst tributary waterways in that catchment are Curlett Stream and Haytons Stream, based on the monitoring at three sites (two in Curlett and one in Haytons). The dominant land use in the catchments of these two streams is industrial.

The parameters of concern are broad, including pH, total suspended solids (TSS)/turbidity, dissolved oxygen/Biochemical Oxygen Demand (BOD_5), dissolved nitrogen and phosphorus, dissolved copper (DCu) and zinc (DZn), and *Escherichia coli* (e.g., Margetts & Marshall, 2020). These contaminants have potential to have both short-term and long-term adverse effects on biota, contribute to proliferation of aquatic plants and/or algae, increase the human health risks from contact recreation, and decrease the aesthetics of the water column.

CCC has also undertaken wet weather monitoring in the catchment which has demonstrated higher contaminant concentrations when compared to those recorded during monthly monitoring. Furthermore, Haytons Stream has been the focus of several water quality investigations instigated by Environment Canterbury (e.g., Moores et al. 2009; O’Sullivan & Charters 2014; Black 2018), that have demonstrated elevated concentrations of nutrients, metals and faecal indicator bacteria during baseflow and storm events. The studies also indicated frequent illicit discharges of contaminants into the stormwater network and streams, contributing to high contaminant levels during both base and storm flows. Despite the number of studies undertaken, the specific sources of contaminants within Haytons and Curlett streams is still not clear. Moreover, the elevated concentrations in Haytons Stream also affect the Ōpāwaho/ Heathcote River, demonstrated by higher ammoniacal nitrogen (ammoniacal-N) and dissolved reactive phosphorus (DRP) concentrations downstream of the tributary confluence compared to upstream (Pattle Delamore Partners, 2007).

Overall, the monitoring and additional studies to date indicate that the upper Ōpāwaho/Heathcote River catchment and, in particular Curlett and Haytons streams, are a high priority for catchment management. These two streams are the focus of several projects by CCC (largely associated with the CSNDC) and Environment Canterbury (ECan) including:

- The CSNDC Ōpāwaho/Heathcote River Stormwater Management Plan;
- CSNDC Industrial site audits within the Haytons and Curlett Stream catchments;
- Development and calibration of the CSNDC contaminant load model and the instream contaminant concentrations model for the Ōpāwaho/Heathcote River catchment, and/or Haytons and Curlett Stream if appropriate;
- The CSNDC Monitoring Performance of Stormwater Treatment Facilities project (Schedule 3, item i); and
- The multi-agency Haytons Stream Action Plan (Moody, 2019).

By focussing the targeted wet weather monitoring project on these two streams, the information obtained from the monitoring can also be used to inform the above projects.

1.3 Aims and objectives of the targeted wet weather monitoring

In accordance with the consent condition, the aims of the targeted wet weather monitoring (TWWM) are to improve knowledge of the state of the receiving environment, contaminant inputs and treatment efficiency, and to inform mitigation options. The TWWM runs for the duration of the consent. Margetts & Poudyal (2020) set out a plan for the TWWM project focussing on Haytons and Curlett Streams from 2021-2023. These specific goals are:

1. To map hotspots or localised discharges (areas with contaminants above guideline values or typical levels) along the length of Haytons and Curlett Streams of a range of parameters, during base flows and storm flows, by the end of 2022.
2. To investigate whether there are also hotspots of other currently unknown emerging or unusual contaminants that may be having an adverse effect on surface water quality within Haytons and Curlett Streams, during base flow and storm flows, by the end of 2023.
3. To establish what discharges from individual sites are contributing to the identified hotspots of contaminants under (1) and (2) above, by the end of 2022 and 2023, respectively.

Consistent with these broader project goals, the first year of monitoring (2021), aimed to collect water samples during storm events at locations within the two catchments that would allow for an adaptive monitoring plan to achieve the above objectives in future years.

2 Sites and Methods

2.1 Overview

This phase of the TWWM project incorporated sampling throughout the Haytons and Curletts Stream catchments, and upstream and downstream within the Ōpāwaho/Heathcote River. Sampling was primarily using autosamplers to collect water samples throughout the duration of a storm event, supplemented with Nalgene Stormwater Sampler bottles to collect "grab" samples during high flow events at additional sites. Sites were monitored collaboratively with Environment Canterbury, University of Canterbury and NIWA running sites, with sampling by all agencies during the same rain events to allow comparisons across the catchment.

2.2 Monitoring sites

2.2.1 Rationale for site selection

The sites monitored in this first phase were selected based on:

- existing knowledge of issues in the catchment (for example in upper sections of Haytons Stream),
- sites at confluences that could provide indications of the presence of upstream contaminant sources (upper Curlett Stream),
- sites that are monitored routinely (monthly) as part of CCC's network, to provide wet weather data to complement the primarily baseflow data (two sites in Curlett Stream),
- sites upstream and downstream of detention basins and wetlands to provide information on treatment, and
- sites in the Ōpāwaho/Heathcote River upstream and downstream of the two tributaries to provide information on the impact of tributary water quality on the downstream river.

2.2.2 Details of sampling locations

The stormwater sampling was undertaken at 15 sites, including two in the Ōpāwaho/Heathcote River at sites upstream and downstream of the two tributaries (Table 2-1 and Figure 2-1). Five sites were located within Haytons Stream, three of which were around the Wigram Retention Basin. Five sites were located in Curlett Stream, including sites upstream and downstream of the Curlett Road wetland system and these were supplemented with an additional three sites using solely Nalgene stormwater sampler bottles.

Table 2-1: Details of sites and monitoring methods. Blue rows are those in the Ōpāwaho/Heathcote River upstream and downstream, respectively, of Haytons and Curletts Streams.

Site Code	Site name	Rationale for selection	Water sampling method	Water level monitoring
HR1	Ōpāwaho/Heathcote River at Warren Crescent footbridge	Upstream of both Haytons and Curlett Streams	Autosampler	Pressure transducer with telemetry
HS1	Haytons Stream downstream of Waterloo Road	Downstream of industrial land; illicit discharges previously detected here	Autosampler	Pressure transducer with telemetry
HS2	Haytons Stream at Washbournes Road culvert	Downstream of stormwater pipe from Ravensdown & other industrial land; illicit discharges previously detected here	Autosampler	Pressure transducer with telemetry
WRB1	Wigram Retention Basin at inlet	Inlet to the Wigram Retention Basin, downstream of all industrial land	Autosampler	Pressure transducer
WRB2	Wigram Retention Basin at outlet	With WRB1, indicates treatment within Wigram Retention Basin comprising an old pond/wetland cell followed by a new retrofitted wetland cell), CCC long-term site (HEATH09)	Autosampler	Pressure transducer
WRB3	Wigram Retention Basin between old and new wetland cells	Outlet of old pond/wetland cell, with WRB1, indicates treatment within old pond/wetland cell, and with WRB2 indicates treatment within new wetland cell.	Autosampler	Pressure transducer
CSAuto1	Curlett Stream at Lunns Road	Downstream of industrial land in eastern part of catchment	Autosampler with bubbler	Pressure transducer with telemetry
CSAuto2	Curlett Stream at Curletts Road	Downstream of industrial land in western part of catchment	Autosampler with actuator	None

Site Code	Site name	Rationale for selection	Water sampling method	Water level monitoring
CSAuto3	Curlett Stream at Southern Motorway	CCC long-term site (HEATH14), upstream of wetland	Autosampler with bubbler	None
CSAuto4	Curlett Stream Downstream of Curlett Wetland	With CSAuto3, indicate treatment through wetland	Autosampler with bubbler	Water level monitored at wetland outlet
CSAuto5	Curlett Stream Upstream of Ōpāwaho /Heathcote River Confluence	Most downstream point in stream, CCC long-term site (HEATH10)	Autosampler with actuator	None
CSNal1	Curlett Stream downstream in Lunns Road branch	Downstream of CSAuto1 and landscaping business	Nalgene bottles	Hobo water level logger installed prior to each event
CSNal2	Curlett Stream Branch	Receives stormwater from branch draining parts of Annex Rd	Nalgene bottles	Hobo water level logger installed prior to each event
CSNal3	Curlett Stream near Cable Street	Most upstream location, stormwater from small but intensive industrial area	Nalgene bottles	Hobo water level logger installed prior to each event
HRAuto2	Ōpāwaho/Heathcote River after Curlett Stream Confluence	With HR1, indicate effect of Haytons and Curlett Streams on Ōpāwaho/Heathcote River water quality	Autosampler with actuator	Pressure transducer with telemetry at Lincoln Rd, 300-400m downstream

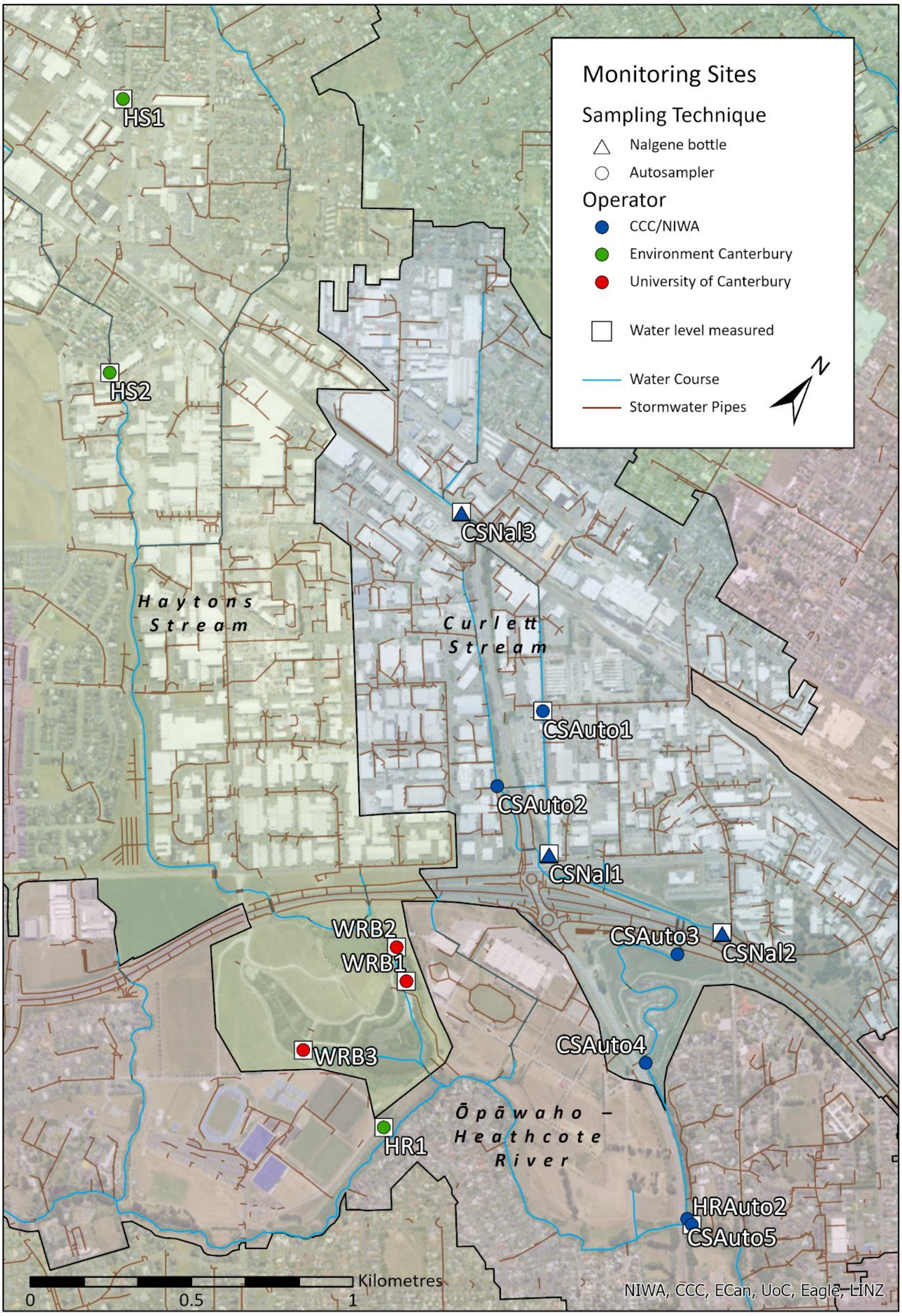

Figure 2-1: Location of water quality monitoring sites in the Hayton and Curlett Stream catchments. Black border and shading indicates stormwater catchment areas.

2.3 Storm criteria

Wet weather samples were collected when the following criteria were met:

- An antecedent dry period of at least 3 days - pollutants build up relatively quickly after a storm event, reaching maximum concentrations at 3-6 antecedent dry days (Poudyal, 2019);
- A total rainfall depth of at least 3 mm [1]; and
- Samples can be retrieved and analysed within 48 hours. For example, storm events on Friday night were not targeted as samples are unlikely to be analysed by the CCC lab until Monday morning, even if retrieved prior to that.

2.4 Sampling methods

2.4.1 Autosampler

Autosamplers (ISCO 6712) were installed at each of the sites listed in Table 2-1. At the sites operated by Environment Canterbury, samplers were connected to water level loggers and a telemetry system that provided in almost real-time a view of the time that samples were collected. For the sites operated by NIWA, CCC supplied an ISCO 6712 with either 730 Bubbler Flow Module or 1640 Liquid Level Sampler Actuator (henceforth termed bubblers and actuators respectively). These do not need a water level recorder/logger to trigger sampling and therefore reduced the costs associated with instrumentation hire and installation. The bubbler uses a pressure transducer and a flow of bubbles to accurately determine the water levels. When the water level reaches the programmed water level, sampling is enabled. The actuator uses a probe assembly installed above the stream at the desired sampling height. When the water rises and liquid touches the stainless steel ring of the probe assembly, the sampler is enabled to begin collecting water samples.

The samplers were programmed to collect samples on a time-weighted basis, based on forecast rainfall duration. Samplers were programmed to collect samples more frequently (e.g., every 30 minutes) at the beginning of a storm event, to target a possible first-flush; and to then collect samples at longer durations (every 4 hours) later in the event. This approach was used at all sites, though for some events longer durations were used at sites upstream and downstream of Curlett wetland system (CSAuto3, CSAuto4, CSAuto5, HRAuto2) and therefore these sites were not expected to demonstrate any first-flush of contaminants.

Approximately 1 L of water was collected from the stream at each sampling interval. Acid-washed polyethylene bottles were used in order to avoid the potential contamination of samples by metals associated with the use of glass and reduce adsorption of metals contained in the water to the sample bottles. Clean bottles were transported to the site capped and gloves were worn when placing in the autosampler and removing the lids.

The autosamplers collected up to 24 bottles during each event. The collected water samples were retrieved by NIWA or Environment Canterbury staff on conclusion of each sampling event.

2.4.2 Nalgene bottles

Nalgene® Storm Water Sampler bottles are commercially produced bottles that collect a grab sample of water, similar to a manual grab[2], but without the requirement for personnel on site. The water bottles fill

---

[1] This rainfall depth is based on modelling by Tom Parsons at CCC for the Avon Stormwater Management Plan that demonstrated this is sufficient rainfall to obtain the first flush of contaminants.

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

once water reaches the intake level when deployed in a stream or drain and close off by means of a float valve (also known as a ball cock), preventing any further water from mixing with the sample.

The bottles were deployed above the baseflow water level prior to each storm event with Hobo water level loggers installed at the same time. Two bottles were deployed at each site, one at 50-60 mm above baseflow to target the early part of the event, and potentially a first-flush; and the second bottle at 150-300 mm above baseflow to target the peak water level. The installation heights (Table 2-2) were determined by NIWA staff based on observations of water levels at the sites and the height for the second bottles (targeting peak flows) was increased from the first event for all subsequent events. Both bottles and the Hobo water level loggers were attached to a section of PVC pipe which was then placed over a waratah that had previously been driven into the stream bed. This enabled the bottles to be quickly installed and safely removed even during high flows as the pipe could be reached from the bank eliminating the need to enter the water.

Figure 2-2: Waratah with two Nalgene sampling bottles installed at the three sampling sites. From left to right: CSNal1, CSNal2 and CSNal3.

Table 2-2: Deployment heights used for Nalgene sampler bottles.

	Event 1		Event 2		Event 3		Event 4	
Sampling location	Lower bottle	Upper bottle	Lower bottle	Upper bottle	Lower bottle	Upper bottle	Lower bottle	Upper bottle
CSNal1	55	165	55	370	60	320	60	320

	Event 1		Event 2		Event 3		Event 4	
Sampling location	Lower bottle	Upper bottle	Lower bottle	Upper bottle	Lower bottle	Upper bottle	Lower bottle	Upper bottle
CSNal2	50	160	50	300	60	320	50	340
CSNal3	75	185	60	250	60	250	50	250

2.5 Sample compositing

To reduce the costs of the monitoring programme, samples were combined prior to laboratory analysis. However, to provide some indication of variability during storm events, samples were combined in up to three groups, representing different parts of the storm event / hydrograph, such as the first-flush (or initial rise), peak flow (or largest peak) and recession. The decision-making regarding the separation of the hydrograph into different parts was undertaken collaboratively between NIWA and Environment Canterbury science staff.

Once the hydrograph was split up, the samples collected during each selected part of the storm event were grouped for compositing in the laboratory.

As water levels were monitored only at a subset of the Curlett Stream sites, event hydrographs from the Lunns Road drain site were used for sites CSAuto2 and CSAuto3. For CSAuto4 and CSAuto5, which were both downstream of the Curlett wetland, the event hydrograph from HRAuto2 was used as a surrogate.

Time-weighted composites were prepared for each site, across the grouping period. Where samples were collected at equal time intervals (e.g., all hourly), an equal volume of water was used in the grouped composites. Where sampling intervals differed, differing volumes of water were used in the composites to achieve a time-weighted average. For example, if a sample group contained bottles 1-10 and bottles 1-5 were collected every 30 minutes and bottles 6-10 every 60 minutes, a 1:2 ratio was used for bottle mixing, whereby the volume used from bottles 1-5 was half that of bottles 6-10. Thus each ml of subsample in the composites represented the same amount of time (e.g., 500 ml per 30 minutes).

For Hayton Stream and the upper Ōpāwaho/Heathcote River site, compositing was undertaken by Environment Canterbury staff. For Curlett Stream and the lower Ōpāwaho/Heathcote River site, compositing was undertaken by staff at the CCC wastewater laboratory. In both cases, the compositing method involved vigorously shaking the samples within the ISCO bottles and measuring the required volume (with a measuring cylinder) into a 10 L plastic container. Subsamples were then taken from that container into laboratory bottles as needed for the required analyses.

2.6 Water sample analyses

A wide range of contaminants were assessed in all composite (or grab for Nalgene sites) water samples (Table 2-3), including nutrients (ammoniacal-N, nitrate-N, DRP), metals (copper, lead and zinc), sediment and oxygen demanding substances (through BOD_5). The turbidity, pH, and hardness (based on dissolved calcium and magnesium) were also measured in each composite (or grab for Nalgene sites) sample as indicators of contamination and/or to assist in ecotoxicology assessments. The additional variables of boron, fluoride, sulfate and manganese were assessed in Haytons Stream only, as indicators of stormwater runoff from the fertiliser manufacturing and storage site in the Haytons Stream catchment. The faecal indicator bacteria *E. coli* was measured in samples collected by Nalgene bottles and in autosampler samples for events 1 and 3 only as these were delivered to the laboratory within 36 hours of sample collection. The selected analytical suite was based on information from previous sampling indicating issues with both nutrients and metals.

Two different analytical laboratories were used for the analyses. Samples from Curlett Stream sites and HRAuto2 were delivered to the CCC Laboratory of the Three Waters Unit, at the Christchurch Wastewater Treatment Plant. All samples collected and processed by Environment Canterbury were delivered to Hill Laboratories, Hornby, Christchurch. For these samples, some analyses were undertaken in Christchurch and some were undertaken in Hamilton, after filtration and sample preservation in Christchurch (see Appendix B Table B-1). Both the CCC and Hill laboratories are accredited by IANZ and all tests were performed in accordance with their terms of accreditation. All analytical methods used by each laboratory are outlined in Appendix B Table B-1. There were only minimal differences between the methods used by each laboratory (e.g., samples for ammoniacal-N were filtered through a 0.7 µm filter by CCC laboratory compared to a 0.45 µm filter by Hill Laboratories) and therefore all results are considered to be comparable.

Table 2-3: Summary of analyses at each site.

Analyte	CCC Nalgene bottle sites	CCC autosampler sites	ECan autosampler sites
TSS; total suspended solids	✓	✓	✓
Turbidity	✓	✓	✓
pH	✓	✓	✓
Dissolved calcium, magnesium, copper, lead and zinc	✓	✓	✓
Total copper, lead and zinc	✓	✓	✓
Total boron, aluminium and manganese	✗	✗	✓
Fluoride	✗	✗	✓
Total ammoniacal-N	✓	✓	✓
Nitrate-N + nitrite-N	✓	✓	✓
DRP	✓	✓	✓
Sulfate	✗	✗	✓
BOD_5, Biochemical Oxygen Demand	✓	✓	✓
DOC; Dissolved Organic Carbon	✓	✓	✓
E. coli	✓	Events 1 & 3 only	✗

2.7 Water quality guidelines used in this report

In this report we have compared the concentrations of contaminants in the streams to guideline values (Table 2-4). These guidelines generally align with the water quality guidelines specified in the CSNDC Environmental Monitoring Programme (EMP) and used in the associated annual water quality monitoring reports (e.g., Margetts & Marshall 2021, 2020). One exception to this was to exclude the turbidity guideline of 5.6 FNU from ANZECC (2000), that is currently used in the CSNDC EMP. This reflects recent guidance that turbidity is not a suitable metric for environmental standards and regulations due to the high variation in outputs between different turbidity sensors (Davies-Colley et al. 2021).

A second exception was the use of the national bottom line threshold for ammoniacal-N from the 2020 version of the National Policy Statement for Freshwater Management (NPS-FM, New Zealand Government 2020), in addition to ammoniacal-N value used in the CSNDC EMP from the Land and Water Regional Plan (LWRP; Environment Canterbury 2019).

Furthermore, the LWRP specifies that for spring-fed urban streams, the 90% level of protection for toxicants should be used and this is reflected in the receiving environment objectives of the CSNDC. The CSNDC and the EMP also specify specific guideline values for the Ōpāwaho/Heathcote River catchment, based on adjustment to 94 mg$CaCO_3$/L. In this report we have used the same hardness adjustment, but used all four protection levels (80-99%, ANZG 2018) to provide some distinction between sites. The EMP also specifies comparing the 95th percentile of measurements over a full year to these guidelines, following the guidance provided by ANZG (2018). However, for this wet weather monitoring, there were only 1 to 4 samples analysed for each event (per site) which is insufficient for calculating percentiles. We have instead compared median concentrations to the guidelines, which we consider appropriate for the primary purpose of assisting in identifying hotspots, rather than to indicate potential ecotoxicological effects.

Table 2-4: Water quality guideline values used in this report.

Canterbury Land and Water Regional Plan				
DRP (mg/L)	0.016			
DIN (mg/L)	1.5			
Ammonia (mg/L)	0.9 *			
pH (lower-upper limit)	6.5-8.5			
E. coli (MPN/100mL)	95th percentile <550			
ANZG (2018) guidelines				
Guidelines for toxicants - all sampling stations	level of protection (% species)			
	99%	95%	90%	80%
Cu (mg/L)	0.0010	0.0014	0.0018	0.0025
Pb (mg/L; adjusted to hardness of 94 mg $CaCO_3$/L)	0.001	0.0034	0.0056	0.0094
Zn (mg/L; adjusted to hardness of 94 mg $CaCO_3$/L)	0.0024	0.008	0.015	0.031
Al (mg/L)	0.027	0.055	0.080	0.15
Mn (mg/L)	1.2	1.9	2.5	3.6
B (mg/L)	0.09	0.37	0.68	1.3
NPS-FM attributes (MfE 2020)				
Ammonia (toxicity) mg NH_4-N/L, national bottom line		Median value < 0.24		Maximum < 0.40
Nitrate (toxicity) mg NO_3-N/L, national bottom line		Median value < 2.4		Maximum < 3.5
Other guidelines				
BOD_5 (mg/L) MfE (1992)	2			
TSS (mg/L) (Hayward et al. 2009)	25			
* Ammonia standards in LWRP are pH adjusted				

3 Results

3.1 Hydrological characteristics of sampled storm events

The characteristics of each storm event are summarised in Table 3-1, and rainfall and hydrographs (water level) are shown in Figure 3-1. The second event, starting on 29th May 2021, was the largest event sampled, with nearly 130 mm (approximately double the normal rainfall in May) of rain falling within 3 days. The rainfall during the most intense 48-hour period of this event has an expected probability of occurring about once every 30 to 40 years. The other three events sampled were each approximately 20 mm over 24 hours, and are of a depth and duration expected to occur multiple times each year. All rainfall events met the storm criteria of a minimum of three antecedent dry periods and a total rainfall depth of at least 3 mm.

Table 3-1: Summary of storm event characteristics. Rainfall as recorded at Christchurch College of Education (approx. 2.2 to 4 km North from the study sites).

Event	Start date and time	End date and time	Antecedent dry period (days)	Total rainfall depth (mm)	Rainfall duration (hours) *
Event 1	11 May 21:15	12 May 23:50	16	19.8	26.5
Event 2	29 May 11:00	1 June 8:00	4	128	69
Event 3	4 October 4:30	5 October 2:30	4	22	22
Event 4	27 November 15:40	28 November 10:40	4	16.2	19

Note: * Rainfall duration was calculated from the start to the end of the main period of rain and does not include minor showers.

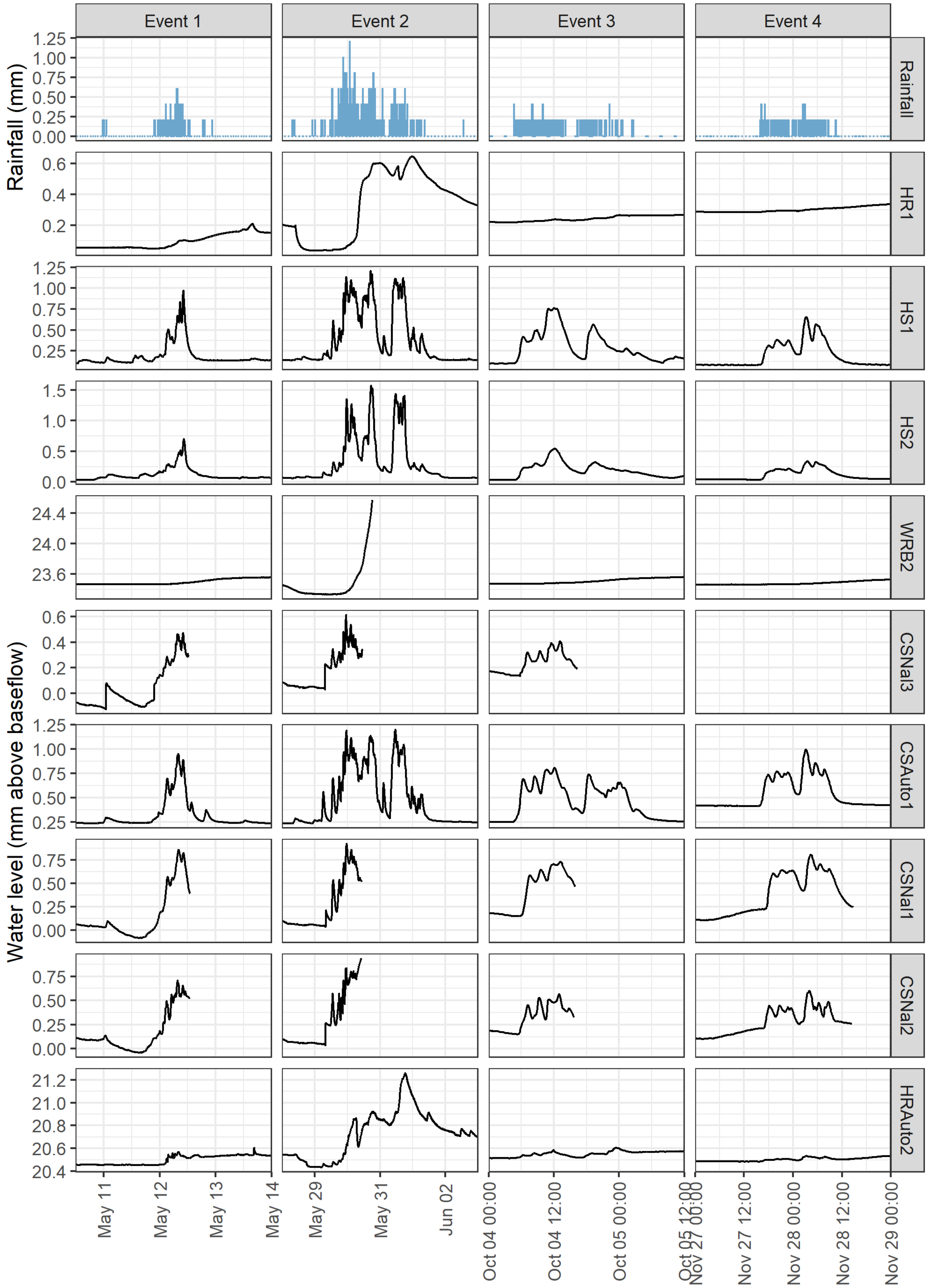

Figure 3-1: Rainfall and water level hydrographs for sites in Ōpāwaho/Heathcote River, and Haytons and Curletts streams during each of the four events. Rainfall as recorded at Christchurch College of Education, Ilam.

3.2 Overview of samples successfully collected

Table 3-2 provides an overview of the sites that were and were not sampled during each event. Not all sites were successfully sampled during each event. In event 1, the sampler at CSAuto1 stopped sampling due to a power failure after collecting only 7 bottles and the autosampler at CSAuto5 did not trigger at all despite a rise in water level that reached the actuator. In the second event, samples were collected at CSAuto3 however the sampler cabinet was flooded due to the high water levels during this storm event, particularly as water backed-up from the downstream detention ponds. No samples were collected at Wigram Retention Basin (WRB) due to lack of University of Canterbury staff availability (Event 1) and then flooding in Event 2 which damaged the equipment and sites, preventing sampling for the remaining events (Events 3 to 4). Data collected by University of Canterbury in June 2020 were used to identify potential treatment of Haytons Stream within the Wigram Retention Basin.

In some cases (e.g., Event 2, CSAuto2; Event 4, HRAuto2), the sample pacing did not work as intended – when the sampler was triggered, it initially collected samples with a longer duration between samples (e.g., 2 to 4 hourly) before changing to an hourly collection (see Figure 3-2).

Table 3-2: Details of sampling success (or otherwise) at each site for each of the four events..

Site Code	Event 1	Event 2	Event 3	Event 4
HR1	Sampled	Sampled	Not sampled	Sampled after peak
HS1	Sampled	Sampled	Missed first-flush	Sampled
HS2	Sampled	Sampled	Sampled	Sampled
WRB1	Not sampled	Flooded	Not sampled	Not sampled
WRB2	Not sampled	Flooded	Not sampled	Not sampled
WRB3	Not sampled	Flooded	Not sampled	Not sampled
CSAuto1	Only partly	Sample pacing issue	Sampled	Sampled
CSAuto2	Sampled	Sample pacing issue	Sampled	Sample pacing issue
CSAuto3	Sampled early	Flooded	Sampled	Sampled
CSAuto4	Sampled	Sampled	Sampled	Fluctuations but mostly as intended
CSAuto5	Did not trigger	Sampled	Sampled	Fluctuations but mostly as intended
CSNal1	Two bottles	Two bottles	Two bottles	Two bottles
CSNal2	Two bottles	Two bottles	Two bottles	Two bottles
CSNal3	Two bottles	Two bottles	Two bottles	Two bottles
HRAuto2	Sampled	Sampled	Sample pacing issue	Sample pacing issue

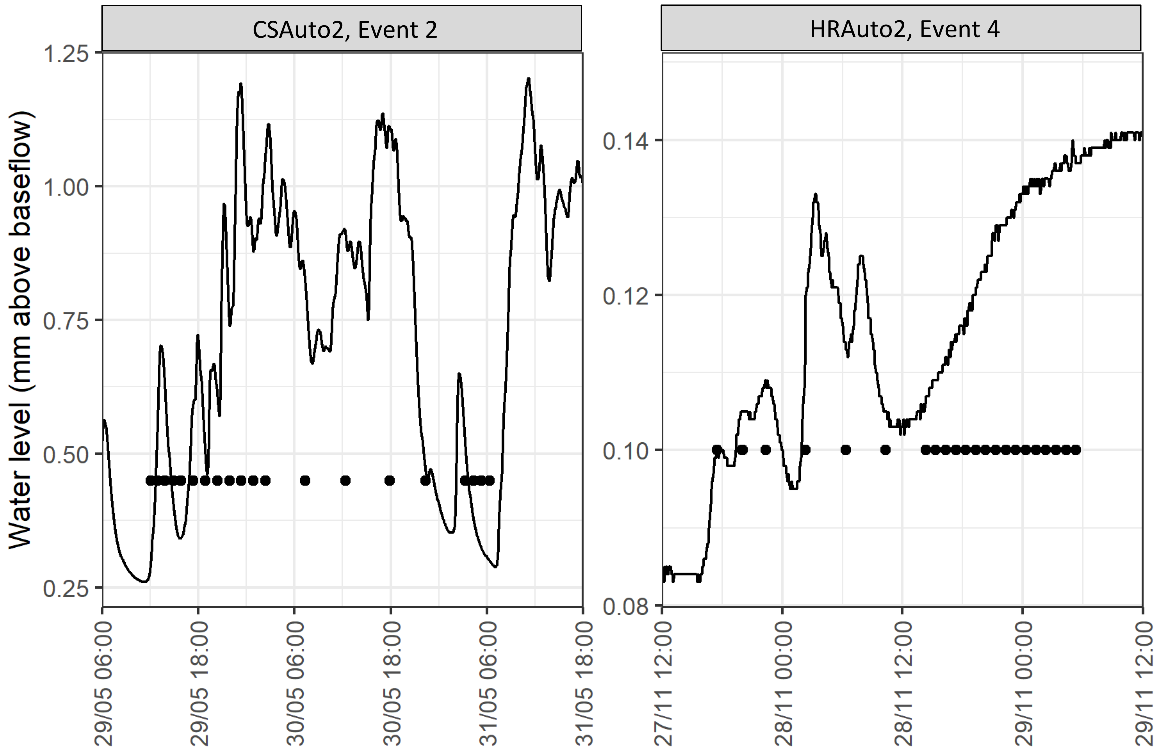

Figure 3-2: Time of individual samples collected by autosamplers at selected sites and events demonstrating that samples were unintentionally collected at a shorter duration near the end of these two events. Vertical position of points is arbitrary. Black lines indicate water level as recorded at CSAuto3 (left panel) and at HRAuto2 (right panel).

Figure 3-3 shows the timing of all individual samples collected by the autosamplers and Nalgene bottles at each site and in each event, coloured by the group those samples were composited into. The water level at each site (where measured) is also displayed. Every site had a slightly different hydrograph and samples were collected at different times at each. As can be seen, although every effort was made to group samples into comparable parts of the hydrograph, this was not always possible. For example, in event 1, samples within group 3 from CSAuto2 were collected over a shorter period than at HS1 and HS2. Depending on the contaminant, and its dynamics during storm events (e.g., increasing with higher flows versus decreasing with higher flows), these concentrations may be either higher or lower than if they were collected over the same duration. This adds some uncertainty in interpreting the results in the following sections. However, as we did collect samples within the same events, multiple samples were collected within each event (at sites using the autosamplers) and, for the most part, across the key parts of the event (initial rise to capture any possible first flush; peak flow; recession) we consider the samples to be broadly comparable for the purposes of investigating differences between sites and to locate potential sources and hot-spots. For the remainder of this results section, the Nalgene bottles are annotated according to the sample group they are most closely related to, e.g., Group 1 or Group 2.

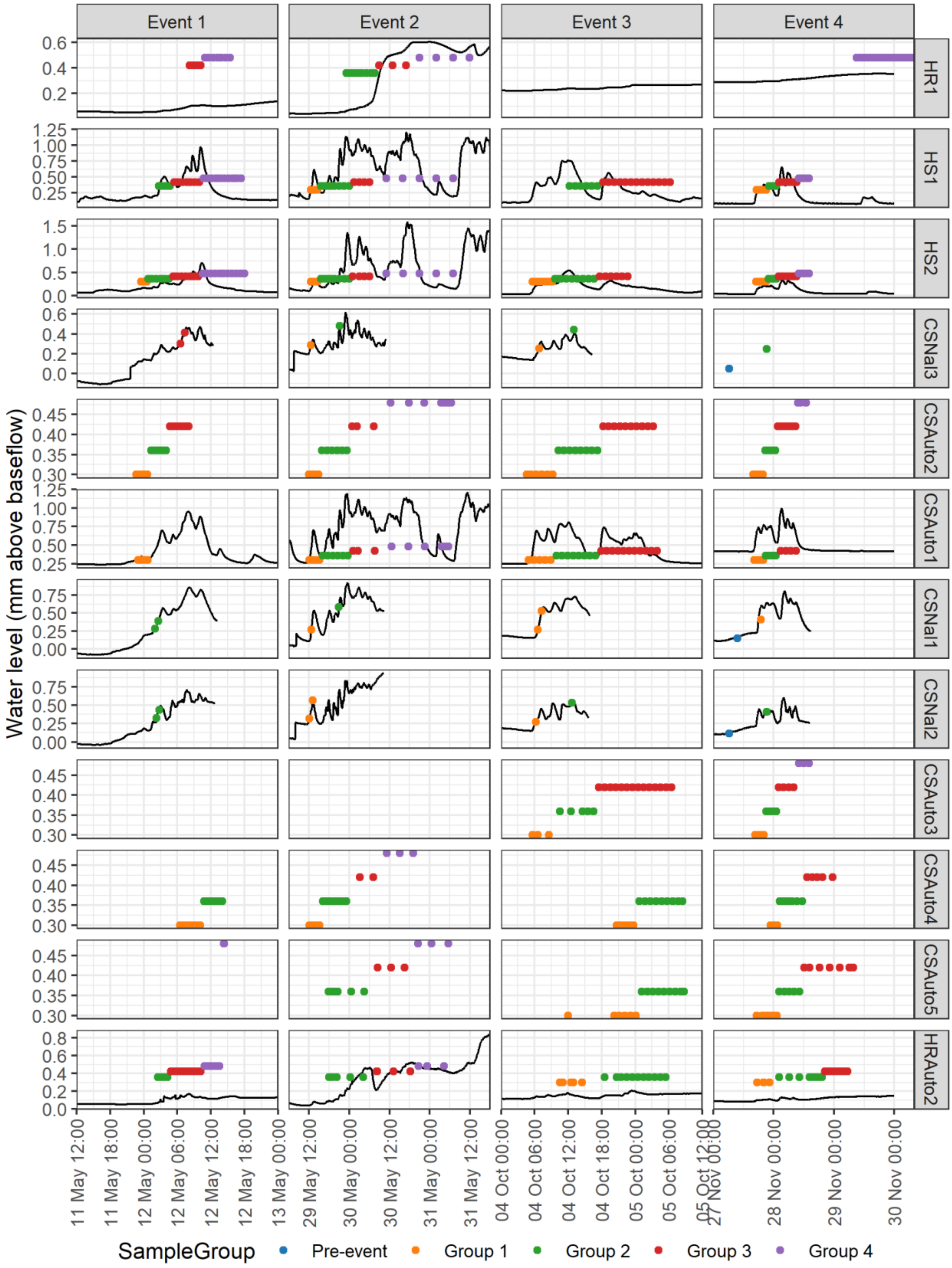

Figure 3-3: Timing of each sample collected by autosampler, for each site and event. Vertical position of points for Nalgene sites is the water level at which samples were collected. Vertical position is arbitrary for autosamplers and merely to differentiate between groups. Colours indicate the groups samples were composited into for analysis. Black lines indicate water level as recorded at each site. Note in event 4 Nalgene samples were filled prior to the rainfall event due to a small rise in water level and are labelled as "Pre-event".

3.3 Water quality results

Table 3-3 and Table 3-4 summarise the water quality results, including a comparison to guideline values.

3.3.1 Solids

Total suspended solids concentrations were above 25 mg/L (guideline from Hayward et al. (2009)) at all sites but HS2 (Table 3-3). Suspended solids and turbidity were highest in the samples collected using Nalgene bottles (with a couple of exceptions, Table 3-4). This was particularly the case for Event 2, where all samples collected with Nalgene bottles contained concentrations greater than 250 mg/L of suspended solids. It is highly likely that this is due to accumulation of sediments within these bottles due to the bottles not completely sealing during this event where water levels were very high for a sustained period (see Figure 3-3). This has been reported previously when using these bottles in streams and open drains (Gadd & Milne 2019; Gadd 2020).

Excluding these values (Nalgene bottles samples), highest total suspended solids concentrations were alternatively observed at either CSAuto2, CSAuto 3, CSAuto4, CSAuto5 or HRAuto2, therefore mainly in the downstream reaches of Curlett Stream (Figure 3-4). Given the high variability of the data, it is unclear why or where main TSS export to Curlett Stream occurred. HRAuto2 (the most downstream site) on Ōpāwaho/Heathcote River exhibited greater concentrations than upstream sites (including Hayton and Curlett streams) during the biggest event (Event 2=128 mm rainfall), suggesting either additional sediment sources between the HR1 and HRAuto2 sites on Ōpāwaho/Heathcote River and/or sediment resuspension of sediment deposited on the river bed, induced by the very high flows associated with Event 2.

Turbidity and TSS were analysed at both CSAuto3 and CSAuto4 sites (upstream and downstream of the Curlett wetland) only for Event 3 and 4. Results are variable and suggest either no treatment within the basin (similar values upstream and downstream in Event 3); or turbidity (usually reflective of fine particles) export and TSS (usually reflective of coarser particles) entrapment (Event 4). It is at this stage therefore not possible to draw any conclusion on the wetland treatment effect although observations suggest it could act as either a sink or a source of sediments (Figure 3-5). On some occasions this sediment remained in suspension to the confluence with Ōpāwaho/Heathcote River, approximately 500 m downstream (Figure 3-6). Previous monitoring of the Wigram Retention Basin (lower Haytons Stream) by University of Canterbury in June 2020 (prior to this project) suggests no specific treatment and sometimes release of TSS although inlet concentrations were low (median TSS <10 mg/L) and therefore most probably close to the irreducible concentrations[3] of the wetland system.

---

[3] The concept of irreducible concentrations recognises that treatment systems cannot reduce concentrations to zero - a minimum concentration is likely regardless of additional treatment volume or area, see: https://owl.cwp.org/?mdocs-file=4745

Table 3-3: Contaminant and physical parameters median values for each sampling site and event (n=1 to 4 depending on events and parameters). Coloured cells indicate the compliance with New Zealand guideline values. Refer to Table 2-4 for detailed guideline values.

Event	Site Code	Copper, dissolved	Copper, total	Zinc, dissolved	Zinc, total	Lead, dissolved	Lead, total	Aluminium, total	Fluoride	Manganese, total	Boron, total	Sulphate	Ammoniacal-N	Nitrate+Nitrite-N	Nitrate-N	Dissolved Inorganic Nitrogen	Dissolved Reactive Phosphorus	BOD5	*E. coli*	Total Suspended Solids	Turbidity	Dissolved Organic Carbon	Hardness	pH
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	MPN/100 mL	mg/L	FTU	mg/L	mg CaCO3/L	-
Event 1	**HR1**	0.0014	0.0027	0.032	0.061	0.0007	0.0028	0.10	0.18	0.059	0.065	2.15	0.010	0.026		0.04	0.138	8.0		34	17	5.9	44.5	7.8
Event 2	**HR1**	0.0029	0.0041	0.043	0.056	0.0003	0.0015	0.30	0.12	0.026	0.054	5.80	0.040	0.21		0.25	0.119	3.0		9	9	5.0	34.0	7.4
Event 4	**HR1**	0.0005	0.0005	0.003	0.006	0.0001	0.0002	0.01	0.05	0.006	0.062	21.00	0.010	4.40		4.41	0.004	2.0		3	2	0.8	109.0	7.8
Event 1	**HS1**	0.0038	0.0100	0.23	0.31	0.0005	0.0079	0.70	0.16	0.0300	0.161	3.30	0.33	0.32		0.58	0.088	5.0		34	36	2.8	17.6	7.2
Event 2	**HS1**	0.0031	0.0076	0.17	0.26	0.0004	0.0067	0.97	0.09	0.0250	0.315	1.60	0.11	0.27		0.38	0.042	4.0		29	34	2.05	14.0	7.3
Event 3	**HS1**	0.0052	0.0103	0.23	0.33	0.0004	0.0062	1.78	0.09	0.0420	0.310	2.15	0.18	0.27		0.44	0.160	4.5		48	67	3.55	12.2	7.2
Event 4	**HS1**	0.0063	0.0083	0.30	0.33	0.0003	0.0017	0.26	0.20	0.0132	0.215	2.40	0.22	0.34		0.53	0.106	4.5		11	14	3.05	13.9	6.9
Event 1	**HS2**	0.0052	0.0107	0.26	0.32	0.0005	0.0045	0.40	0.32	0.0245	0.062	4.80	0.57	0.52		1.09	0.195	5.0		24	20	4.4	18.2	7.2
Event 2	**HS2**	0.0030	0.0073	0.13	0.19	0.0003	0.0055	0.68	0.27	0.0206	0.121	2.75	0.18	0.23		0.41	0.141	2.5		24	23	1.95	10.6	7.2
Event 3	**HS2**	0.0058	0.0114	0.19	0.27	0.0004	0.0045	0.62	0.14	0.0270	0.119	2.90	0.51	0.28		0.79	0.185	4.0		25	29	3.9	10.0	7.1
Event 4	**HS2**	0.0097	0.0124	0.24	0.27	0.0002	0.0014	0.17	0.25	0.0110	0.111	2.90	0.35	0.33		0.62	0.208	3.5		7	7	3.05	11.8	6.9
Event 1	**CSAuto2**	0.0110	0.0210	1.0	1.1	0.0006	0.0046						1.20	0.37	0.33	1.60	0.520	6.4	6600	19	22			6.9
Event 2	**CSAuto2**	0.0032	0.0124	0.30	0.36	0.0003	0.0068						0.24	0.22	0.20	0.45	0.065	3.1		32	27	4.1	15.5	7.0
Event 3	**CSAuto2**	0.0080	0.0240	0.38	0.59	0.0003	0.0140						0.29	0.31	0.31	0.58	0.110	6.0	17000	66	65	5.2	19.0	6.9
Event 4	**CSAuto2**	0.0075	0.0140	0.50	0.60	0.0014	0.0038						0.44	0.25	0.23	0.78	0.375	3.7		19	13	7.7	24.0	6.7
Event 1	**CSNal3**	0.0140	0.0210	1.1	1.1	0.0008	0.0093						0.22	0.19	0.18	0.41	0.053	4.1	6900	94	13			6.8
Event 2	**CSNal3**	0.0067	0.0550	0.38	0.72	0.0002	0.0495						0.13	0.24	0.23	0.37	0.039	7.0	1550	485	89			6.8
Event 3	**CSNal3**	0.0097	0.0265	0.42	0.63	0.0008	0.0146						0.16	0.31	0.30	0.35	0.056	6.1	1380	87	49			6.9
Event 4	**CSNal3**	0.0138	0.0290	0.42	0.50	0.0012	0.0102						0.10	0.31	0.29	0.40	0.057	10.2	4950	66	29			6.8
Event 1	**CSAuto1**	0.0840	0.0950	2.2	2.4	0.0028	0.0098						0.023	0.80	0.75	0.82	0.160	4.8	220	7	6			7.0
Event 2	**CSAuto1**	0.0120	0.0350	0.36	0.47	0.0006	0.0190						0.031	0.28	0.27	0.35	0.046	2.4		33	30	2	9.3	6.9
Event 3	**CSAuto1**	0.0200	0.0530	0.39	0.51	0.0008	0.0230						0.23	0.25	0.23	0.68	0.064	3.8	1400	32	24	3.9	9.7	6.9
Event 4	**CSAuto1**	0.0270	0.0340	0.51	0.53	0.0010	0.0087						0.11	0.26	0.24	0.37	0.071	3.5		15	8	5.6	12.0	6.6
Event 1	**CSNal1**	0.0048	0.2300	0.39	1.8	0.0006	0.0770						0.35	0.57	0.53	0.92	0.300	12.0	1400	570	190			7.0
Event 2	**CSNal1**	0.0069	0.2950	0.23	1.7	0.0003	0.1040						0.35	0.34	0.32	0.68	0.073	6.9	6350	690	225			7.2
Event 3	**CSNal1**	0.0202	0.2345	0.64	1.9	0.0011	0.0845						0.30	0.51	0.49	0.82	0.125	18.8	1000	370	95			7.0
Event 4	**CSNal1**	0.0225	0.2225	0.75	2.2	0.0035	0.0725						1.13	0.12	0.02	1.26	1.755	22.7	2780	390	109			7.1
Event 1	**CSNal2**	0.0021	0.0620	2.3	2.9	0.0003	0.0340						0.31	0.25	0.24	0.56	0.091	20.0	290	180	65			6.4
Event 2	**CSNal2**	0.0059	0.0780	0.77	1.3	0.0003	0.0320						0.09	0.45	0.44	0.54	0.041	8.5	910	420	64			6.8
Event 3	**CSNal2**	0.0063	0.0340	1.1	1.6	0.0004	0.0114						0.12	0.31	0.29	0.43	0.074	10.0	665	79	25			6.8
Event 4	**CSNal2**	0.0043	0.0275	0.85	1.3	0.0004	0.0112						0.17	0.32	0.31	0.49	0.061	4.7	3400	80	22			7.1
Event 3	**CSAuto3**	0.0160	0.0380	0.36	0.42	0.0005	0.0110						0.19	0.24	0.22	0.42	0.061	4.2	3100	32	34	3.3	12.0	6.8
Event 4	**CSAuto3**	0.0260	0.0330	0.41	0.47	0.0008	0.0041						0.27	0.24	0.22	0.51	0.270	3.6		10	8	6.5	14.0	6.7
Event 1	**CSAuto4**	0.0059	0.0160	0.083	0.16	0.0005	0.0074						0.37	0.17	0.15	0.54	0.098	5.2	4900	147	169			7.2
Event 2	**CSAuto4**	0.0081	0.0150	0.12	0.15	0.0003	0.0049						0.11	0.29	0.28	0.40	0.026	2.5		37	46	3.6	28.5	7.0
Event 3	**CSAuto4**	0.0120	0.0195	0.13	0.16	0.0009	0.0049						0.09	0.20	0.19	0.29	0.076	4.4	4950	38	41	7.7	49.0	7.3
Event 4	**CSAuto4**	0.0059	0.0130	0.026	0.078	0.0008	0.0076						0.09	0.08	0.07	0.18	0.033	4.8		72	97	13	68.0	7.2
Event 1	**CSAuto5**	0.0081	0.0370	0.099	0.30	0.0004	0.0120						0.10	0.16	0.14	0.26	0.054	5.4	4400	180	97			6.8
Event 2	**CSAuto5**	0.0081	0.0230	0.17	0.28	0.0003	0.0072						0.06	0.21	0.20	0.23	0.038	3.0		49	44	3.9	30.0	6.9
Event 3	**CSAuto5**	0.0069	0.0140	0.053	0.094	0.0005	0.0046						0.10	0.13	0.13	0.24	0.058	3.2	1775	36	42	7.5	60.0	7.1
Event 4	**CSAuto5**	0.0013	0.0032	0.009	0.020	0.0004	0.0025						0.20	0.01	0.01	0.21	0.011	2.2		24	31	10	85.0	7.0
Event 1	**HRAuto2**	0.0017	0.0024	0.036	0.039	0.0003	0.0011						0.074	0.31	0.29	0.37	0.047	4.5	2900	13	11			7.1
Event 2	**HRAuto2**	0.0028	0.0230	0.061	0.220	0.0002	0.0110						0.010	0.34	0.33	0.35	0.045	3.4		110	96	3.2	36.0	6.9
Event 3	**HRAuto2**	0.0015	0.0033	0.028	0.042	0.0001	0.0016						0.019	2.3	2.30	2.30	0.016	1.7	555	14	12	3.2	77.5	7.2
Event 4	**HRAuto2**	0.0012	0.0023	0.017	0.023	0.0001	0.0010						0.033	1.9	1.90	1.90	0.004	1.4		9	9	3.8	96.0	7.2

Legend for metals and metalloids: meet ANZG (2018) guideline values for the protection of:

🟩	99% of species
🟦	95% of species
🟨	90% of species
🟧	80% of species
🟥	does not meet any ANZG (2018) guideline values

Legend for other contaminants:

🟥	exceed LWRP standards (pH-adjusted for ammoniacal-N); other guidelines in Table 2-4
🟧	exceed NPS-FM national bottom line for ammoniacal-N or nitrate-N

Note: No compliance check was performed for fluoride, sulphate, DOC and hardness for which no guideline value exists. Total concentrations were used for comparison to ANZG (2018) guideline values for aluminium, manganese and boron as dissolved concentrations were not analysed for these parameters.

Table 3-4: Contaminants and physical parameters median values for each sampling site and event (n=1 to 4 depending on events and parameters). Bar size represents lowest to highest values amongst all sampling sites for each parameter. Shaded cells indicate potential overestimation of concentrations (see Section 3.3.1).

Event	Site Code	Copper, dissolved mg/L	Copper, total mg/L	Zinc, dissolved mg/L	Zinc, total mg/L	Lead, dissolved mg/L	Lead, total mg/L	Ammoniacal-N mg/L	Nitrate+ Nitrite-N mg/L	Dissolved Reactive Phosphorus mg/L	BOD5 mg/L	E. coli MPN/100mL	Total Suspended Solids mg/L	Turbidity FTU	Dissolved Organic Carbon mg/L	Hardness mg CaCO3/L	pH -
Event 1	**HR1**	0.0014	0.0027	0.032	0.0610	0.0007	0.0028	0.01	0.03	0.138	8		34	17	5.9	45	7.8
Event 2	**HR1**	0.0029	0.0041	0.043	0.0560	0.0003	0.0015	0.04	0.21	0.119	3		9	9	5.0	34	7.4
Event 4	**HR1**	0.0005	0.0005	0.003	0.0058	0.0001	0.0002	0.01	4.40	0.004	1.999		3	2	0.8	109	7.8
Event 1	**HS1**	0.0038	0.0100	0.230	0.3100	0.0005	0.0079	0.33	0.32	0.088	5		34	36	2.8	18	7.2
Event 2	**HS1**	0.0031	0.0076	0.170	0.2605	0.0004	0.0067	0.11	0.27	0.042	4		29	34	2.1	14	7.3
Event 3	**HS1**	0.0052	0.0103	0.228	0.3300	0.0004	0.0062	0.18	0.27	0.160	4.5		48	67	3.6	12	7.2
Event 4	**HS1**	0.0063	0.0083	0.295	0.3250	0.0003	0.0017	0.22	0.34	0.106	4.5		11	14	3.1	14	6.9
Event 1	**HS2**	0.0052	0.0107	0.260	0.3200	0.0005	0.0045	0.57	0.52	0.195	5		24	20	4.4	18	7.2
Event 2	**HS2**	0.0030	0.0073	0.134	0.1920	0.0003	0.0055	0.18	0.23	0.141	2.5		24	23	2.0	11	7.2
Event 3	**HS2**	0.0058	0.0114	0.188	0.2700	0.0004	0.0045	0.51	0.28	0.185	4		25	29	3.9	10	7.1
Event 4	**HS2**	0.0097	0.0124	0.240	0.2650	0.0002	0.0014	0.35	0.33	0.208	3.5		7	7	3.1	12	6.9
Event 1	**CSAuto2**	0.0110	0.0210	1.000	1.1000	0.0006	0.0046	1.20	0.37	0.520	6.4	6600	19	22			6.9
Event 2	**CSAuto2**	0.0032	0.0124	0.295	0.3600	0.0003	0.0068	0.24	0.22	0.065	3.1		32	27	4.1	16	7.0
Event 3	**CSAuto2**	0.0080	0.0240	0.380	0.5900	0.0003	0.0140	0.29	0.31	0.110	6.0	17000	66	65	5.2	19	6.9
Event 4	**CSAuto2**	0.0075	0.0140	0.500	0.5950	0.0014	0.0038	0.44	0.25	0.375	3.7		19	13	7.7	24	6.7
Event 1	**CSNal3**	0.0140	0.0210	1.100	1.1000	0.0008	0.0093	0.22	0.19	0.053	4.1	6900	94	13			6.8
Event 2	**CSNal3**	0.0067	0.0550	0.375	0.7200	0.0002	0.0495	0.13	0.24	0.039	7.0	1550	485	89			6.8
Event 3	**CSNal3**	0.0097	0.0265	0.415	0.6250	0.0008	0.0146	0.16	0.31	0.056	6.1	1380	87	49			6.9
Event 4	**CSNal3**	0.0138	0.0290	0.420	0.5000	0.0012	0.0102	0.10	0.31	0.057	10.2	4950	66	29			6.8
Event 1	**CSAuto1**	0.0840	0.0950	2.200	2.4000	0.0028	0.0098	0.02	0.80	0.160	4.8	220	7	6			7.0
Event 2	**CSAuto1**	0.0120	0.0350	0.360	0.4700	0.0006	0.0190	0.03	0.28	0.046	2.4		33	30	2.0	9	6.9
Event 3	**CSAuto1**	0.0200	0.0530	0.390	0.5100	0.0008	0.0230	0.23	0.25	0.064	3.8	1400	32	24	3.9	10	6.9
Event 4	**CSAuto1**	0.0270	0.0340	0.510	0.5300	0.0010	0.0087	0.11	0.26	0.071	3.5		15	8	5.6	12	6.6
Event 1	**CSNal1**	0.0048	0.2300	0.390	1.8000	0.0006	0.0770	0.35	0.57	0.300	12.0	1400	570	190			7.0
Event 2	**CSNal1**	0.0069	0.2950	0.230	1.7000	0.0003	0.1040	0.35	0.34	0.073	6.9	6350	690	225			7.2
Event 3	**CSNal1**	0.0202	0.2345	0.640	1.9000	0.0011	0.0845	0.30	0.51	0.125	18.8	1000	370	95			7.0
Event 4	**CSNal1**	0.0225	0.2225	0.745	2.2150	0.0035	0.0725	1.13	0.12	1.755	22.7	2780	390	109			7.1
Event 1	**CSNal2**	0.0021	0.0620	2.300	2.9000	0.0003	0.0340	0.31	0.25	1.755	20.0	290	180	65			6.4
Event 2	**CSNal2**	0.0059	0.0780	0.765	1.2500	0.0003	0.0320	0.09	0.45	0.091	8.5	910	420	64			6.8
Event 3	**CSNal2**	0.0063	0.0340	1.115	1.5650	0.0004	0.0114	0.12	0.31	0.041	10.0	665	79	25			6.8
Event 4	**CSNal2**	0.0043	0.0275	0.850	1.2500	0.0004	0.0112	0.17	0.32	0.074	4.7	3400	80	22			7.1
Event 3	**CSAuto3**	0.0160	0.0380	0.360	0.4200	0.0005	0.0110	0.19	0.24	0.061	4.2	3100	32	34	3.3	12	6.8
Event 4	**CSAuto3**	0.0260	0.0330	0.410	0.4700	0.0008	0.0041	0.27	0.24	0.061	3.6		10	8	6.5	14	6.7
Event 1	**CSAuto4**	0.0059	0.0160	0.083	0.1555	0.0005	0.0074	0.37	0.17	0.270	5.2	4900	147	169			7.2
Event 2	**CSAuto4**	0.0081	0.0150	0.120	0.1500	0.0003	0.0049	0.11	0.29	0.098	2.5		37	46	3.6	29	7.0
Event 3	**CSAuto4**	0.0120	0.0195	0.128	0.1550	0.0009	0.0049	0.09	0.20	0.026	4.4	4950	38	41	7.7	49	7.3
Event 4	**CSAuto4**	0.0059	0.0130	0.026	0.0780	0.0008	0.0076	0.09	0.08	0.076	4.8		72	97	13.0	68	7.2
Event 1	**CSAuto5**	0.0081	0.0370	0.099	0.3000	0.0004	0.0120	0.10	0.16	0.033	5.4	4400	180	97			6.8
Event 2	**CSAuto5**	0.0081	0.0230	0.170	0.2800	0.0003	0.0072	0.06	0.21	0.054	3.0		49	44	3.9	30	6.9
Event 3	**CSAuto5**	0.0069	0.0140	0.053	0.0935	0.0005	0.0046	0.10	0.13	0.038	3.2	1775	36	42	7.5	60	7.1
Event 4	**CSAuto5**	0.0013	0.0032	0.009	0.0200	0.0004	0.0025	0.20	0.01	0.058	2.2		24	31	10.0	85	7.0
Event 1	**HRAuto2**	0.0017	0.0024	0.036	0.0390	0.0003	0.0011	0.07	0.31	0.011	4.5	2900	13	11			7.1
Event 2	**HRAuto2**	0.0028	0.0230	0.061	0.2200	0.0002	0.0110	0.01	0.34	0.047	3.4		110	96	3.2	36	6.9
Event 3	**HRAuto2**	0.0015	0.0033	0.028	0.0420	0.0001	0.0016	0.02	2.30	0.045	1.7	555	14	12	3.2	78	7.2
Event 4	**HRAuto2**	0.0012	0.0023	0.017	0.0230	0.0001	0.0010	0.03	1.90	0.016	1.4		9	9	3.8	96	7.2

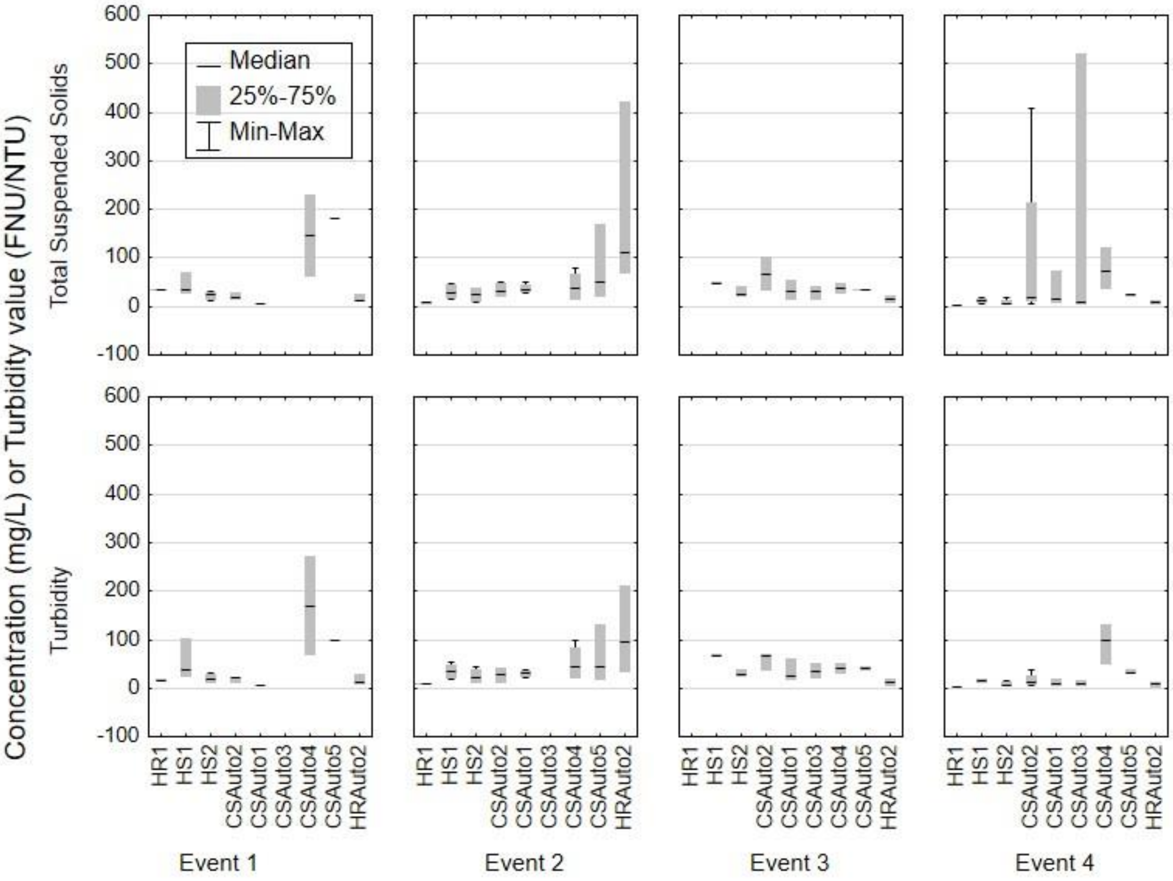

Figure 3-4: Turbidity and total suspended solids concentrations at autosampler sites for each event. HS1 and HS2: on Haytons stream from upstream to downstream, CSAuto2 to CSAuto5: on Curlett stream, HR1 and HRAuto2: on Heathcote river, upstream and downstream respectively of tributaries. Note that turbidity measurements at sites HR1, HS1 and HS2 were made with a different instrument to other sites and results are therefore only broadly comparable (Davies-Colley et al. 2021).

While usually lower concentrations were observed on Haytons Stream than on Curlett Stream, higher concentrations were observed on 2 occasions (Event 1 and Event 3) at HS1 compared to its downstream site (HS2) suggesting inputs from the upper part of the catchment (containing industrial land) are occasionally elevated above those from other parts of the catchment.

Figure 3-5: Curlett wetland inlet (top) and outlet (bottom). Photos taken 28 November 2021 (the day after Event 4). Note water is more turbid at the outlet than the inlet.

Figure 3-6: Sediment-laden Curlett Stream at confluence with Ōpāwaho/Heathcote River on 23 September 2021. Photo taken during dry weather conditions, prior to event 3. HRAuto2 site is approximately 400 m downstream of this confluence (to the left of the photo).

3.3.2 Metals

Copper (Cu) and Zinc (Zn) concentrations were highly variable between sites, within events and between events, though in most cases concentrations were lowest at sites HR1 and HRAuto2 (Figure 3-7). The upstream site (HR1) usually exhibited lower concentrations than the downstream site (HRAuto2) suggesting metal exports from Haytons and Curlett streams. Despite this likely export, copper and zinc event median concentrations at HRAuto2 met the ANZG (2018) guideline values for the protection of 90% of species or higher (Table 3-3), except for during the largest event (Event 2 = 128 mm). This suggests that the Cu and Zn contribution from the Haytons and Curlett streams was in most cases sufficiently diluted not to increase metals concentrations in the main river above these guideline values.

As explained for TSS (Section 3.3.1), sediments and therefore total metal concentrations (which includes particulate metals – those that are adsorbed to sediment) are likely to have been overestimated in samples collected in the Nalgene bottles, therefore only dissolved form concentrations will be discussed here for sites CSNal1, CSNal2 and CSNal3 sites.

Haytons Stream DCu and DZn water quality did not meet the ANZG (2018) guidelines in any sampled event at any site based on median concentrations. There were usually minimal differences between HS1 and HS2 metal concentrations, except on one occasion (Event 4) where a higher dissolved Cu (DCu) first flush concentration was observed in HS1 (6.5 times higher than the first flush concentration at HS2) despite being the smallest monitored rainfall event (16.8 mm) of moderate intensity (Figure 3-1). This suggests occasional DCu input in upper Haytons Stream that may come from stormwater runoff from upstream industrial activities. Wigram Retention Basin (lower Haytons Stream) data collected by University of Canterbury in June 2020 (prior to this project) showed reduction of median concentrations from ~5µg/L to <1.8 µg/L for DCu and from 300-400 µg/L to

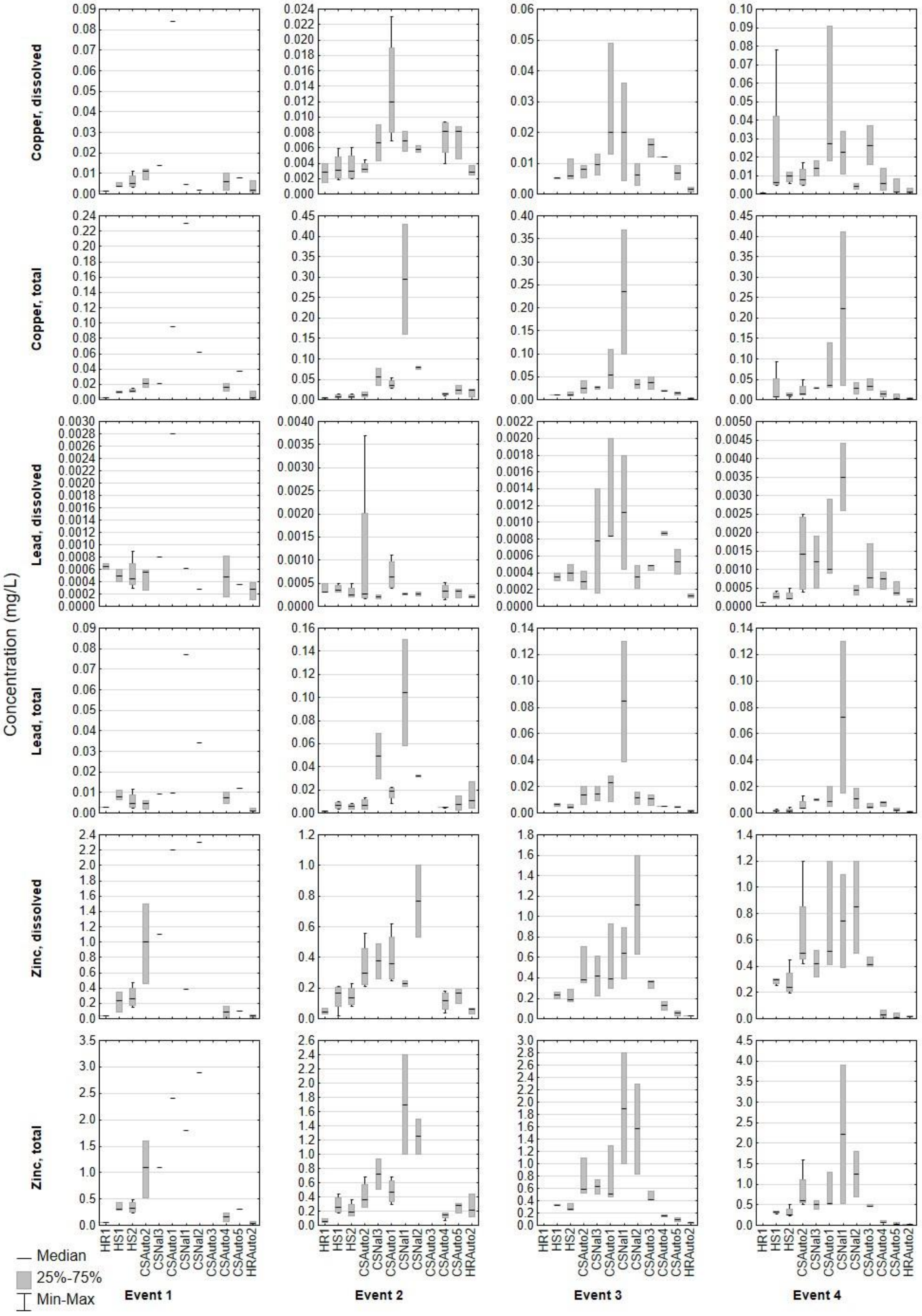

Figure 3-7: Metals concentrations for each sampling site for each event. HS1 and HS2: on Haytons stream from upstream to downstream; CSAuto2 to CSAuto5: on Curlett Stream; HR1 and HRAuto2: on Ōpāwaho/Heathcote River, upstream and downstream respectively of tributaries. Note that the y-axis scales for each parameter vary from event to event.

<40 µg/L for Zn (dissolved and total concentrations) within the basin, suggesting potential for treatment before the confluence with Ōpāwaho/Heathcote River.

Haytons Stream was likely not the main contributor to metal input to Ōpāwaho/Heathcote River – metal concentrations in Curlett Stream were much higher. The majority of Curlett Stream's sites' samples were also above the Cu and Zn ANZG (2018) guideline values, including all upstream of the wetland system. Highest DCu concentrations were observed at CSAuto1 (Figure 3-7) suggesting that sources from the upstream industrial land contribute copper to the upper Lunns Road branch of the Curlett Stream. DCu stayed relatively stable at sites upstream of and including CSAuto3 (downstream of the Southern Motorway) then generally decreased through the Curlett wetland with DCu median concentration reduced by 25 to 77% at CSAuto4 compared to CSAuto3 (Table 3-4). DCu was further reduced downstream at CSAuto5 and HRAuto2. Total Copper (TCu) followed similar trends as DCu except at CSAuto5, where higher concentrations were observed compared to upstream site CSAuto4 for Event 1 and 2, either related to the higher TSS concentrations at those times or suggesting occasional TCu input.

DZn concentrations were generally higher at CSAuto1, CSNal1 and CSNal2 sites (up to 2.3mg/L) than other sites, and sometimes reached high concentrations at CSAuto2 (up to 1.5 mg/L during Event 1), suggesting that DZn input to both eastern branches of Curlett Stream, and sometimes to the western branch, occurred. High concentrations observed at CSNal3 and CSAuto2 (medians of 1 and 1.1 mg/L respectively) occurred during Event 1 which had the longest antecedent dry period (16 days) suggesting potential for higher Zn accumulation in the small intensive industrial contributing subcatchments. Excluding the Nalgene bottles, total Zinc (TZn) followed similar trends as DZn (higher at CSAuto2 and CSAuto1) and remained relatively stable down to site CSAuto3. Dissolved and particulate forms of Zn were then reduced in the Curlett wetland, exhibiting from 60 to 94% lower median outlet concentrations.

While total and dissolved lead (Pb) event median concentrations were below ANZG (2018) guidelines (Table 3-3) for all sites, higher concentrations (especially in particulate form) were observed at CSNal1. Because of their association with TSS concentrations, these may have also been overestimated (Section 3.3.1).

The presence of a first-flush for the metals was investigated by plotting the samples collected at each site in order of collection (Figure 3-8). A first flush pollution effect was visible at most sites (except for CSAuto4 and downstream sites) with the first composite sample being on average 1.4 to 1.7 higher than the second sample, and as high as 12 times higher at HS1 (Event 4 for DCu). This phenomenon was particularly visible at CSNal3, CSAuto2, CSAuto1 and CSNal2 (for Cu, Zn, Pb; Figure 3-8). The combined effect of the hydrological buffer provided by the Curlett wetland and dilution in Ōpāwaho/Heathcote River most probably diminished this phenomenon for sites CSAuto4 to HRAuto2.

Figure 3-8: Copper, lead and zinc concentrations for each site, each event and sample group. Colour of bar represents the sample group (i.e., the composite group made of multiple samples collected by the autosampler). Reduction in height of bar from group 1 to 4 represents a declining concentration, i.e., a first-flush effect.

Although the EMP uses guideline values based on adjustment to hardness of 94 mg $CaCO_3$/L for the Ōpāwaho/Heathcote catchment (excluding Cashmere Stream), the hardness was consistently lower than this value in Haytons and Curlett streams, with the exception of site CSAuto5 (Figure 3-9) and was in fact lower than 30 mg $CaCO_3$/L at most sites, suggesting guidelines should not be adjusted for hardness in these locations. Hardness also varied within an event – highest concentrations were usually measured at the start of the event (e.g., group 1 samples) and decreased as water level increased. These samples were often those with highest metal concentrations and a positive correlation between hardness and zinc was measured at HS2, CSAuto1 and CSAuto2 (Figure 3-10); however this was not the case at sites near or downstream of the Curlett wetland or in the Ōpāwaho/Heathcote River.

Increased Dissolved Organic Carbon (DOC) is known to be a toxicity modifying factor (De Schamphelaere 2004, Heijerick 2002) for metals, with reduced toxicity at higher DOC concentrations. DOC concentrations ranged from 1.5 to 30 mg/L with a median concentration across all sites and events of 4.35 mg/L, suggesting relatively low effect towards toxicity reduction, due to generally low DOC concentrations (Figure 3-9). At some sites (e.g., CSAuto1, CSAuto2), higher dissolved copper and zinc concentrations were associated with higher DOC concentrations implying the toxicity of high polluting events could be modified by elevated DOC, though this was not consistent across sites (Figure 3-10).

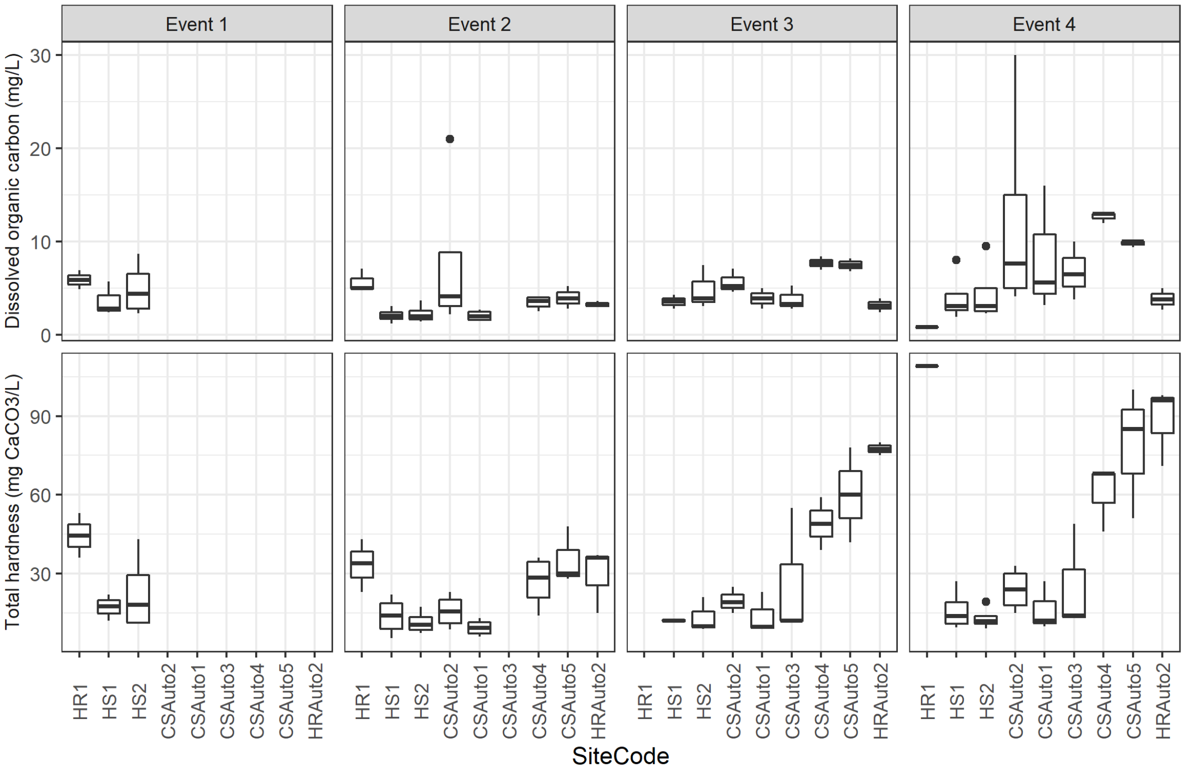

Figure 3-9: DOC and hardness concentrations at each site. Hardness was lower in Haytons and Curlett streams than in the Ōpāwaho/Heathcote River.

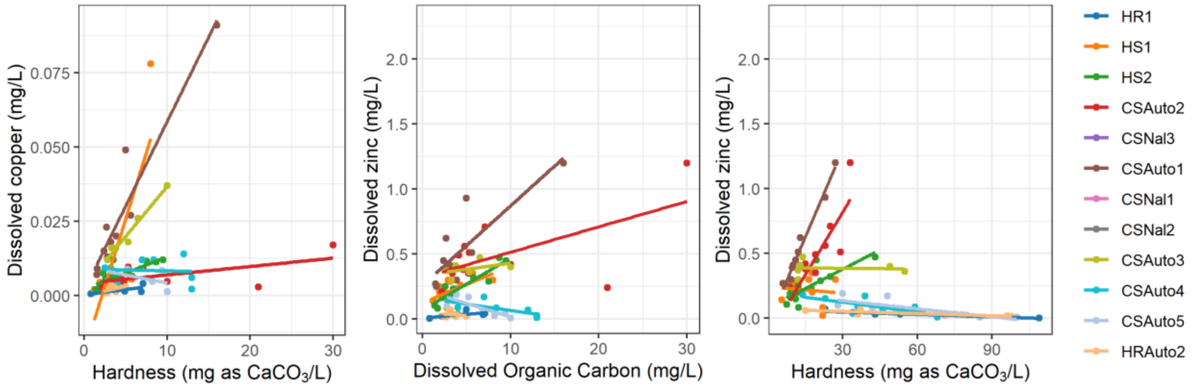

Figure 3-10: Dissolved metals concentrations versus dissolved organic carbon and hardness concentrations. Coloured lines represent linear regressions fitted for each site.

3.3.3 Nutrients

Nutrient concentrations were highly variable between sites, within events and between events, though in most cases concentrations were lowest at sites CSAuto3, CSAuto4 and CSAuto5, suggesting dilution of contaminant sources and some removal within the pond/wetland treatment system in the Curlett Stream catchment (Figure 3-11).

Compared to the upstream and downstream Ōpāwaho/Heathcote River sites, ammoniacal-N concentrations were elevated within both Hayton and Curlett streams (Figure 3-11, Figure 3-12), with highest concentrations measured in HS1, HS2, CSAuto2 and CSNal1 and almost invariably during the initial part of each storm event. A maximum of 2.9 mg N/L was measured in Curlett Stream at site CSAuto2 (in the western branch of the catchment, Figure 1-1). This would exceed a guideline value of 2.5 mg/L based on the LWRP and adjusted for the pH measured in that sample (6.5). When the concentration is adjusted, as required for comparison to the NPS-FM numerical attributes, this is equivalent to a concentration at pH 8 of 1.1 mg/L, which exceeds the National bottom line threshold of 0.40 mg N/L in the NPS-FM for an annual maximum, but does not exceed the C/D threshold of 2.2 mg/L. Therefore, this results in a grading of C, with an associated expectation of reduced survival of the most sensitive aquatic species.

Nitrate+nitrite-N concentrations were more consistent across the sites and events, with most samples measuring between 0.1 and 0.5 mg N/L, and generally with the highest concentrations measured in the samples collected at the start of the event (particularly during events 2 and 3). Almost all samples were below the Land and Water Regional Plan (LWRP) standard of 1.5 mg/L for dissolved inorganic nitrogen (which includes nitrate-nitrite-N + ammoniacal-N).

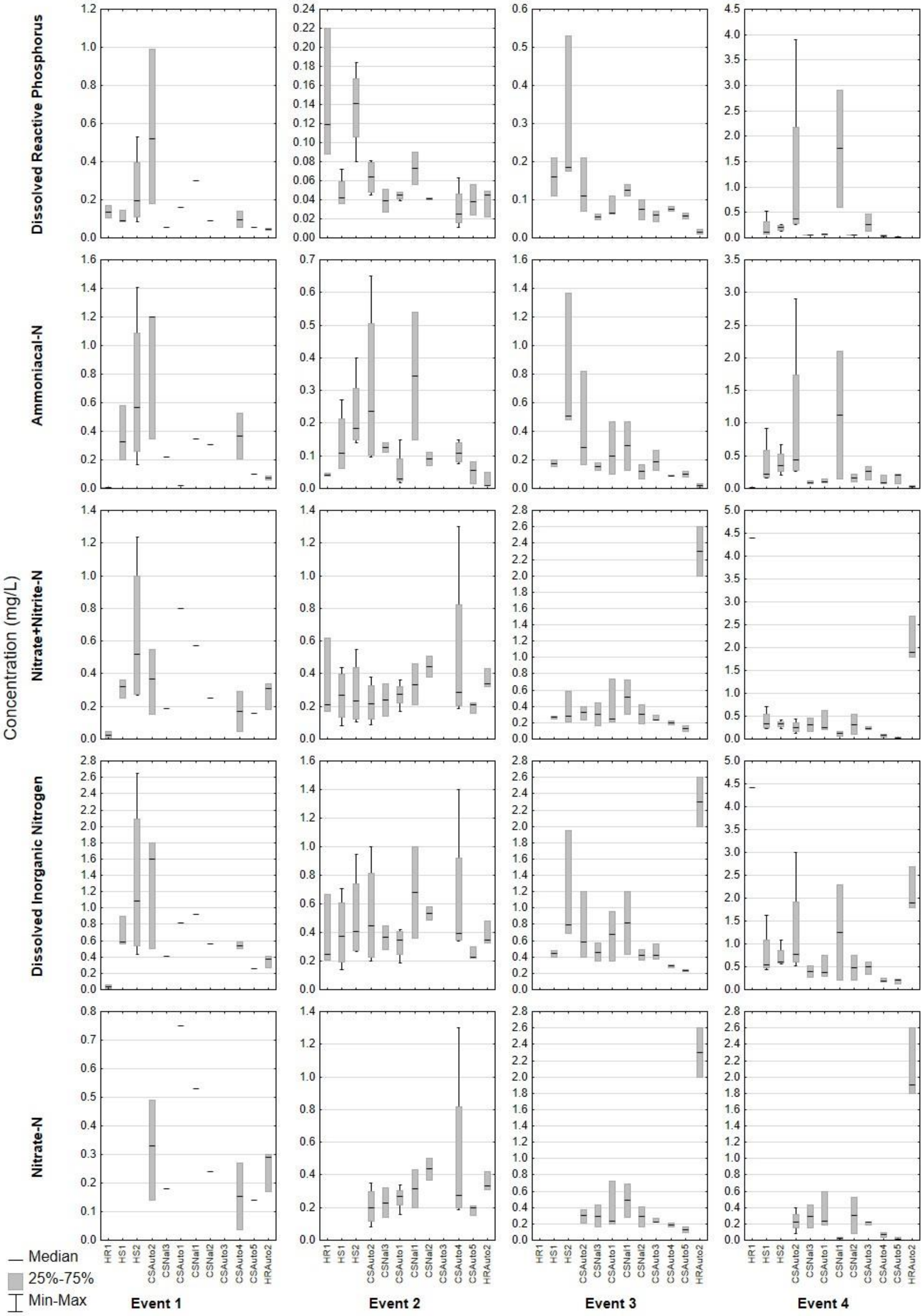

Figure 3-11: Ammoniacal-N, nitrate+nitrite-N, nitrate-N and dissolved reactive phosphorus concentrations for each sampling station for each event. HS1 and HS2: on Haytons Stream from upstream to downstream; CSAuto2 to CSAuto5: on Curlett Stream; HR1 and HRAuto2: on Ōpāwaho/Heathcote River, upstream and downstream respectively of tributaries. Note that the y-axis scales for each parameter vary from event to event.

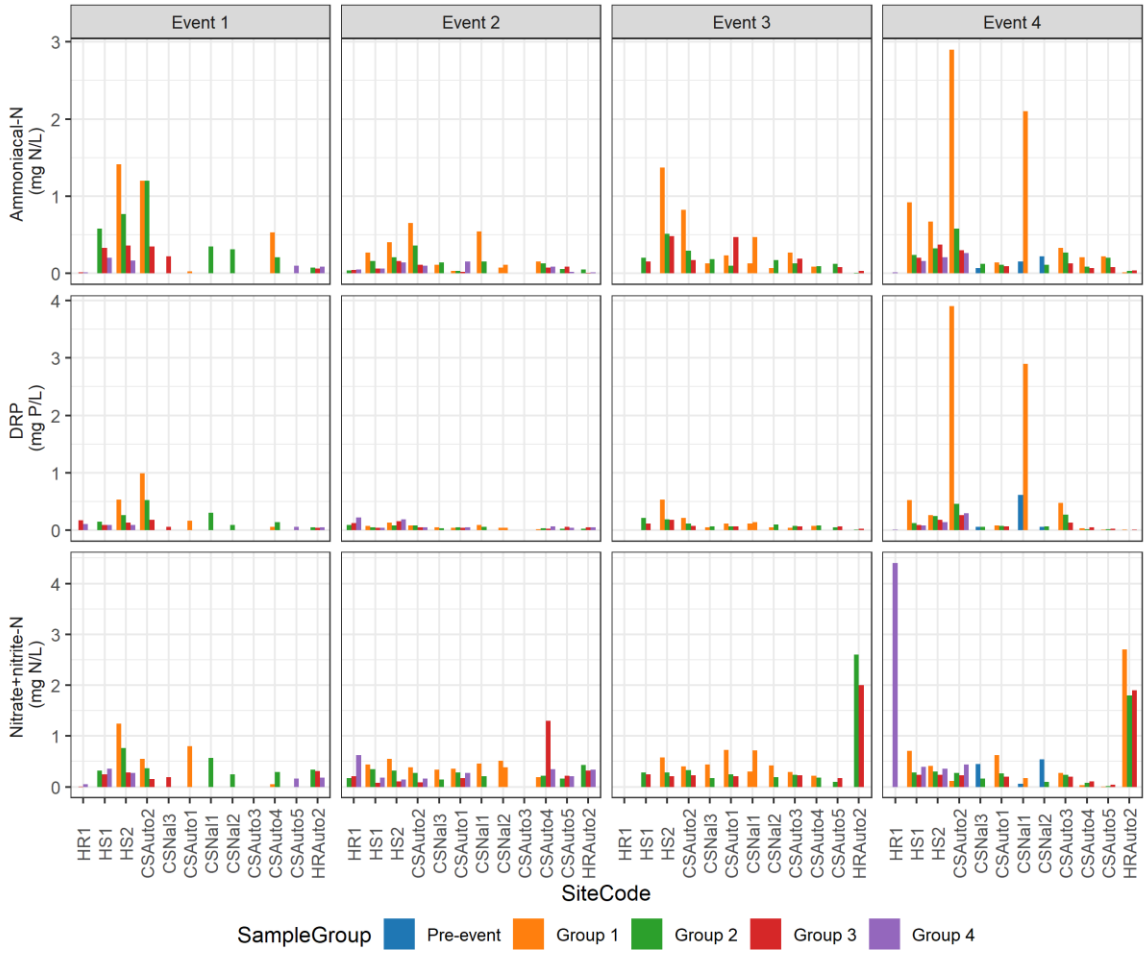

Figure 3-12: Ammoniacal-N, nitrate+nitrite-N and dissolved reactive phosphorus concentrations for each sampling station for each event. Colour of bar represents the sample group. Reduction in height of bar from group 1 to 4 represents a declining concentration, i.e., a first-flush effect. HS1 and HS2: on Haytons stream from upstream to downstream, CSAuto2 to CSAuto5: on Curlett stream, HR1 and HRAuto2: on Heathcote river, upstream and downstream respectively of tributaries.

However, during event 3 and 4, very high nitrate+nitrite-N concentrations were measured at the two Ōpāwaho/Heathcote River sites. The concentration was around 2 mg/L at the downstream site (HRAuto2), substantially higher than in any of the samples collected in the tributaries. It seems likely that this is due to high concentrations in the upper Ōpāwaho/Heathcote River. Although this was sampled after the storm event (see Figure 3-3), the nitrate+ nitrite-N concentration here was 4.4 mg N/L, based on a composite of 24 samples collected over 24 hours. That concentration is consistent with monthly monitoring undertaken by CCC at the same site (range of 4.4-5.6 mg N/L for 2020; Margetts & Marshall 2021). This is well over the guideline value of 1.5 mg/L for a spring-fed plains urban stream, exceeds the national bottom line for nitrate-N (toxicity) based on a maximum in a sample, and is also above the guideline value of 3.8 mg/L based on protection of 90% of species (Hickey 2013), suggesting the likelihood for reduced reproduction, growth and/or survival of the most sensitive aquatic species in this location.

DRP concentrations consistently exceeded the LWRP receiving water standard of 0.016 mg/L at all sites and in all samples, with the exception of some samples from Ōpāwaho/Heathcote River at HR1 and HRAuto2 and in Curlett Stream downstream of the wetland at CSAuto4 and CSAuto5. University of Canterbury Wigram retention basin data from 2020 (prior to this project) suggest that DRP inlet median concentrations of ~0.07 mg/L could be reduced below 0.04 mg/L suggesting moderate treatment. DRP concentrations were highly elevated in two samples from Event 4: the first composite from CSAuto2 (3.9 mg P/L) and the storm sample for CSNal1 (2.9 mg P/L), downstream of the confluence of the western (CSAuto2) and eastern (CSAuto1) branches. DRP concentrations were then substantially lower (<0.5 mg P/L) in subsequent samples at CSAuto2. A sample at CSNal1 collected as water rose before the storm event also had higher DRP concentrations than most other samples / sites (0.61 mg P/L) though not as high as the sample during the storm event that followed. The DRP concentrations at CSAuto3 were lower, suggesting some dilution of these high DRP concentrations from other water sources in Curlett Stream, and concentrations were lower again downstream of the wetland. In Events 1 and 3, DRP was higher at HS2 than at HS1, but in event 4 the reverse occurred, suggesting multiple sources of DRP in the upper Haytons Stream catchment.

Aluminium, sulphate, fluoride, boron and manganese were also measured in the upper Ōpāwaho/Heathcote River and at the two Haytons Stream sites as potential indicators of stormwater contamination associated with the fertiliser manufacturing and storage site in the Haytons Stream. Elevated sulfate and fluoride could indicate association with that site. A correlation plot (Figure 3-13) and principal component analysis (PCA, Figure 3-14) indicate that levels of ammoniacal-N and DRP are related to levels of fluoride and to a lesser extent, sulfate, at both the HS1 and HS2 sites, but not at the HR1 site. The PCA did not show clear differences between sites based on these water quality parameters as there is no clustering by site. Samples with the highest ammoniacal-N, DRP and fluoride were most frequently from site HS2, but also from HS1. Site HS1 had the highest concentrations of boron and samples with high boron were associated with lower DRP and ammoniacal-N. Aluminium and manganese were associated with total suspended solids concentrations and to a lesser extent turbidity (based on correlation coefficients, not shown here) and were not related to the presence of high DRP or ammoniacal-N.

These results suggest nutrient concentrations at both HS1 and HS2 could be influenced by the fertiliser manufacturing and storage operations. However, as of June 2020, stormwater from that site discharges to trade waste except for rainfall events of 20 mm or more, when excess stormwater is discharged to the stormwater network between the HS1 and HS2 sites. Therefore, there is no clear pathway for stormwater or nutrients from that site to HS1, or to HS2 during two of the four events monitored, though it cannot be ruled out that the elevated nutrients are due to their presence in stream bed sediments or shallow groundwater from historical contamination. Alternatively, there may be another source (or multiple sources) of ammoniacal-N and DRP upstream of HS1, as noted in previous studies (e.g., Moores et al. 2009; O'Sullivan & Charters 2014; Black 2018). This explanation also seems feasible as similarly elevated ammoniacal-N and DRP concentrations were at times measured in Curlett Stream, which has no fertiliser works in the catchment.

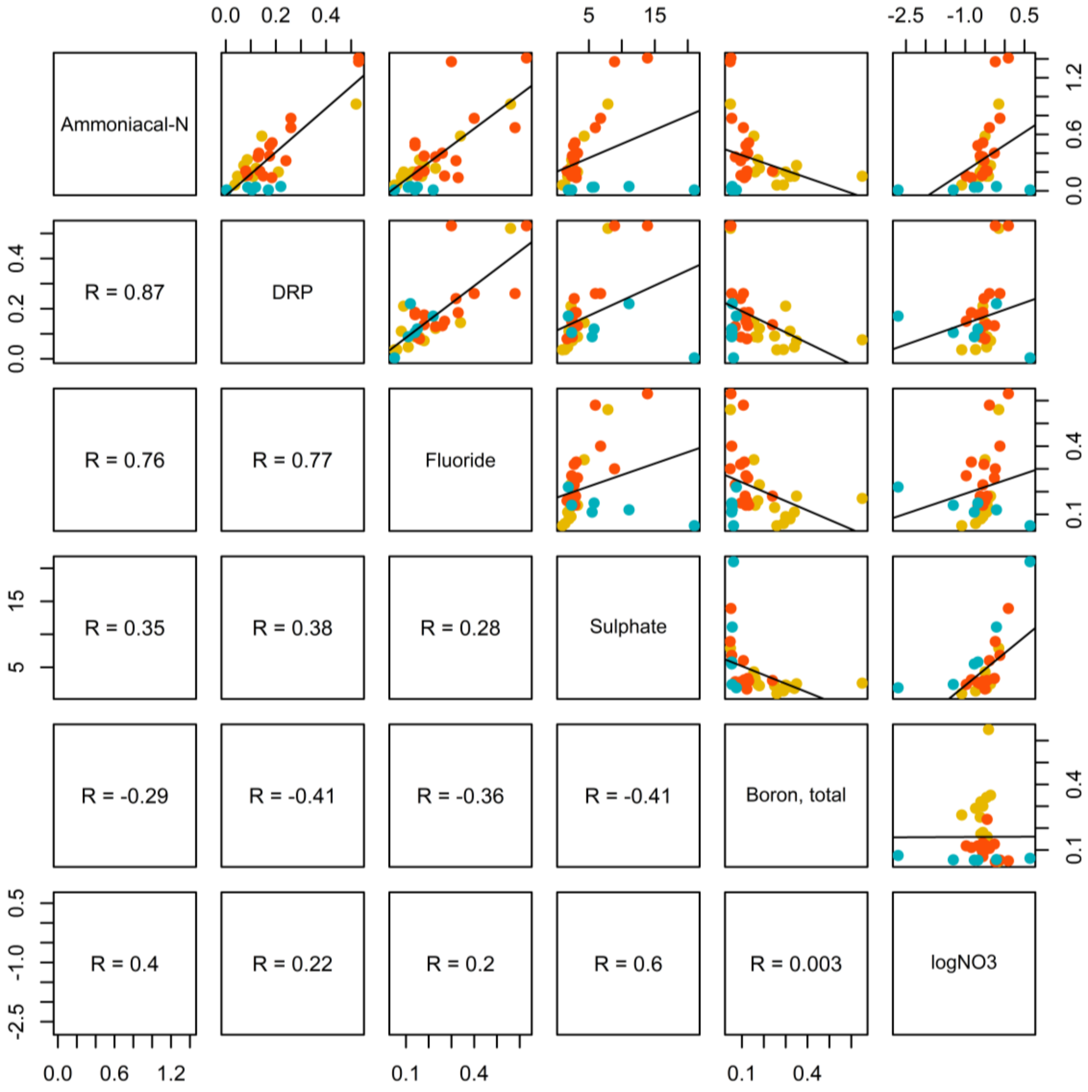

Figure 3-13: Correlation matrix for nutrients and fertiliser indicators at sampling sites in Haytons Stream (sites HS1 and HS2) and upstream in Ōpāwaho/Heathcote River (site HR1). In upper section relationships between data on each column and row are shown. Different coloured points indicate different sites as follows HR1 = blue, HS1 = yellow, HS2 = red. R value in lower section shows the Pearson's correlation between each parameter. LogNO3 = Log10 of nitrate+nitrite-N. R value of 0.76 between ammoniacal-N and fluoride indicates strong correlation. Site HS2 (in red) is associated with higher DRP, ammoniacal-N and fluoride.

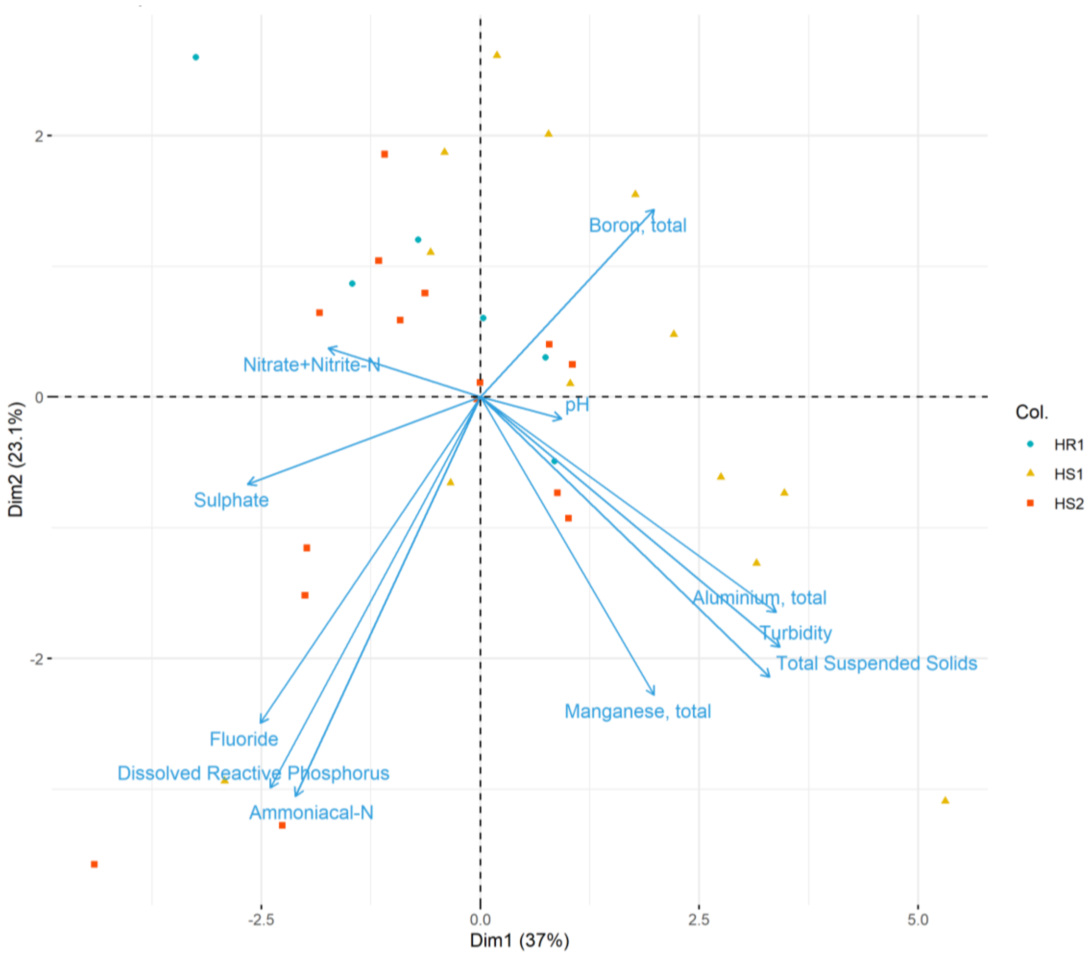

Figure 3-14: Principal component analysis (PCA) of nutrients and fertiliser indicators at sampling sites in Haytons Stream (sites HS1 and HS2) and upstream in Ōpāwaho/Heathcote River (site HR1). Different sites are indicated by different coloured key. Most samples from HR1 are grouped near top of plot, HS1 to the right and samples from HS2 are scattered around, showing there are not clear differences between the sites in terms of these water quality parameters. Arrows indicate how strongly each water quality parameter influences each principal component. Fluoride, DRP and ammoniacal-N are positively correlated, and negatively correlated to boron. Samples associated with higher DRP, ammoniacal-N and fluoride are mostly found at HS2 but sometimes at HS1.

The overall contribution of Haytons and Curlett Streams to nutrient concentrations in Ōpāwaho/Heathcote River is not clear due to a lack of data from the outlet of Haytons Stream, downstream of the Wigram Basin and incomparable data for Events 3 and 4 due to the sampler not triggering (event 3) or a different time period for the sampling (Event 4). There were therefore only two events that allow for comparisons (events 1 and 2). In Event 1 ammoniacal-N and nitrate+nitrite-N were higher at the Ōpāwaho/Heathcote River downstream site than at the upstream site, suggesting these two tributaries contribute both forms of nitrogen; whereas DRP was lower downstream than upstream. However, in Event 2 ammoniacal-N and DRP concentrations were mostly lower downstream, though nitrate+nitrite was mostly higher. In Event 4, although samples were collected at different times, the concentrations of nitrate+nitrite-N were very high at HR1 and HRAuto2, substantially higher than in the two tributaries, suggesting they are not the major (or only) source.

3.3.4 Oxygen demand and faecal indicator bacteria

BOD_5 and *E. coli* were consistently above freshwater quality guidelines at all sites but HRAuto2 (for BOD_5 Event 3 and 4 only).

Highest BOD_5 concentrations were observed at CSNal1 or CSNal2 (Figure 3-15) However as this contaminant can be in particulate form it might have been overestimated in Nalgene bottles (as explained for TSS in section 3.3.1). BOD_5 was indeed positively correlated with TSS (Figure 3-16), supporting this explanation. Therefore, while the high BOD_5 concentrations could be indicative of a wastewater effluent source upstream of CSNal1 and CSNal2, further investigation is needed to provide greater certainty on sources and/or to quantify the contribution.

Excluding the Nalgene bottle samples, highest BOD_5 concentrations were alternatively observed at CSAuto2 and/or HRAuto2 - therefore mainly at, and sometimes downstream, of the western Curlett Stream branch. *E. coli* concentration were higher at CSNal3, CSAuto2 or CSNal1 suggesting potential sources to both branches of the Curlett stream (Figure 3-15). BOD_5 and *E. coli* concentrations were sometimes above laboratory upper quantification limits (>24000 MPN/100ml and >32 mg/L for BOD_5) suggesting potential discharge of wastewater effluent upstream of CSAuto2. Curlett wetland did not seem to have an impact on BOD_5 concentrations while a relatively high *E. coli* concentration (4950 MPN/100mL) was observed downstream of the wetland (Event 3) compared to 3100 MPN/100mL at the upstream site (CSAuto3). No investigation of *E. coli* was performed on Haytons Stream.

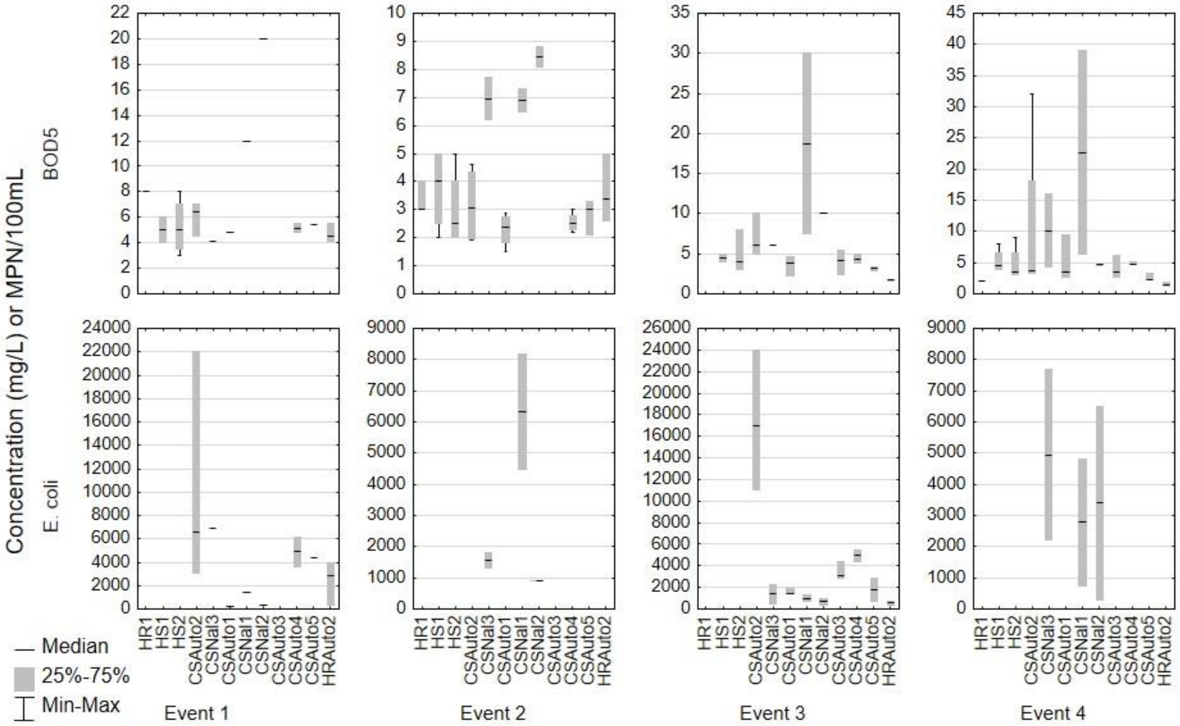

Figure 3-15: E. coli and BOD5 concentrations for each sampling sites for each event. HS1 and HS2: on Haytons Stream from upstream to downstream, CSAuto2 to CSAuto5: on Curlett Stream, HR1 and HRAuto2: on Ōpāwaho/Heathcote river, upstream and downstream respectively of tributaries. Note that the y-axis scales for each parameter vary from event to event. Some samples exceeded the upper quantification limit for BOD_5 and have been plotted at that limit.

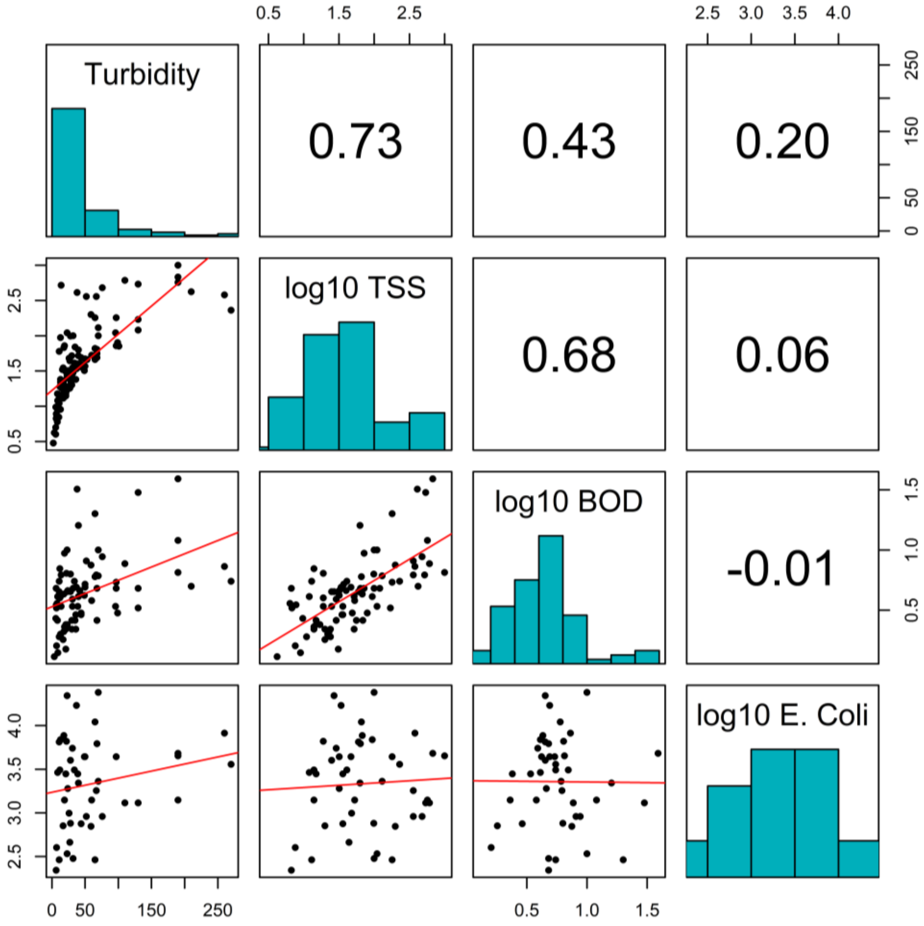

Figure 3-16: Correlation matrix for Turbidity, TSS, BOD$_5$ and *E. coli*. In upper section value shows the Pearson's correlation between each parameter. Numbers close to 1 indicate a close correlation. In lower section, relationships between data on each column and row are shown. Red line is the linear regression between the two variables plotted. Histograms show the distribution of each water quality parameter plotted.

4 Summary and recommendations

4.1 Summary of water quality results

Overall, water quality data suggest that the Curlett Stream subcatchments were the main contributors of metals, solids, BOD_5 and *E. coli*, although some high concentrations were occasionally observed at HS1 (upper Haytons Stream) for TSS and DCu. However, some uncertainties persist due to either the variability of the locations presenting the highest concentrations for each event, or the possible overestimation of pollutants (especially particulate forms) in samples collected by Nalgene bottles at some sites. Key areas of uncertainty include the following: (1) Although high concentrations of both DCu and DZn were identified at the Curlett Stream site “CSAuto1” , it was not possible to identify which upstream subcatchment was the highest contributor of metals, as no upstream monitoring station was installed on the eastern branch; and (2) For some pollutants such as DCu, no decrease in concentration was observed until after the Curlett wetland suggesting that copper is released in several locations along the upper part of the Curlett Stream and precise source identification is therefore not yet feasible.

Overall, nutrient water quality data suggest that both Haytons (upstream HS2) and Curlett (upstream CSAuto2 and/or CSNal1) streams received DRP, NH_4 and NO_3 input, sometimes simultaneously with *E. coli* and BOD_5 (especially at CSAuto2). Observations of nutrients in combination with sulphate and fluoride suggest potential input from fertiliser manufacturing and storage operations to Haytons Stream but the lack of data further downstream limit the identification of any additional contributions. High nitrate concentrations were observed at the downstream site on the Ōpāwaho/Heathcote River for Event 3 and 4, and although the upstream site (HR1) was not sampled on these occasions it is likely that these were due to upstream (spring) sources.

Finally, it is clear that the current land use of the Curlett Stream subcatchment comprises many potential pollutant sources (various industrial sites, scrap metal yards, railway, machinery manufacturing sites). It will be difficult to achieve the third objective of the targeted wet weather monitoring project (i.e. identification of individual sites contributing to hot spots) without putting in place a widespread monitoring programme to collect samples at the scale of individual potential contributing sites. We recognise that this may not be technically nor economically feasible, particularly within the specified timeframe of by the end of 2022. A more realistic approach may be to use trade waste and industrial audit teams to assist in identifying high risk sites, and to work on this objective over a longer period of time.

4.2 Performance of monitoring methods

Nalgene bottles were used at three sites to supplement the data collected using autosamplers. Samples were collected at all sites, though during Event 4 the first bottle was filled before the rainfall event started as the water level rose due to some other reason. The very high TSS concentrations measured in the bottles on some occasions coincided with times that the bottles were submerged underwater for an extended period, leading to potential for sediment to accumulate in the bottles.

The ISCOs with liquid level actuators were less reliable in terms of triggering the collection of water samples. In one case, the actuator did not trigger sampling at all (Event 1, CSAuto3). Most of the time samplers did trigger samples, however in some cases multiple samples were collected straight away, possibly due to the trigger turning on and off. Furthermore, the variable sample pacing did not work as intended on several occasions. It appears that this is may be because the sample timing starts when the samplers are turned on (prior to a storm event), although sampling doesn't begin until the start of the rainfall and rise in water level. Therefore, by the time the first samples are triggered, the programme is already past the intensive sampling phase and into the longer duration phase. However, there may be other reasons for the sample pacing not working, including the actuators triggering on and off and/or operator error. Until the reason for this issue can be found and resolved, these trigger systems are less suitable for sites where there is a need to have more intensive and less intensive sampling, for example to investigate the presence of a first-flush.

4.3 Recommendations for future monitoring

Reflecting the various areas of uncertainty encountered in sampling to date, in order to gain a better understanding of the main contributing sources to the Haytons and Curlett streams, a number of actions are recommended as below.

Sampling sites:

- The autosamplers at HR1, HRAuto2 and CSAuto5 can be removed. Upstream and downstream sites on Ōpāwaho/Heathcote River showed relatively lower and less variable concentrations than the Curlett and Haytons streams (except for nitrate-N) and therefore would appear as stations of lower interest from a hotspot identification perspective (except for nitrate hotspot identification). CSAuto5 showed usually lower concentrations than CSAuto4 suggesting no additions between these sites and CSAuto5 could therefore be removed, relying on CSAuto4 as an indication of the output from the Curlett Stream catchment.

- Replace the single autosampler located at CSAuto1 with two autosamplers located just upstream, on each of the western and eastern branches. This would enable us to identify which of these two branches contributes the majority of contaminants to the current CSAuto1 site (see Figure 4-1).

- Move the equipment at CSAuto3 to a slightly higher position to avoid possible flooding in the future.

- If possible, coordinate sampling with University of Canterbury in order to collect water quality data at the inlet and outlet of the Wigram Retention Basin. This would improve understanding of whether additional sources to Haytons Stream exist downstream of HS2.

Sampling methods:

- Replace Nalgene bottles with autosamplers to provide more reliable estimates of contaminant concentrations. Autosamplers from HR1, HRAuto5 and CSAuto5 could be moved to the Nalgene sites (CSNal3, CSNal1 and CSNal2) to provide more reliable estimates of contaminant concentrations.

- Replace the liquid level actuators on ISCOs with a more reliable triggering system (such as connecting to a pressure transducer and logger) as these systems seemed prone to issues including: a) not triggering sampling at all (event 1, CSAuto3); b) collecting multiple samples straight away, possibly due to the trigger turning on and off; and c) the variable sample pacing not working as intended. If pressure transducers are included at all sites to measure water level (and flow) there is no additional cost or equipment required for this.

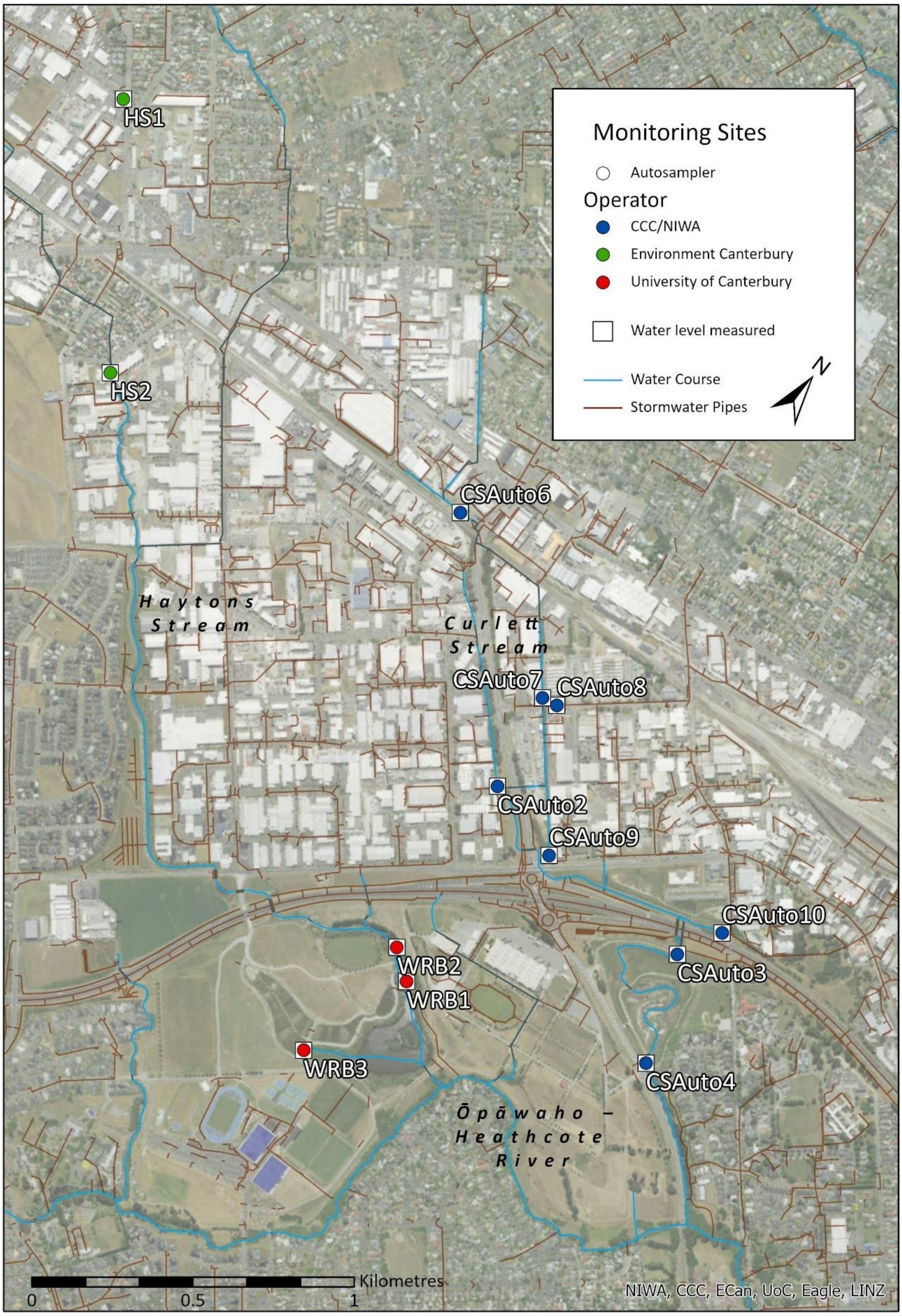

Figure 4-1: Recommended locations for further sampling in the Curlett Stream catchment. Note that site numbers are not contiguous as some locations monitored in 2021 are to be discontinued.

- Where variable sample pacing is used to target first-flush, ensure the sample pacing is different downstream of the wetlands where flows are attenuated and remain high for a longer duration. Although this approach was attempted in some storm events, it should be used in all events.
- Measure the flow at each site: this would allow for flow-weighted composite sampling and estimation of the actual mass of pollutants at each site as opposed to concentrations. Comparison solely of pollutant concentrations between sites and /or branches of stream does not allow for hot spot identification as inputs to the streams are diluted to different degrees depending on stream flows. In particular, flow measurement is crucial to precisely identify which branch of the Curlett Stream actually receives most of the pollutant loads. This would involve additional cost, as this would likely require a series of gaugings at each site to relate water level to flow. In some locations (not within the stream due to fish passage issues) it may be feasible to install a rated structure (e.g., a weir or flume) to relate water level to flow, which may be more cost-effective than gaugings (but still at additional cost).
- If flow weighted sampling is performed at each site (implying flow measurement at each site) then only one sample (flow weighted composite sample) could be analysed at each site (as opposed to 3 or 4 as in 2021). These measures would reduce analytical costs.
- Use information from this monitoring to determine trigger levels for sampling to ensure samples are collected from all sites during the same parts of the hydrograph to improve comparability of data.
- Sample 8 additional storm events to better account for the variability of pollutant export between events, with a review of the results and information obtained after four additional events.
- Due to low Pb concentrations observed at all sites, remove this parameter from the monitoring programme. However all other parameters should be continued if possible.

Additional tasks:

- Reconsider how hardness-adjusted guidelines for zinc are used for the Ōpāwaho/Heathcote catchment as hardness was lower than 30 mg $CaCO_3$/L within the Haytons and Curlett streams.
- Investigate the use of nitrate isotopes (δ15N and δ18O of NO_3) in assessing the contribution of nitrogen from the fertiliser manufacturing and storage site to Haytons Stream. Isotopic methods should be able to distinguish between nitrogen sources that enter the stream from fertiliser via surface or subsurface flows (close to the sampling sites) and those from deeper Canterbury aquifers with greater distance between nitrogen sources and the Haytons Stream sampling sites.
- In order to map hot spots during base flow conditions (one of the objectives of the “wet weather monitoring”), some dry weather investigations need to be performed over 2022-2023. This could include dry weather sampling at the current and/or proposed wet weather monitoring stations and where resource permits, additional sites in between. Alternatively, instrumentation could be installed to measure water level, and water quality indicators such as pH, conductivity and turbidity. These approaches have been used in the Haytons Stream catchment previously, identifying the presence of dry weather discharges and with some success in identifying possible sources of contamination.

5 Acknowledgements

The authors would like to acknowledge the work by all staff involved in undertaking this monitoring, particularly Marty Flanagan (NIWA), Rachel Herbert and David Ashby-Coventry (ECan) who went out on short notice, during early mornings and in floods to set up samplers and retrieve samples. We also thank Belinda Margetts and Salina Poudyal for designing the targeted wet weather monitoring, and Michele Stevenson for input at multiple stages, particularly discussions on sample compositing.

6 References

ANZECC. (2000) Australian and New Zealand guidelines for fresh and marine water quality. Volume 1: The guidelines. Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand.

ANZG (2018). Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Governments and Australian state and territory governments, Canberra, ACT, Australia. https://www.waterquality.gov.au/anz-guidelines

Black, L. (2018) Understanding and Quantifying Contaminant Discharges to Haytons Stream. MSc thesis in Environmental Science, University of Canterbury.

Davies-Colley, R.; Hughes, A.O.; Vincent, A.G.; Heubeck, S. (2021). Weak numerical comparability of ISO-7027-compliant nephelometers. Ramifications for turbidity measurement applications. Hydrological Processes 35(12).

De Schamphelaere, K. A. C.; Janssen, C. R. (2004). Effects of Dissolved Organic Carbon concentration and source, pH, and water hardness on chronic toxicity of copper to Daphnia magna. Environmental Toxicology and Chemistry 23(5): 1115-1122.

Environment Canterbury. (2019). Canterbury Land and Water Regional Plan. Environment Canterbury Regional Council, Christchurch.

Gadd, J. (2020). Testing new methods for storm event sampling. Riccarton Stream and Addington Brook case study. Report No. 2020016AK prepared for Environment Canterbury. NIWA, New Zealand.

Gadd, J. and Milne J. 2019. Monitoring water quality in urban streams and stormwater: Guidance for New Zealand practitioners. NIWA Client Report 2019168AK prepared for Envirolink. MBIE ContractNo. CO1X1701.

Hayward, S., Meredith, A., & Stevenson, M., 2009. Review of proposed NRRP water quality objectives and standards for rivers and lakes in the Canterbury region. Environment Canterbury Repot R09/16, March 2009.

Heijerick, D. G.; Janssen, C. R.; De Coen, W. M., The Combined Effects of Hardness, pH, and Dissolved Organic Carbon on the Chronic Toxicity of Zn to D. magna: Development of a Surface Response Model. Archives of Environmental Contamination and Toxicology 2002, 44, 210-2

Hickey, C. W. (2013). Updating nitrate toxicity effects on freshwater aquatic species. NIWA Client Report HAM2013-009. Prepared for Ministry of Building, Innovation and Employment: Funded by Envirolink. January 2013. 39 p.

Margetts, B and Marshall W. (2021) Christchurch City Surface Water Quality Annual Report 2020. Prepared to meet the Requirements of CRC214226 Christchurch City Council. June 2021. 112 p.

Margetts, B. and Marshall, W. (2020). Surface water quality monitoring report for Christchurch City waterways: January - December 2019. Christchurch City Council, Christchurch.https://ccc.govt.nz/assets/Documents/Environment/Water/Monitoring-Reports/2019-reports/City-wide-surface-water-quality-report-2019.pdf

Margetts, B and Poudyal S. (2020) Comprehensive Stormwater Network Discharge Consent: Targeted Wet Weather Monitoring Project Scope. Christchurch City Council. November 2020. 21 p.

MoE/MoH (2003). Microbiological water quality guidelines for marine and freshwater recreational areas. Ministry for the Environment and Ministry of Health, Wellington, New Zealand.

Ministry for the Environment. (1992). Water Quality Guidelines No. 1. Guidelines for the control of undesirable biological growths in water. ME91. Ministry for the Environment, Wellington.

Moody, N. (2019). Haytons-Paparua Stream – cleaning up the most polluted waterway in Christchurch and giving the Ōpāwaho-Heathcote River a better start in life. Environment Canterbury, Christchurch, New Zealand.

Moores, J., Gadd, J., Wech, J. & Flanagan, M (2009). Haytons Stream catchment water quality investigation. Environment Canterbury Report No. R09/105. Prepared for Environment Canterbury by NIWA.

New Zealand Government. (2020). National Policy Statement for Freshwater Management 2020. Ministry for the Environment, Wellington, New Zealand.

O'Sullivan, A. & Charters, F. (2014). Haytons Stream 2013 water quality investigation at Gerald Connolly Place. Environment Canterbury Report No. R14/33. Prepared for Environment Canterbury by University of Canterbury.

Pattle Delamore Partners. (2007). Avon/Otakaro and Heathcote/Opawaho rivers: analysis of water quality data from 1992-2006. Report No. U07/42 Prepared for Environment Canterbury. Pattle Delamore Partners, New Zealand.

Poudyal, S. (2019). Characterising stormwater pollutant yields from urban carparks in a low intensity rainfall climate. PhD thesis. Department of Civil and Natural Resources Engineering. University of Canterbury, Christchurch, New Zealand.

Appendix A Sampling site locations

Table A-1: Full details of sampling site locations.

Site Code	Site Name	Easting (NZTM)	Northing (NZTM)	Party responsible	Sampling method
HS1	Haytons Stream downstream of Waterloo Road	1562985	5179378	ECan	Autosampler
HS2	Haytons Stream at Washbournes Road culvert	1563905	5178733	ECan	Autosampler
CSAuto1	Curletts Stream at Lunns Road	1565615	5178705	CCC / NIWA	Autosampler
CSAuto2	Curletts Stream at Curletts Road	1565648	5178423	CCC / NIWA	Autosampler
CSAuto3	Curletts Stream at Southern Motorway	1566405	5178358	CCC / NIWA	Autosampler
CSAuto4	Curletts Stream Downstream of Curletts Wetland	1566531	5178025	CCC / NIWA	Autosampler
CSAuto5	Curletts Stream upstream of Ōpāwaho/Heathcote River Confluence	1566928	5177711	CCC / NIWA	Autosampler
CSNal1	Curletts Stream upstream of Curletts Stream Branch	1565905	5178350	CCC / NIWA	Stormwater sampler bottles
CSNal2	Curletts Stream Branch	1566466	5178498	CCC / NIWA	Stormwater sampler bottles
CSNal3	Curletts Stream near Cable Street	1565046	5179028	CCC / NIWA	Stormwater sampler bottles
WRB1	Wigram Retention Basin at old pond	1565760	5177829	UC	Autosampler
WRB2	Wigram Retention Basin at wetland outlet	1565793	5178189	UC	Autosampler
WRB3	Wigram Retention Basin at wetland inlet	1565676	5177419	UC	Autosampler
HR1	Ōpāwaho/Heathcote River at Warren Crescent footbridge	1566043	5177050	ECan	Autosampler
HR2	Ōpāwaho/Heathcote River after Curletts Stream Confluence	1566975	5177716	CCC / NIWA	Autosampler

Appendix B Analytical methods used

Table B-1: Summary of analytical methods used in this study by each laboratory.

Analyte	Method used by CCC laboratory	Method used by Hill Laboratories
TSS; total suspended solids	Filtration using Whatman filters (nominal pore size 1.2 - 1.5µm), dried at 103-105°C, gravimetric determination (APHA 2540 D 23rd ed. 2017).	Filtration using Whatman 934 AH, Advantec GC-50 or equivalent filters (nominal pore size 1.2 - 1.5µm), gravimetric determination (APHA 2540 D (modified) 23rd ed. 2017). Analysed at Hill Laboratories, Christchurch.
Turbidity	Optical turbidimeter (Hach TL230, ISO 7027)	Analysis using a Hach 2100 Turbidity meter. Analysed at Hill Laboratories, Christchurch. APHA 2130 B 23rd ed. 2017 (modified).
pH	pH meter. (APHA 4500-H+ B)	pH meter. Analysed at Hill Laboratories, Christchurch. APHA 4500-H+ B 23rd ed. 2017. Note: It is not possible to achieve the APHA Maximum Storage Recommendation for this test (15 min) when samples are analysed upon receipt at the laboratory, and not in the field. Samples and Standards are analysed at an equivalent laboratory temperature (typically 18 to 22 °C). Temperature compensation is used
Dissolved calcium, magnesium, copper, lead and zinc	Filtered through a nylon 0.45 µm filter, acidified with nitric acid then analysed by ICP-MS (APHA 3125 B modified)	Filtered through a 0.45 µm filter then acidified and analysed by ICP-MS (APHA 3125 B 23rd ed. 22-42, 2017.)
Total copper, lead and zinc	Nitric acid digestion (APHA 3030 E) then analysed by ICP-MS (APHA 3125 B modified)	Nitric acid digestion APHA 3030 E (modified) 23rd ed. 2017; analysed by ICP-MS (APHA 3125 B / US EPA 200.8)
Total boron, aluminium and manganese	Not analysed	Nitric acid digestion APHA 3030 E (modified) 23rd ed. 2017; analysed by ICP-MS (APHA 3125 B / US EPA 200.8)
Fluoride	Not analysed	Direct measurement, ion selective electrode. APHA 4500-F- C 23rd ed. 2017
Total ammoniacal-N	Sample filtered through 0.7 µm filter Phenol/hypochlorite colourimetry. Segmented flow analyser. (APHA 4500-NH3 G modified)	Filtered Sample from Hill Laboratories, Christchurch. Phenol/hypochlorite colourimetry. Flow injection analyser. (NH4-N = NH4+-N + NH3-N). APHA 4500-NH3 H (modified) 23rd ed. 2017.\

Analyte	Method used by CCC laboratory	Method used by Hill Laboratories
Nitrate-N + nitrite-N	Sample filtered through 0.7 µm filter. Cadmium reduction. Segmented flow analyser (APHA 4500-NO3 F)	Filtered sample from Hill Laboratories, Christchurch. Total oxidised nitrogen. Automated cadmium reduction, flow injection analyser. APHA 4500-NO3- I (modified) 23rd ed. 2017
DRP	Sample filtered through a 0.45 µm filter, Molybdenum blue colourimetry analysed by Segmented flow analyser (APHA 4500-P F)	Filtered sample from Hill Laboratories, Christchurch. Filtered through a 0.45 µm filter then analysed by flow injection analysis with Molybdenum blue colourimetry. APHA 4500-P G (modified) 23rd ed. 2017
Sulfate	Not analysed	Filtered sample from Christchurch. Ion Chromatography. APHA 4110 B (modified) 23rd ed. 2017
BOD5	Total BOD5 Incubation 5 days at 20°C. DO meter, no nitrification inhibitor added, seeded (APHA 5210 B)	Total BOD5 Incubation 5 days, DO meter, no nitrification inhibitor added, seeded. Analysed at Hill Laboratories, Christchurch. APHA 5210 B (modified) 23rd ed. 2017
DOC	Sample filtered through a GF/F filter, inorganic carbon removed by acidification and nitrogen purging, persulfate-ultraviolet oxidation method, CO2 analysis by segmented flow analyser (APHA 5310C)	Acidification, purging to remove inorganic C, super-critical persulphate oxidation at 375°C, IR detection. APHA 5310 C (modified) 23rd ed. 2017
E. coli	Colilert method. Enzyme substrate test. Incubated 35°C for 24 hours (APHA 9223 B)	