YRIRP Report

Effective monitoring and assessment of contaminants impacting on the lower to middle sections of the Yarra River

Scientific report

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Executive summary

This study aimed to identify the levels and variability of an array of pollutants in urban stormwater systems that drain into Melbourne's Yarra River. A monitoring program was conducted in three residential and three industrial catchments. Dry weather flows and wet weather events were monitored for heavy metals, two indicator microorganisms (*Escherichia coli* and enterococci) and Total Petroleum Hydrocarbons (TPHs).

Dry weather data was collected from the six catchments using an intensive monitoring regime. Over a seven day period, three samples per day were withdrawn from each catchment's outlet pipes. Wet weather data was also collected from the outlet pipes of two catchments, one residential and one industrial. In total, four rainfall events were monitored in both catchments using autosamplers that withdrew samples from the stormwater at flow-weighted intervals.

Pollutant levels varied *between catchments* (i.e. from one catchment to another), temporally *within catchments* (i.e. from one sampling time to another at the same location) and temporally during wet weather events (i.e. pollutant concentrations vary over the hydrograph). The magnitude of this variability was found to be specific to both the pollutant type and the catchment, with some pollutants exhibiting considerable variability at one catchment and minimal variability at another.

This was even the case between catchments of very similar land uses, levels of imperviousness and degrees of development. For example, aluminium concentrations varied greatly at two of the catchments (one industrial and one residential), while the concentrations remained largely similar at two other catchments (again, one industrial and one residential).

Some pollutants exhibited a constant amount of variability across all catchments. Strontium was the most constant within all catchments during dry and wet weather events, with standard deviations always far less than its mean concentration (indicating a low relative variation). While strontium's variability was small *within* each catchment, concentrations were often different *between* catchments.

Other pollutants exhibiting a constant variability across all catchments were *E. coli* and enterococci. These bacterial indicators constantly had the highest variation within all six catchments, with standard deviations generally being greater than their means. Both bacterial indicators also varied significantly between each catchment during dry weather flows, with *E. coli* showing no real difference between land uses, but enterococci always being less evident at the industrial catchments.

The variability of pollutants was found to have a large influence on the accuracy of certain sampling strategies for load estimations. For example, accurately estimating dry weather loadings for a pollutant with concentrations that vary considerably requires more samples than a pollutant with low variability.

This also applies to wet weather sampling, with the variability in the pollutant's concentrations governing the number of samples required during each event for accurate wet weather pollutant load estimates. This finding has important implications on future sampling designs, and will help to achieve more accurate load estimates and reduce monitoring costs.

Analyses were conducted to explain some of the observed variations. The correlation of pollutants during both dry and wet weather was most apparent for heavy metals, with many catchments showing statistically significant correlations between an array of different metals. Few metals were correlated with flow rates and indicator organisms were most significantly correlated with one another. However, during wet weather the indicator organisms were also correlated with some heavy metals – although never consistently at both wet weather catchments.

Many of the heavy metals at the residential catchment showed a decline in concentrations from the start of wet weather events. This indicates that a first flush effect might be present for these metals at this catchment. Only a few heavy metals at the industrial catchment showed such a trend, but loads were always less significant than that found at the residential catchment. *E. coli* and enterococci showed no consistent first flush trend at either of the two catchments.

Comparisons between estimated yearly dry and wet weather loads showed that for the residential catchment, the total annual load was mainly sourced from wet weather events. The opposite was true for the industrial catchment, with generally less than half of the total annual pollutant load being sourced from wet weather events.

These results were highly dependent on the dry weather flow regimes found within each catchment; the large residential catchment had very low flow rates, while very high dry weather flows were found at the small industrial catchment. This was an interesting finding, since baseflow rates found in stormwater are theoretically proportional to the size of the catchment (mainly the size of the pervious soil system). These results clearly demonstrate that anthropogenic sources of water exist in the industrial catchment and that these sources of water can result in high dry weather pollutant loads.

Although this dataset helps to understand the variability of pollutants between and within each study catchment, there is insufficient data to extrapolate these findings directly to other catchments. More data collection is required to understand

the underlying population distribution of each pollutant at a range of different catchments. This population distribution can then be used to estimate the likely pollutant load coming from an unmonitored catchment. Until this is completed, it will be necessary to monitor catchments to understand their pollutant levels and associated variability.

This study has helped to inform these future monitoring regimes by understanding:

- the connection between pollutant variability and sampling frequency
- the typical variability of an array of pollutants in residential and industrial catchments during both dry and wet weather flows.

Key messages

- Pollutant levels varied *between catchments* (i.e. from one catchment to another), temporally *within catchments* (i.e. from one sampling time to another at the same location) and temporally during wet weather events (i.e. pollutant concentrations vary over the hydrograph).
- The variability of pollutants was found to have a large influence on the accuracy of certain sampling strategies for load estimates.
- Comparisons between estimated yearly dry and wet weather loads showed that for the residential catchment, the total annual load was mainly sourced from wet weather events. For the industrial catchment, generally less than half of the total annual pollutant load was sourced from wet weather events.
- Results clearly demonstrate that anthropogenic sources of water existed in the industrial catchment and that these sources of water can result in high dry weather pollutant loads.

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1 Introduction

The Yarra River is a major waterway and natural feature of Melbourne's landscape. It has shaped Melbourne's development and growth, supports industry and tourism, and is highly valued as an environmental and recreational asset.

The Environment Protection Authority (EPA) Victoria is a statutory environmental regulator. It is specifically concerned with illegal pollution discharging from industrial estates via stormwater drainage systems to receiving waterways, including the Yarra River.

In 2006, EPA developed and implemented the Yarra River Investigation and Response Program (YRIRP). This four year program focused on scientific analysis, knowledge transfer and statutory enforcement to meet the ongoing challenge of managing water quality in the Yarra River.

This report outlines the research methods used to effectively monitor and assess contaminants impacting on the middle to lower sections of the Yarra River.

2 Research background

Characterising pollutant levels from urban stormwater drains during dry and wet weather periods is important for a number of reasons, including:

- assessing and improving Water Sensitive Urban Design WSUD treatment technologies
- assessing the impacts of stormwater run-off on downstream systems
- for modelling purposes.

Accurate monitoring methodologies must be used in order to accurately characterise pollutant loads and concentrations. The sampling of dry weather urban stormwater flows is often conducted using a 'grab' sampling methodology (e.g. Leecaster et al. 2002; Fletcher & Deletic 2007; Francey et al. in press). Grab sampling of wet weather flows in urban systems is often used to characterise a site's pollution level (e.g. Eleria & Vogel 2005; Fletcher & Deletic 2007; Soonthornnonda & Christensen 2008).

Most bacterial and toxicant sampling in rivers and drains conducted by EPA is from a single sampling point using a grab sample methodology, the adequacy of which largely depends on:

- the pollutant's variability (both spatially and temporally)
- the frequency of the sampling and the corresponding time period that is being characterised (e.g. daily, weekly, monthly or annual loads).

The representativeness of this form of sampling in terms of quantifying pollutant levels is therefore unknown.

Discharges of faecal contamination in many stormwater drains discharging to the Yarra River were found to be highly variable (Melbourne Water & EPA Victoria 2007a). An independent scientific review of the above investigation supported the recommendation to further characterise the degree of spatial and temporal variability of pollutant loads within the system (Melbourne Water & EPA Victoria 2007b).

While a sampling program has been undertaken by EPA to assess the spatial variability of pollutants in the lower and middle Yarra River, temporal scale variability of pollutants entering the river is yet to be fully investigated.

3 Scope

A monitoring program was conducted at three residential and three industrial catchments in the greater Melbourne area.

Both dry weather flows and wet weather events were monitored for heavy metals, two indicator microorganisms (*Escherichia coli* and enterococci) and Total Petroleum Hydrocarbons (TPHs).

Dry weather data was collected from the six catchments using an intensive monitoring regime. Over a seven day period, three samples per day were withdrawn from each catchment's outlet pipes.

Wet weather data was also collected from the outlet pipes of two of the catchments, one residential and one industrial. In total, four rainfall events were monitored at both catchments using autosamplers that withdrew samples from the stormwater at flow-weighted intervals.

4 Purpose

The primary aim of this program was to identify the temporal variability of pollutants in urban stormwater feeding into the Yarra River.

Several objectives were established to address the overall aim, including:

- To identify and report the variability of each pollutant during *dry* weather periods to help understand this variability in industrial and residential catchments. This variability includes:
  - how the pollutant varies between different study sites and within each study site
  - how the pollutant varies within each day.
- To identify and report significant correlations between all dry weather pollutant levels and flow rates to help determine whether the behaviour and or source of one pollutant is captured in another, or is explained by flow rates.
- To determine the errors associated with using just one grab sample per day to characterise weekly pollutant loads.
- To identify and report the variability of each pollutant during *wet* weather periods to help understand this variability in industrial and residential catchments. This variability includes:
  - how the pollutant varies between different study sites and within each study site
  - how the pollutant varies within each wet weather event.
- To identify and report significant correlations between all wet weather pollutant levels and flow rates, to help determine whether the behaviour and/or source of one pollutant is captured in another, or is explained by flow rates.
- To determine the errors associated with using just one, two, three or four randomly taken samples during rainfall events to characterise a pollutant's wet weather event loads.
- To identify differences in pollutant behaviour between dry and wet weather periods and determine whether dry or wet weather pollutant loads contribute the most to total annual loads.
- To determine the uncertainty in the analytical procedure for measuring typical stormwater pollutants.

5 Methods

5.1 Site selection

Three residential and three industrial sites in Melbourne were carefully selected as the study sites, based on criteria which included:

- a good representation of the required land use, with the majority of the catchment classified as either residential or industrial
- prior knowledge of key drains that had shown to be influenced by microorganisms, heavy metals or hydrocarbons
- relative proximity to the base location of the sampling team (Monash University, Clayton)
- locations that were safe for sampling staff to access and where the likelihood of vandalism was minimal
- established catchments to ensure that construction and remediation works were kept to a minimum during the sampling period.

Table 1 below summarises the characteristics of the selected sites and is followed by brief descriptions of each site.

Flow rates and physical parameters (including temperature, pH and electric conductivity) were monitored at each site during both dry and wet weather events using in-situ probes located at each catchment's outlet.

Other stormwater quality parameters were monitored at each site using grab sampling methodologies, but at varying times as indicated below.

Table 1. Site descriptions and catchment characteristics

Site name	Melways reference of outlet	Primary land use[1]	Total catchment area[2] (ha)	Total imperviousness[2] (% of area)	Catchment's outlet pipe dimensions (m)	Latitude, Longitude
Hedgeley Dene Main Drain, Malvern East	59 K10	Residential - medium density	160	45%	Square - 1.83W x 1.20H	37°51'57.70"S, 145° 3'36.87"E
Lara Street Main Drain, Malvern East	59 E5	Residential - medium density	110	55%	Circular - 0.61rad	37°50'48.32"S, 145° 2'24.08"E
Fairfield Main Drain, Fairfield	31 A11	Residential - medium density	337	68%	Circular - 1.00rad	37°46'57.69"S, 145° 1'19.48"E
Thornton Crescent, **Nunawading**	48 H10	Industrial, with a small proportion residential (<15%)	11	85%	Circular - 0.375rad	37°49'8.98"S, 145°11'15.30"E
Lexton Road, **Box Hill**	47 F7	Industrial, with a small proportion residential (<20%)	16	80%	Circular - 0.375rad	37°48'39.05"S, 145° 8'5.77"E
Railway Road, **Blackburn**	47 K10	Industrial, with some residential (<38%) and commercial (<30%)	44	65%	Circular - 0.525rad	37°49'13.19"S, 145° 9'7.05"E

Figure 1. Location of the six study sites in relation to Monash University and Melbourne's Central Business District.

Hedgeley Dene Main Drain, Malvern East

This is one of the largest sites, with a total catchment area exceeding 160 ha. The site mainly comprises medium density residential developments with a small number of commercial developments within its stormwater boundaries.

Stormwater quality parameters were monitored during *both* dry and wet weather periods.

Figure 2. Aerial photographs of the Hedgeley Dene site showing the approximate stormwater boundaries and a typical streetscape found within this site. ✕ marks the location of the catchment outlet pipe/access pit used for sampling and installation of equipment.

Lara Street Main Drain, Malvern East

This is the smallest residential development, with a catchment area of approximately 110 ha. Located quite close to the Hedgeley Dene site, this site has a similar level of imperviousness (55%) and also contains mainly medium density residential developments within its stormwater boundary, with just a small number of commercial properties.

Stormwater quality parameters were monitored *only* during dry weather periods.

Figure 3. Aerial photographs of the Lara Street site showing the approximate stormwater boundaries and a typical streetscape found within this site. ✕ marks the location of the catchment outlet pipe/access pit used for sampling and installation of equipment.

Fairfield Main Drain, Fairfield

This is the largest residential site, with a catchment area of over 330 ha. It is also the most impervious residential catchment, due to its level of development and proximity to Melbourne's CBD. Commercial precincts within the catchment represent less than five % of the total area.

Stormwater quality parameters were monitored *only* during dry weather periods.

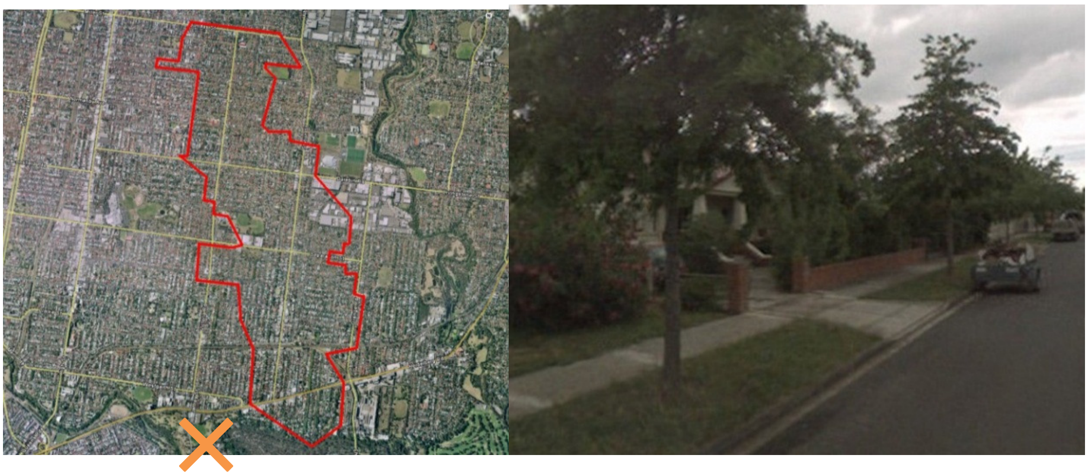

Figure 4. Aerial photographs of the Fairfield site showing the approximate stormwater boundaries and a typical streetscape found within this site. ✕ marks the location of the catchment outlet pipe/access pit used for sampling and installation of equipment.

Thornton Crescent, Nunawading

This is the smallest industrial site, with a catchment area of just 11 ha. The majority of the site is classified as industrial, with only a small portion of the catchment made up of residential premises (< 15%). The medium to high level of development produces a very high level of total imperviousness (85%).

Stormwater quality parameters were monitored during *both* dry and wet weather periods.

Figure 5. Aerial photographs of the Nunawading site showing the approximate stormwater boundaries and a typical streetscape found within this site. ✕ marks the location of the catchment outlet pipe/access pit used for sampling and installation of equipment.

Lexton Road, Box Hill

This is a small, undulating catchment with an area of around 16 ha, of which around 80% is impervious. The site is mostly comprised of industrial developments, but a small portion of the catchment contains medium density residential land uses (< 20%).

Stormwater quality parameters were monitored *only* during dry weather periods.

Figure 6. Aerial photographs of the Box Hill site showing the approximate stormwater boundaries and a typical streetscape found within this site. ✕ marks the location of the catchment outlet pipe/access pit used for sampling and installation of equipment.

Railway Road, Blackburn

While this is the largest of the industrial catchments (44 ha), it also has the lowest level of imperviousness (65%). This may be due to the relatively high proportion of medium density residential development located within this site, occupying around 30% of the catchment.

Stormwater quality parameters were monitored *only* during dry weather periods.

Figure 7. Aerial photographs of the Blackburn site showing the approximate stormwater boundaries and a typical streetscape found within this site. ✕ marks the location of the catchment outlet pipe/access pit used for sampling and installation of equipment.

5.2 Equipment and installation

5.2.1 Obtaining permits

As each site was selected, it was necessary to consult with local councils and water authorities to obtain permits for the installation of the sampling equipment.

Each site had to be equipped with instruments to measure flow rates and physical water quality parameters. This equipment needed to be fixed to the inside of the stormwater pipe and confined space entry permits had to be acquired from the appropriate authority. For the residential catchments, this was Melbourne Water, since all drains were Melbourne Water assets, while for the industrial sites the local council (City of Whitehorse) was the authorising body.

For the two sites being monitored during wet weather events (Hedgeley Dene and Nunawading), some equipment also needed to be installed on the surface of the catchment to allow for automatic sampling. These sites required extra permits from the local council for the installation of monitoring huts, as they were to be located on nature strips of property owners and were close to roads (see Figure 2 and

Figure 5 for these locations).

Figure 8. An example of the monitoring huts located at the Hedgeley Dene and Nunawading sites. These huts contained the autosampling equipment required to conduct wet weather sampling at these sites.

5.2.2 Flow measurement

Each site was equipped with a flow meter and a flow probe installed in the invert of the outlet pipe (HACH 910 at sites monitored for dry weather only and HACH 950 for sites monitored for both dry and wet weather – see Figure 9).

These flow meters measure stormwater depths using pressure transducers to calculate the 'wetted area' of the flow using the measured pipe radius or cross section (see Table 1).

They also employ two ultrasonic transducers to estimate the average velocity of the flow by converting Doppler shifts in returned ultrasounds to velocity readings (see HACH 2005 for more information).

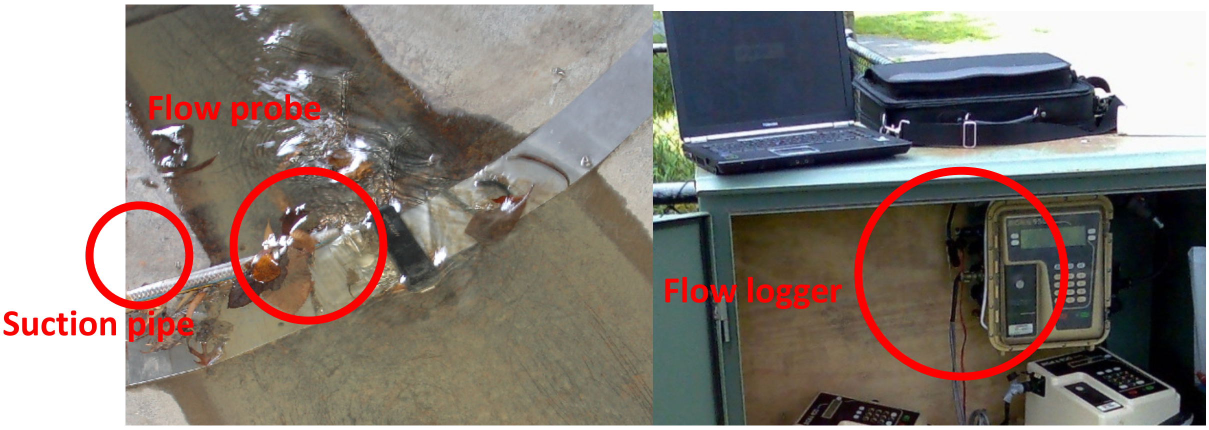

Figure 9. Typical installation of the flow sensor (left) and the above ground logger (right) installed at the Hedgeley Dene and Nunawading sites.

Prior to installation within the pipe, these flow probes and meters were calibrated using a flume within Monash University's hydraulics laboratory. Each probe (and associated meter) was placed within the flume and water with three known flows (measured using a magnetic based flow meter), velocities (measured using a velocity probe) and depths (measured using a ruler) was passed through the flume. These known parameters were then compared with the parameters estimated by the probe, and any discrepancies were minimised by the calibration of the device.

Once installed, the accuracy of the depth measurement was checked every two weeks If any discrepancy was detected the meter and probe were calibrated in-situ to ensure an accurate reading was obtained. The calibration of the velocity measurement in-situ was not possible, however the checking of the probe prior to and after use showed that the probe's velocity measurement did not drift from calibration.

The meters were set to log water depth, water velocity and calculated water flow rates at six minute intervals (it was sometimes possible to achieve slightly better resolution for some probes). The meters were downloaded on a weekly basis.

These flow meters are usually able to measure water depths to a reasonably low level. For depths less than 1–2 cm, however, the measurement can be inaccurate. Velocity measurement is often not possible at low water depths because the device measuring the Doppler shift is not submerged. They also have limited velocity measurement accuracy, so velocities of less than 0.01 m/s are not recorded.

It was therefore difficult to achieve accurate flow measurements during dry weather flows.

In some catchments the dry weather flow depth was so low that not only was the depth measurement inaccurate, the velocity was often not recorded because the device was not properly submerged.

Monash tried many different weir formations to try and alleviate this situation, however even a very small weir downstream of the probe resulted in problems. Increasing the depth of the water usually meant creating a dam, which reduced water velocity often to levels below detection (i.e. < 0.01 m/s). The creation of the weir also led to blockages which, even when cleaned on a weekly basis, meant that the probe was inundated with sediment and litter, rendering it useless for accurate measurements.

After much trial and error these weirs were removed, as it was decided that the measurement of higher flow rates (which could be detected without a weir) was better than having no measurements at all due to obstruction. This was only a real problem at two sites: Hedgeley Dene and Box Hill.

5.2.3 In-situ water quality probes

In-situ water quality probes were installed at the invert of each outlet pipe for the six study catchments to measure physical (and one chemical) properties of the stormwater, including:

- temperature
- dissolved oxygen (DO)
- pH
- electric conductivity (EC)
- turbidity
- ammonium.

The probes were installed to provide results for at least 14 days of dry weather flows prior to any water quality sampling (whether dry or wet weather). The probes were therefore in position for over a month prior to sampling. Wet weather events often occurred during these periods and the stormwater levels had to return to dry weather levels before it could be counted as a dry weather day. Three days were normally required to allow drains to return to baseflow conditions after more than 1 mm of rainfall.

This data was used to identify peaks in pollutant levels during dry weather periods, which helped select the dry weather grab sampling times. For the analysis used to determine these peak dry weather pollutant levels, see Appendix 1.

Three types of in-situ water quality probes were used for this study:

- Greenspan CS304 – temperature, DO, pH, EC
- Hydrolab MS5a – temperature, pH, EC, turbidity, ammonium
- Hydrolab MS5b – temperature, DO, pH, EC, turbidity

Figure 10. Water quality probes used in this study: the Greenspan CS304 (left) and the Hydrolab MS5 (right).

At the sites where dry and wet weather water quality sampling was conducted (Hedgeley Dene and Nunawading), both Greenspan CS304 and Hydrolab MS5a probes were installed in the invert of each catchment's outlet pipes.

It was decided that the sites that had wet weather sampling should also have the better water quality probes, which also monitor turbidity and ammonium (i.e. the MS5a probe). Installing two probes in the same drain provided an extra degree of redundancy.

The Hydrolab MS5b probe was used at the Blackburn site because concurrent work was being conducted by EPA and the probe was already installed. Standard Greenspan CS304 probes were installed at the rest of the study sites: Lara Street, Fairfield and Box Hill.

Apart from the MS5b probe, which was not installed by Monash University, calibration of all parameters was conducted prior to installation to ensure that the probes were functioning correctly and producing accurate results.

The DO probes were calibrated using the method outlined in the user manual, which involves assuming the zero value of the probe does not drift (which is a safe assumption according to the manufacturers) and using the current atmospheric pressure. For calibration results, see Appendix 1.

To ensure the probes operated correctly for the span of the project, post-calibration was also conducted once they were removed from the stormwater drains.

The probes were set to log at six minute intervals, except for the Blackburn site, where the data was collected using 15 minute intervals. This was because EPA had already set this value and it was decided that the entire dataset was best kept in the same format.

This high resolution of logging for most of the probes caused two major problems:

- The battery consumption of the MS5 probes was very high and the batteries needed replacement each week.
- The significant amount of data logged over a one week span meant that the probes had to be downloaded every week to avoid excessive downloading times.

It was therefore necessary to remove the probes from the invert of the pipe every week, replace the batteries, clean the probes and download the information logged.

Weirs were installed downstream of each water quality probe to ensure it was submerged in the stormwater during dry weather periods. These dams were thoroughly cleaned out each week, but still did not always prevent sediment and litter building up around the probes, with a potentially adverse affect on the results.

5.2.4 Wet weather sampling equipment

Wet weather water quality sampling was conducted at two of the study sites: one residential (Hedgeley Dene) and one industrial (Nunawading).

To facilitate this sampling, two automatic samplers were installed in each of the site's monitoring huts. These autosamplers were programmed to collect up to 24 1 L samples according to flow-weighted intervals during any one event.

Clean, reinforced sampling tubes were installed from each autosampler to the outlet pipe's invert. The tubes were installed 3 cm above the invert of the pipe to avoid debris and sediment causing blockages. The position of the tubes was near the outlet of the catchment (see Figures 2–7 for these locations).

Prior to and after withdrawing the sample from the stormwater, the autosamplers go through a purge process designed to clean the suction pipes. This involves withdrawing water from the pipe up until it reaches the pump located on the sampler. Water is then pushed back out of the suction pipe, and the process is repeated.

Figure 11. An example of the autosamplers used for wet weather water quality sampling. Two samplers were required for the samples analysed.

5.3 Rainfall data

Rainfall data for the two wet weather sampling sites was obtained from Melbourne Water. The files listed rainfall totals in six minute intervals, and included data from the start of 2007 until 24 June 2009.

The Gardiner gauge was selected as representative of the Hedgeley Dene site (Melbourne Water gauge ID 229624), and the Mitcham gauge was used for Nunawading (Melbourne Water gauge ID 586006).

5.4 Dry weather sampling

Dry weather samples were taken from the stormwater pipes and analysed for a range of water quality constituents. Three samples per day were taken from each of the six drains in order to identify the variability in pollutants during the day. This was conducted for a seven day period in order to determine any variability in the diurnal fluctuation of pollutants between different days of the week.

For the residential sites, the dry weather sampling was conducted on seven consecutive days, from 10–16 February 2009 (including weekends).

For the industrial sites it was unfortunately not possible to conduct the sampling in seven consecutive days, due to a very small amount of rainfall within the catchment areas. The sampling was conducted from 12–19 May 2009, with part of May 15 and 16 missing due to this minor rainfall (< 1 mm fell during this event).

The times at which samples were withdrawn from the stormwater pipes were based on criteria that ensured that the times selected:

- captured the probable variation in each constituent during each day (i.e. using the results of the analysis found in Appendix 2, the times at which peak physical characteristics occurred are adequately sampled)
- maintained a safe working environment for the sampling staff (i.e. samples could only be taken during daylight hours to ensure visibility was satisfactory, and needed to be spaced far enough apart to ensure staff were well rested for each sampling run)
- enabled the majority of samples to be taken straight to the laboratory, or taken to a laboratory within 12 hours of collection
- meant that there was enough time to get from one site to another, to the analysis laboratories and back to the base at Monash University by the time the next sample was due.

It should be noted that while the dry weather sampling for the residential catchments was conducted during daylight saving time, the industrial sampling was conducted in May and had to finish much earlier.

For ease of comparison, the three sampling times each day will be referred to as *Morning*, *Afternoon* and *Evening* in the rest of this report.

Table 2. Sampling times chosen for the six study sites, labelled as Morning, Afternoon and Evening samples for ease of comparison.

Site	Morning	Afternoon	Evening
Hedgeley Dene	7:00am	1:30pm	8:00pm
Lara Street	7:30am	2:00pm	8:30pm
Fairfield	8:00am	2:30pm	9:00pm
Nunawading	8:00am	12:45pm	5:30pm
Box Hill	7:00am	11:45am	4:30pm
Blackburn	7:30am	12:15pm	5:00pm

The dry weather samples were withdrawn from the invert of the stormwater pipe using a clean, sterile procedure to prevent contamination of the sample. This included using sterilised (or clean where appropriate) sampling bottles, sampling collection tools (such as disposable gloves etc.) and most importantly, always sampling water upstream of the sampler.

The collected sample was equally divided into sample bottles (one for each water quality parameter being tested) using a method that ensured even replication between samples (McCarthy et al. 2008).

The sample bottles were arranged in a circle and the sample was poured in increments, so that at the end of each rotation each sample bottle had received 10% of the container's volume. A total of around 10 rotations were required to fill all of the sample bottles.

At the end of each rotation, the sample being distributed was rapidly shaken to ensure suspension/mixing was maintained. The samples were then placed in a cooler to ensure that all bottles were kept at 4 °C during transportation to their respective laboratories for analysis.

Morning and Afternoon samples were taken immediately to the laboratory (i.e. within one hour of collection), while Evening samples were kept in the fridge overnight and delivered to the laboratory with the samples taken on the next Morning sampling run.

Whenever a dry weather sample was collected, an estimation of the flow rate was performed by collecting the entire stormwater flow in a large plastic bag and timing the length of time used to fill this bag. The contents of the bag were then estimated using a measuring cylinder.

This was undertaken because, despite the efforts of constructing many types of weirs and water control, some of the dry weather flows were so low that the flow probes were not sensitive enough to accurately measure them. While the process produced only a very rough estimate of the flow rate, it was considered having this type of estimate was better than having no estimate at all.

5.5 Wet weather sampling

Samples were withdrawn during a number of wet weather events at the Hedgeley Dene and Nunawading sites using two automatic samplers. These samplers were programmed to take samples using flow weighted intervals and were arranged so that each autosampler (containing 24 sample bottles) would be triggered at the same time.

One autosampler contained cleaned and sterilised plastic bottles, and was dedicated to collecting samples for microbiological and heavy metal analyses. The other contained cleaned glass bottles and was dedicated to collecting samples for hydrocarbon analyses.

While the intervals used for the two sites were different, due to their varying degree of impervious areas, each site was programmed so that a 30 mm rainfall event could be captured without having to refill the autosamplers. This setup was based on a large history of sampling wet weather events in Melbourne, and was primarily focused on capturing a one-in-three month average recurrence interval event.

To more properly ascertain whether a first flush effect was present, the collection of samples was skewed so that the initial portion of the event was characterised by more samples than the end of the event.

It was initially proposed that three wet weather events, with around 15 samples in each, would be collected from these two sites (i.e. 45 samples from each site). It was subsequently decided that the collection of events would continue until a total of 45 samples was reached, meaning that more or less than three events could be monitored, depending on the size of these events.

5.6 Laboratory analyses and uncertainty analysis

The collected wet weather samples and the 126 dry weather samples were analysed by NATA accredited laboratories using standard laboratory techniques.

The following water quality parameters were quantified for each collected sample using the named laboratories (detection limits are presented in square brackets).

Ecowise Environmental, Scoresby, Victoria

- *E. coli* (Colilert technique) [1 MPN/100 mL]
- Enterococci (Enterolert technique) [1 MPN/100 mL]
- Heavy metals (aluminium [0.1 mg/L], antimony [0.01 mg/L], arsenic [0.01 mg/L], barium [0.01 mg/L], beryllium [0.01 mg/L], boron [0.2 mg/L], cadmium [0.002 mg/L], chromium [0.01 mg/L], cobalt [0.01 mg/L], copper [0.01 mg/L], iron [0.2 mg/L], lead [0.01 mg/L], manganese [0.01 mg/L], mercury [0.001 mg/L], molybdenum [0.01 mg/L], nickel [0.01 mg/L], selenium [0.01 mg/L], silver [0.01 mg/L], strontium [0.01 mg/L], thallium [0.01 mg/L], tin [0.01 mg/L], titanium [0.01 mg/L], vanadium [0.01 mg/L] and zinc [0.01 mg/L])

Leeder Consulting, Mitcham, Victoria

- Total Petroleum Hydrocarbons (TPHs) [0.01 mg/L]

Water Studies Centre, Monash University, Australia

- Total Nitrogen (TN) and nitrogen species (NOx, NH_3)

(This data is not included in the analysis of the report – see Appendix 3 and 4.)

On one occasion at each site, extra sample volume was collected from the stormwater drains during the dry weather sampling period. This extra volume was used to create triplicate samples in order to test the accuracy of the laboratory analyses. Once the sample was withdrawn, it was decanted into three separate bottles, filling each bottle a maximum of 10% during each rotation. This procedure ensured that each sample was as close as possible to 'true' replicates.

Using these results, it is possible to determine the uncertainty in the laboratories' analytical procedures (see McCarthy et al. 2008 for more information on this sampling method).

5.7 Analysis and presentation of collected data

5.7.1 Analysis of dry weather data

Between- and within-site variability

Summary descriptive statistics have been presented earlier for pollutants that were regularly above their corresponding detection limits. Mean pollutant concentrations, together with Relative Standard Deviations (RSD = the coefficient of variation expressed as a percentage) of the collected pollutants were calculated for each site, using all 21 samples collected during the regime.

If the pollutant was not detected in all samples, then these samples were removed from the calculation of the mean and RSD for that pollutant, and the final number of samples used in the analysis was presented. Removal of these numbers was necessary since their absolute number was not known.

For visual comparisons, it was decided to display the results of selected pollutants using boxplots. Each boxplot contains the pollutant concentrations obtained from the 21 samples collected at the respective study site. When samples had pollutant levels less than their detection limit, these samples were left out of the boxplot.

For comparative purposes, boxplots of the measured flow rates at the catchments were also provided.

Within-day variability of pollutants

Boxplots were created to help visualise how some pollutants vary between Morning, Afternoon and Evening samples. As the aim was to determine diurnal variations, the variability between days was removed from the analysis by standardising all concentrations using the daily averages (i.e. each of the seven Morning [M], Afternoon [A] and Evening [E] sample concentrations obtained from a site were divided by their respective daily average for that site). These standardised values for each pollutant and site were then plotted in three boxplots, each containing the Morning, Afternoon and Evening values.

Since there are seven days of collection (and hence seven Morning, seven Afternoon and seven Evening samples per site), each boxplot has a maximum of seven standardised values (some have less due to pollutant levels being below detection limits).

Providing boxplots for all pollutants was not possible because of the space required for these plots. Instead, Student's t-tests were performed to determine whether there were significant differences in Morning, Afternoon and Evening samples. These tests were performed with the same dataset used to create the above boxplots (i.e. standardised values were used), and tests were performed for each pollutant at each site to determine:

- whether there was a significant difference between Morning and Afternoon sample concentrations (reported as MvA)

- whether there was a significant difference between Morning and Evening sample concentrations (reported as MvE)
- whether there was a significant difference between Evening and Afternoon sample concentrations (reported as EvA).

If there was a statistically significant difference (at the 95% level) in concentrations, then the corresponding p-value was reported in the Results section.

There was often insufficient data to conduct the statistical testing (due to pollutants being below their detectable level). If the number of values used for the testing of a variable (i.e. the number of samples above detection in either M, A or E) was less than five, then no testing was performed for this variable.

This is because with samples of less than five, these statistical tests are not robust. In fact, even with the seven samples used in each variable, the results of these tests should be used with caution.

Correlation analyses

A correlation analysis was conducted to determine whether any pollutants had significant relationships with other pollutants or flow rates. Correlation coefficients (*R*) were calculated for every combination of pollutants and flow rates.

Statistical tests were performed to determine the significance of these correlation coefficients, and only correlations which were statistically significant at the 95% significance level were reported.

The correlation analysis was conducted for each of the six sites, indicating a maximum of 21 data points were available in each of the two variables used in the analysis (i.e. 21 variable pairs). However, since the pollutants were sometimes below their detection limit, this number varied considerably.

As with the previous section, correlation coefficients that were estimated using less than five variable pairs were not reported, even if the statistical test showed it was significant. This was because statistical tests are not robust when using such small numbers of points.

Since so many variable pairs were significantly correlated, it was not possible to report on all of these within this report. Instead, this report concentrates on those variable pairs that were significantly correlated at three or more sites, with Appendix 5 giving a full list of all correlations found.

Errors in weekly loads using just one sample per day

The following analysis was conducted to determine whether randomly taking one sample per day is sufficient to estimate weekly pollutant loads.

One sample was randomly selected from the three available samples for that day. This was repeated for each of the seven days of the week and these seven samples were then used to estimate the weekly pollutant load by multiplying the total volume measured each day by the corresponding sample concentration. The total of the seven loads is referred to as the 'estimated' weekly pollutant load.

This process was repeated 500 times to capture most of the possible pollutant concentration combinations. These 500 estimated pollutant loads were compared to the pollutant load calculated when using all samples collected during the monitoring program (referred to as the 'actual' weekly load). Ratios of estimated to actual pollutant loads were used to determine the amount of error in the estimated load. In total, 500 ratios were calculated for each pollutant at each study site and the results are presented using boxplots.

Since it was not possible to present all pollutants using boxplots, it was decided to represent the spread of these boxplots using the 95% confidence interval from the 500 ratios calculated for each pollutant at each site.

The spread of the boxplots helps identify the most probable amount of error involved in predicting weekly pollutant loads using just one sample per day. The calculation of this confidence interval was not possible for some pollutants, where a number of samples were below their detection limit.

For pollutants where there were more than five samples (out of the 21 taken at each site) that were less than their respective detection limit, the confidence interval was not reported.

This decision was based on the fact that for samples that were less than the detection limit, the concentration used in this analysis was specified as half of the detection limit. If more than five samples with these values were used in the analysis, it would skew the results to a point where the confidence interval was no longer truly representative of the errors involved in this process (because there would be five constant numbers, which would lead to narrow confidence intervals).

5.7.2 Analysis of wet weather data

Between- and within-site variability

As with the dry weather data, summary descriptive statistics have been provided for pollutants that were regularly above their corresponding detection limits. Mean pollutant concentrations, together with the RSD of the collected pollutants were calculated for each site, using all wet weather samples collected.

If the pollutant was not detected, then these samples were removed from the calculation of the mean and RSD for that pollutant, and the final number of samples used in the analysis was presented.

For visual comparisons, it was again decided to display the results of select pollutants using boxplots. Each boxplot contains the pollutant concentrations measured in all wet weather samples.

If some of the samples had levels of the pollutant of less than its detection limit, then these samples were left out of the boxplot.

Within-event variability of pollutants

In order to understand whether the pollutants at the two wet weather sites experienced a first flush, plots of pollutant concentrations against cumulative run-off depth (i.e. cumulative volumes converted to run-off depth using the effective impervious area for the site) were created for select pollutants.

These boxplots contain the results from all samples collected from all wet weather events. If samples were below detection they were included on the plot, for illustrative purposes only, at half of their detection limit. One plot was constructed for each study site.

It was not possible to present a boxplot of wet weather concentrations against cumulative run-off depths for each pollutant. Instead, a linear correlation analysis was conducted to determine whether any significant trends were present.

Only statistically significant correlation coefficients are presented in the Results section. This correlation analysis was not performed on pollutants which had less than five data points for the analysis due to non detection.

Correlation analyses

As with the dry weather dataset, a correlation analysis was conducted to determine whether any pollutants had significant relationships with other pollutants or flow rates.

Correlation coefficients (R) were calculated for every combination of pollutants and flow rates. Statistical tests were performed to determine the significance of these correlation coefficients, and only correlations which were statistically significant at the 95% significance level were reported.

The correlation analysis was conducted using all the data collected during wet weather flows. Again, correlation coefficients which were estimated using less than five variable pairs were not reported, even if the statistical test showed it was significant (because statistical tests are not robust when using such small numbers of points).

Errors in event loads using a few samples in each event

A boot strapping methodology was employed to determine the impact of randomly taking a grab sample during a wet weather event to estimate total wet weather event loads. This method was employed to determine the accuracy of using one, two, three and four randomly selected samples to estimate the total wet weather pollutant load.

Using the 'three samples per event' as an example, three samples were randomly selected from each wet weather event using a uniform distribution (i.e. each sample had the same probability of being selected, but no sample could be picked more than once). The concentrations in these three samples were then averaged and multiplied by the total event volume to achieve the event's total estimated pollutant load.

This was repeated for each event monitored at the specific site. The summed loads from all events (known as the 'estimated' total load) were then compared to the loads calculated using all of the samples collected within the events (referred to as the 'actual' wet weather event load). This actual event load is estimated using a flow-weighted approach. The process was repeated 500 times to ensure that the most possible combinations were captured.

Once again, boxplots of ratios between 'estimated' and 'actual' total wet weather loads are presented in the Results section.

Since it was not possible to present all pollutants using boxplots, it was decided to represent the spread of these boxplots using the 95% confidence interval from the 500 ratios calculated for each pollutant at each site. However, the calculation of this confidence interval was not possible for some pollutants, where a number of samples were below the detection limit.

For pollutants where there were more than five samples that were less than their respective detection limit, the confidence interval was not reported. This decision was based on the same explanation provided above in section 5.7.1: Errors in weekly loads using just one sample per day.

5.7.3 Comparison between wet weather and dry weather pollutant levels

Boxplots were constructed for the two wet weather monitoring sites to compare the concentrations obtained in dry weather with those obtained in wet weather events for select pollutants.

The following procedure was conducted for each pollutant in order to compare the importance of dry weather loads against wet weather loads.

Using the 'actual' dry weather and wet weather loads it was possible to extrapolate this data to estimate the approximate contribution of each to total annual pollutant loads. To obtain annual dry weather pollutant loads, it was assumed that the monitored week is representative of the pollutant characteristics for an entire year. The weekly load was therefore multiplied by 52 to obtain an approximate annual dry weather load.

There are obviously huge issues related to such an assumption, and the results from this section of the report are for indicative purposes only.

The wet weather events taken at each site were also assumed to be somewhat representative of the pollution levels found in typical rainfall events. The total 'actual' load from the monitored events was therefore divided by the total rainfall in these events and this was subsequently multiplied by the site's average annual rainfall to achieve an approximate annual wet weather pollutant load.

As above, this is a large assumption and these results are to be used with caution.

6 Results and discussions

Dry and wet weather results have been presented in four separate sections:

- **Between- and within-site variability** – to provide details about how each pollutant is varying between and within each different site during dry weather periods
- **Within-day variability** – to provide information about how each pollutant varies diurnally (i.e. within each day)
- **Correlation analysis** – to determine the relationship between pollutant concentrations, and other pollutants and flow rates for dry weather flows
- **Errors in weekly load estimations** – to assess the accuracy of random grab sampling methodologies during dry weather events to estimate total weekly dry weather loads.

6.1 Dry weather data

6.1.1 Between- and within-site variability

Appendix 3 shows detailed data for all pollutants monitored during the dry weather campaign, while Table 3 shows only the mean and Relative Standard Deviations (RSD = coefficient of variation divided by the mean expressed as a percentage) for the detected pollutants for each study site. Figure 12 shows boxplots for the 21 concentrations obtained during the monitoring period for iron, zinc, *E. coli* and enterococci. Flow rates are also shown in this figure for comparative purposes.

Table 3. Mean and Relative Standard Deviations (RSD = standard deviation divided by the mean, expressed as a percentage) of detected constituents in the 21 dry weather samples collected at each study site.

Pollutant	Hedgeley Dene	Lara Street	Fairfield	Box Hill	Blackburn	Nunawading
Aluminium	1.09 (142%)[16]	0.52 (49%)[20]	0.22 (75%)[20]	0.21 (35%)[20]	2.14 (307%)[11]	0.17 (25%)
Barium	0.06 (50%)	0.04 (40%)	0.03 (19%)	0.07 (38%)	0.04 (145%)	0.03 (7%)
Copper	0.03 (74%)[14]	0.02 (29%)	0.02 (71%)[2]	0.07 (95%)[17]	0.04 (106%)[9]	ND
Iron	2.65 (108%)[11]	0.45 (36%)[20]	0.60 (0%)[2]	1.03 (54%)	1.73 (271%)[14]	0.33 (14%)
Lead	0.05 (90%)[7]	0.01 (0%)[1]	ND	0.02 (76%)[2]	0.03 (143%)[3]	0.01 (0%)[1]
Manganese	0.16 (129%)[11]	0.01 (0%)[1]	0.03 (94%)[2]	0.08 (53%)	0.06 (199%)[14]	0.06 (9%)
Molybdenum	ND	0.01 (0%)[1]	ND	0.03 (88%)[9]	0.10 (138%)[2]	ND
Nickel	0.01 (43%)[3]	ND	ND	0.10 (108%)	0.01 (93%)[3]	ND
Strontium	0.22 (33%)	0.21 (37%)	0.05 (16%)	0.09 (15%)	0.04 (32%)	0.08 (3%)
Titanium	0.04 (106%)[10]	0.03 (41%)[15]	0.01 (43%)[3]	0.02 (76%)[5]	0.02 (79%)[4]	ND
Zinc	0.30 (108%)	0.08 (21%)	0.10 (156%)	1.17 (50%)	0.64 (99%)	0.07 (60%)
E. coli	655 (134%)	2732 (196%)	12360 (103%)	2374 (168%)	2361 (117%)	3 (71%)[9]
Enterococci	1331 (165%)	1326 (117%)	4746 (148%)	80 (98%)[19]	112 (305%)	2 (86%)[17]
TPHs	0.15 (0%)[1]	ND	0.19 (0%)[1]	0.42 (100%)[16]	0.42 (126%)[9]	ND

A superscript indicates the number of samples used to calculate the mean and RSD, with all other samples not detected (ND). Absent superscripts indicate all samples were above detection. Heavy metals and TPHs are measured in mg/L, *E. coli* and enterococci are both measured in MPN/100 mL.

- Antimony was only detected four times at Box Hill (0.01 mg/L and 0.02 mg/L).
- Arsenic was only detected five times at Hedgeley Dene (0.01 mg/L) and nine times at Lara Street (0.01 mg/L to 0.02 mg/L).
- Beryllium was not detected at any site.
- Boron was only detected at Box Hill (0.6 mg/L) and Blackburn (0.5 mg/L).
- Cadmium was detected once at Fairfield (0.003 mg/L).
- Chromium was only detected once each at Hedgeley Dene (0.01 mg/L), Box Hill (0.001 mg/L) and Blackburn (0.04 mg/L).
- Cobalt was detected nine times at Box Hill (between 0.01 mg/L and 0.05 mg/L) and once at Blackburn (0.01 mg/L).
- Mercury was not detected at any site.
- Selenium was not detected at any site.
- Silver was detected eight times at Blackburn (between 0.01 mg/L and 0.16 mg/L).
- Thallium was not detected at any site.
- Tin was only detected once at the Box Hill site (0.001 mg/L).
- Vanadium was only detected twice at Hedgeley Dene (0.01 mg/L and 0.02 mg/L) and once at Blackburn (0.02 mg/L).

A number of heavy metals were not detected at any of the study sites during the seven day program: beryllium, mercury, selenium and thallium. Others were only detected in a minimal number of samples: antimony, arsenic, boron, cadmium, chromium, cobalt, silver, tin and vanadium.

Silver was only detected at the Blackburn site, and this could be indicative of illegal discharges, albeit intermittent, from coating/plating businesses located in this industrial catchment. The eight detections always occurred in pairs (in the Afternoon 12pm and Evening 5:00pm samples) and never in the Morning samples (7:30am).

Nickel was only regularly detected at the Box Hill site (with all samples being above detection), with a general trend that the Evening samples were higher than the Morning samples. This again indicates the possibility of illegal releases into the stormwater system, also probably from the coating/plating industries located within this catchment.

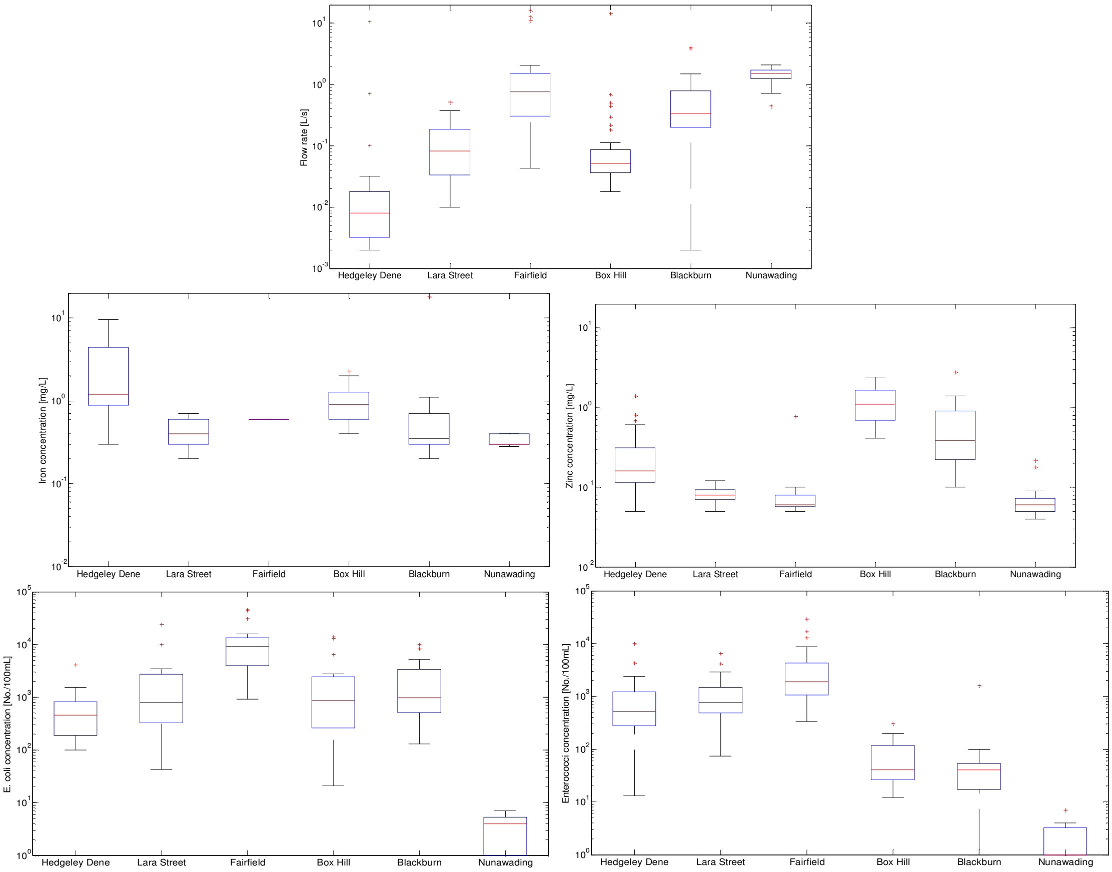

Figure 12. Boxplots showing the distributions of flow rates (top) and dry weather sample concentrations found at each study site for iron (middle left), zinc (middle right), *E. coli* (bottom left) and enterococci (bottom right).

Aluminium was regularly detected at all the study sites, with positive detection in 86% of the samples collected at the six study sites (Table **3**).

The variability of this constituent between sites was particularly high, while its variability within a site was very much site dependent. For example, Blackburn had the highest average concentration (2.14 mg/L) and the highest RSD (307%), while Nunawading had the lowest average aluminium concentration (0.17 mg/L) and the lowest RSD (25%).

Iron (detected in 71% of samples) and zinc (detected in all samples) followed a similar trend to that of aluminium and this is reflected in Figure **12**, which shows the high variability of these constituents between sites, and sometimes extreme variability within sites (e.g. at Hedgeley Dene).

There seems to be an inverse relationship between the flow rate and the concentrations of these two pollutants (Figure **12**), with sites that have higher flow rates obtaining lower iron and zinc concentrations. Dilution of the pollutants in higher flow rate systems could explain this inverse relationship.

In fact, section 6.1.3 shows there is a significant negative relationship between flow and zinc concentrations. Figure 12 also indicates there is a positive correlation between iron and zinc concentrations, and section 6.1.3 investigates this correlation in more detail.

Barium (detected in 100% of samples), copper (detected in 51% of samples), lead (detected in just 11% of samples) and titanium (detected in 30% of samples) all follow a slightly different trend to aluminium, iron and zinc, with fairly consistent concentrations between study sites and usually low variability within each site.

Strontium was the only detected constituent that had a consistently low variability within each study site, with a maximum RSD of just 37% (compared to its closest pollutant, copper with a maximum RSD of 106%). However this heavy metal still varied considerably between sites.

Detection of TPHs was generally low, with just 21% of samples having TPH levels above detection. There was a significant variability between sites, however, with some sites having nearly 80% of its samples above detection, while other sites' samples were never above detection.

The most interesting trend was that the industrial sites had a much higher detection rate of TPHs (40 %) and concentrations (up to 1.8mg/L) than the residential sites (3% and up to 0.2mg/L, respectively), indicating that the sources of hydrocarbons are more prevalent in industrial stormwaters. This is logical, since all of the industrial catchments have motor repair businesses within their catchment boundaries.

Hydrocarbons were mostly detected at the Box Hill site, where oil slicks in the stormwater, together with occasional petroleum smells within the stormwater drain, were recorded when sampling. Detection at the Blackburn site was less common, with less than 50% of samples taken at this site being above detection. No samples taken at the Nunawading site had detectable levels of hydrocarbons, possibly due to its very high, constant flow rate, which may have diluted the concentrations to below detection.

As might be expected, the variability of the two microbial indicators (*E. coli* and enterococci) between-sites and within-sites was large (Table **3** and Figure **12**). Mean *E. coli* concentrations varied by over one order of magnitude between the three residential sites, and over two orders of magnitude between the three industrial sites. Variability of enterococci between sites was generally smaller. Detection for both indicators was high at all sites except Nunawading, where less than half of the samples had detectable levels of *E. coli* (most samples had detectable levels of enterococci).

As opposed to iron and zinc, neither of the microbial indicators followed the trend of higher concentrations in catchments with lower flow rates. In fact, for the residential catchments the opposite was true, with sites having higher flow rates also having higher indicator organism concentrations.

Another trend observed in Figure **12** is that the *E. coli* and enterococci concentrations found at the residential sites were often very similar (in median values and ranges), whereas large differences (in median values and ranges) were found at the industrial sites.

The results presented in Appendix 3, Table **3** and Figure **12** all indicate that the presence, variability and magnitude of pollutants is different for different land uses, and often different for catchments that have the same land use.

This makes it difficult to extrapolate this type of information to other catchments, even if they have similar land uses. Only the collection of more data from different catchments could potentially yield enough information to help identify the real population distributions of these pollutants, which could then be used for extrapolation.

The immense variability observed for many of the pollutants within a site over just one week in a year also raises more concerns.

Many of the pollutants varied so much during one week that even routine weekly, or more commonly monthly, grab sampling methodologies (often employed to estimate annual pollutant loading rates to downstream systems) will not accurately portray a yearly loading rate. Since these pollutant levels (and flow rates) will more than likely vary from week-to-week, these sampling methodologies may become even less accurate for load estimations (especially for routine monthly methods).

Section 6.1.4 will investigate this type of accuracy problem in more detail. Appendix 6 also describes an analysis conducted to determine the number of samples required per year in order to accurately estimate annual sediment loads from an urban catchment not used in this study.

This study found that two samples were required to be taken each week (randomly) to estimate mean annual sediment loads to within 50% of the actual values.

6.1.2 Within-day variability of pollutants

While the previous section focused on the variability of the pollutants between- and within- sites, this section focuses on how these pollutants vary within each day. In particular, it attempts to determine whether there is any consistent diurnal variation of the pollutants during the day (i.e. are pollutant concentrations generally higher in the morning than in the evening? etc.).

The boxplots in Figure 13 help identify the diurnal variation of pollutants at each site (note the standardised values on the y-axis). Table 4 identifies statistically significant differences in concentrations of pollutants between different times of the day for each study site.

The significance values presented in Table 4 were created using the same dataset from that used to create Figure 13, and indicate whether there are any statistical differences in the Morning, Afternoon and Evening samples for each pollutant at each site. Many pollutants are either missing from this table, or blank cells are located in the table, which indicate there was insufficient data to perform statistical analyses (mainly caused by detection limits).

For the four pollutants plotted in Figure 13, there was no consistent trend for any of the pollutants at all sites. For example, iron concentrations at the Box Hill site appeared to increase from morning to night, while the same pollutant decreased at the Lara Street site (even though the two sites have similar land-uses). These differences were found to be statistically significant at both sites (see Table 4).

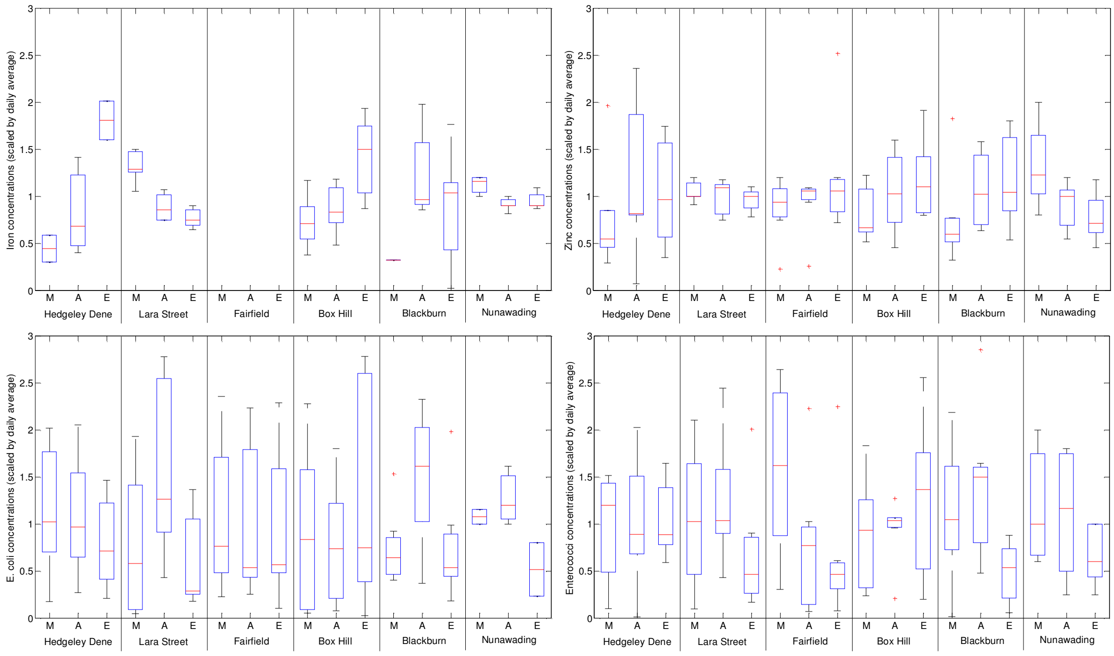

Figure 13. Boxplots showing the diurnal variation of iron (top left), zinc (top right), *E. coli* (bottom left) and enterococci (bottom right). As an example, data in each 'M' boxplot are comprised of ratios between the Morning sample concentrations and the daily average concentration (taken as the average of the Morning [M], Afternoon [A] and Evening [E] sample concentrations). Missing boxplots indicates that not enough data was available for plotting (i.e. samples were below detection).

Figure 13 shows some correlation between the behaviour of the two heavy metals (iron and zinc) during the day, within each study site (see section 6.1.3 for more information on this correlation). That is, if iron tended to increase throughout the day, zinc generally increased also at that catchment. This trend could indicate similar sources of these two heavy metals within each catchment.

It is interesting to note that although not as strong, this trend is also observed for the indicator organisms (i.e. a site which showed a diurnal pattern for E. coli generally showed a similar pattern for enterococci).

It should be stressed that the dataset used for this type of analysis is very small, so it is difficult to identify these trends accurately. This caution also applies to the statistical information presented in Table 4.

Table 4. Significant probabilities (p-values < 0.05) obtained using a Student's t-test to determine whether the null hypothesis that the two datasets (either M vs. A, M vs. E or E vs. A) are from the same population.

Pollutant	T-test	Hedgeley Dene	Lara Street	Fairfield	Box Hill	Blackburn	Nunawading
Al [mg/L]	MvA		0.00				
	MvE		0.00				
	EvA				0.04		
Ba [mg/L]	MvA						
	MvE		0.04		0.02	0.04	
	EvA						
Cu [mg/L]	MvA			NA		NA	NA
	MvE			NA	0.01	NA	NA
	EvA			NA			NA
Fe [mg/L]	MvA		0.00	NA		NA	0.00
	MvE	NA	0.00	NA	0.00	NA	0.00
	EvA			NA	0.01		
Mn [mg/L]	MvA		NA	NA			0.02
	MvE	NA	NA	NA	0.00		
	EvA		NA	NA	0.01		
Ni [mg/L]	MvA	NA	NA	NA		NA	NA
	MvE	NA	NA	NA	0.02	NA	NA
	EvA	NA	NA	NA		NA	NA
Sr [mg/L]	MvA						
	MvE		0.00				
	EvA	0.03					
Zn [mg/L]	MvA						0.05
	MvE						0.02
	EvA						
E. coli [MPN/100 mL]	MvA					0.03	
	MvE						
	EvA		0.03			0.04	
Enterococci [MPN/100 mL]	MvA						
	MvE					0.06	
	EvA					0.02	

Blanks indicate the two datasets were not statistically different (i.e. $p > 0.05$) and NA indicates there was not enough data to calculate the p-value. The number of points in these tests is unusually low, with each dataset containing only seven values. No adjustment has been made for this small number of data points.

6.1.3 Correlations between pollutants and flow rates

Appendix 5 shows a matrix of the significant correlation coefficients between two measured water quality pollutants (from the dry weather sampling). These correlation coefficients are presented for each of the six study sites. As a summary, the pairs of water quality parameters which were found to be statistically correlated at three or more sites are provided in Table 5.

Table 5. Statistically significant (i.e. p > 0.05) correlation coefficients (*R*) between water quality pollutants and flow rates monitored during dry weather periods

Study sites	Pollutant	Al [mg/L]	Cu [mg/L]	Fe [mg/L]	Sr [mg/L]	*E. coli* [MPN/100 mL]	Flow [L/s]
Hedgeley Dene/Lara St/ Fairfield	Ba [mg/L]	0.88 / -- / 0.53	0.9 / -- / --	0.92 / -- / --	0.68 / 0.95 / 0.7		
Box Hill /Blackburn/ Nunawading		0.61 / 0.9 / --	0.62 / 0.72 / --	0.81 / 0.91 / --	0.43 / -- / --		
Hedgeley Dene/Lara St/ Fairfield	Fe [mg/L]	0.98 / 0.86 / --					
Box Hill /Blackburn/ Nunawading		0.47 / 0.99 / --					
Hedgeley Dene/Lara St/ Fairfield	Mn [mg/L]			0.97 / -- / --			-- / -- / --
Box Hill /Blackburn/ Nunawading				0.44 / -- / 0.6			-- / -- / 0.59
Hedgeley Dene/Lara St/ Fairfield	Zn [mg/L]	0.99 / 0.45 / 0.54	0.95 / 0.44 / --	0.98 / 0.7 / --	-- / -- / 0.59		-- / -- / --
Box Hill /Blackburn/ Nunawading		-- / -- / --	0.53 / -- / --	0.45 / -- / --	-- / 0.88 / -0.49		-- / -0.48 / --
Hedgeley Dene/Lara St/ Fairfield	Enterococci [MPN/100 mL]					0.93 / 0.45 / 0.48	
Box Hill /Blackburn/ Nunawading						-- / 0.65 / --	
Hedgeley Dene/Lara St/ Fairfield	Flow [L/s]	-- / 0.46 / 0.59			-- / -- / --		
Box Hill /Blackburn/ Nunawading		-- / -- / --			-- / -0.51 / --		

Only pairs of pollutant variables which had $p < 0.05$ at three or more sites are presented (see Appendix 5 for a full list).

A number of metals were significantly correlated with one another, indicating positive relationships between certain heavy metals. For example, aluminium was positively correlated with barium, iron and zinc, while zinc was also found to be significantly correlated to iron, copper and strontium at more than three of the six study sites.

These correlations provide evidence that the sources and behaviour of these metals were similar at some study sites, but these sources/behaviours were not consistent at all study sites.

While Appendix 5 indicates that some metals, at some sites, were correlated with *E. coli* or enterococci, no metal or TPH was significantly correlated to these indicators at more than three study sites (Table 5). As expected, *E. coli* and enterococci were significantly correlated, but only at four of the study sites.

The lack of correlation between these two microbial indicators at the Nunawading site could be explained by the *very* low numbers of organisms at this site (with all samples having concentrations of less than 7 MPN/100 mL for both indicators).

There is generally a much higher uncertainty in the estimation of these indicators at this level of concentration, and it is hypothesised that the variability in these parameters at this site is predominantly due to measurement errors. This makes it difficult to obtain good correlation results.

The absence of a significant correlation between *E. coli* and enterococci at the Box Hill site is more difficult to explain. However, when investigating the data in more detail, the significant correlation found at the only industrial site (Blackburn) between the two indicators is largely controlled by one very polluted sample (15 May, Afternoon) with *E. coli* of 10000 MPN/100 mL and enterococci of 1600 MPN/100 mL. This was atypical of what was usually found at this site, with average *E. coli* concentrations of around 2400 MPN/100 mL and enterococci never being higher than 100 MPN/100 mL.

As displayed in Appendix 3, this sample was noted to have a brownish colour, not dissimilar to that of diluted sewage. The removal of this ‘outlier’ reduced the correlation between *E. coli* and enterococci at the Blackburn site to just 0.4 ($p > 0.05$).

Taking the above into consideration, it can be concluded that none of the industrial sites have a true significant correlation between *E. coli* and enterococci, while all three of the residential sites showed significant positive relationships.

This could indicate that, except for the one sample at the Blackburn site, the sources and behaviour of *E. coli* are not the same as that for enterococci at the industrial sites, whereas the opposite is true for the residential sites.

It could also be because all industrial sites had low enterococci levels (which generally have higher associated uncertainties) causing these correlations to be unidentifiable at these sites.

6.1.4 Errors in weekly loads using just one sample per day

The boxplots shown in Figure 14 display the accuracy in using one sample per day to estimate weekly loads of different pollutants at the six study sites. The boxplots were created using the results of the 500 iterations whereby one sample was randomly selected from each of the three available (per day) for the seven day monitoring period. Each randomly selected sample concentration was multiplied by the daily stormwater volume to get a daily load estimation, and the sum of these seven daily load estimations was the estimated weekly load.

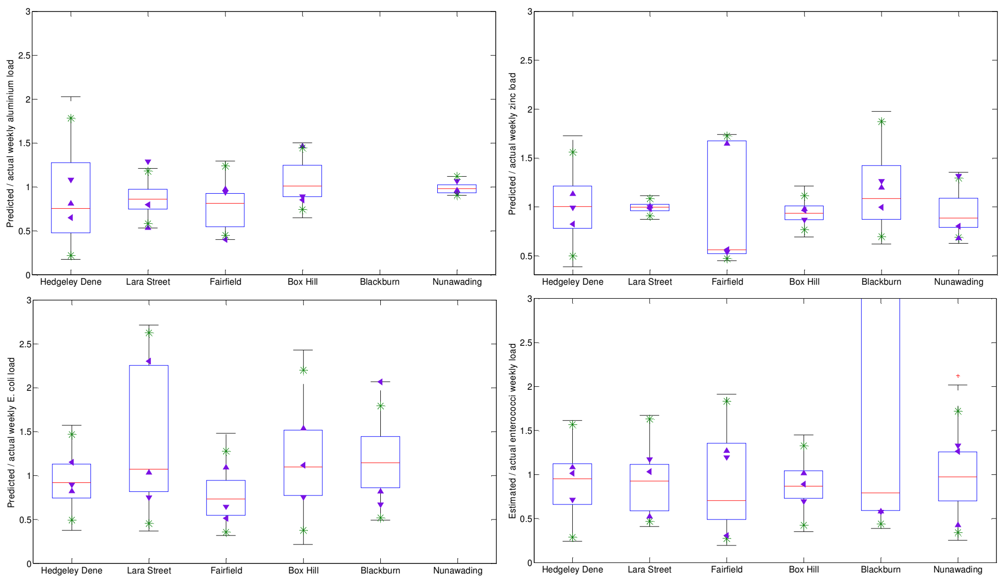

Figure 14. Boxplots showing the accuracy of using just one sample per day (randomly selected from each of the three taken each day) to estimate weekly loads for aluminium (top left), zinc (top right), *E. coli* (bottom left) and enterococci (bottom right). Green stars indicate upper and lower points in 95% confidence boundaries. Purple triangles that point down represent the weekly load if only Morning samples were used to estimate the weekly load, while those that point left and up are similar but for Afternoon and Evening samples, respectively.

Figure 14 indicates that while using one sample per day for weekly load estimations can be accurate for some pollutants at some sites, for other pollutants the error in the weekly load was large. There seems to be no real agreement between catchments, with some sites having very narrow boxplots (indicating high accuracy, such as for aluminium at Nunawading), and other sites having broad boxplots for the same pollutant (indicating high uncertainty, such as for aluminium at the Hedgeley Dene site).

In general, it is shown that the error when using one sample per week to estimate weekly loads is higher for the indicator organisms than for the two heavy metals (Figure 14).

To investigate this for all pollutants, the 95% confidence intervals (and upper and lower bounds) are presented in Table 6. This table reiterates that shown in Figure 14, demonstrating that for some heavy metals (aluminium, barium, zinc, etc.) the accuracy of using just one sample per day to estimate weekly loads varied between the study sites.

This table also reinforces the fact that the error when using one sample per week to estimate weekly indicator organism loads was consistently high (and most often higher than those found for heavy metals).

Table 6. 95% confidence intervals for estimating a pollutant's weekly load using just one sample per day (randomly selected from the three taken for each day).

Pollutant	Hedgeley Dene	Lara Street	Fairfield	Box Hill	Blackburn	Nunawading
Al [mg/L]	1.57 (0.22,1.78)[16]	0.6 (0.58,1.18)[20]	0.78 (0.45,1.24)[20]	0.7 (0.74,1.45)[20]		0.22 (0.9,1.12)
Ba [mg/L]	0.62 (0.68,1.3)	0.32 (0.84,1.16)	0.19 (0.88,1.06)	0.47 (0.85,1.32)	1.75 (0.62,2.38)	0.05 (0.98,1.03)
Cu [mg/L]		0.41 (0.79,1.19)		1.36 (0.3,1.66)[17]		
Fe [mg/L]		0.32 (0.77,1.1)[20]		0.66 (0.72,1.38)		0.18 (0.88,1.07)
Mn [mg/L]				0.61 (0.69,1.3)		0.11 (0.94,1.05)
Ni [mg/L]				0.98 (0.51,1.49)		
Sr [mg/L]	0.42 (0.77,1.19)	0.28 (0.87,1.15)	0.17 (0.92,1.09)	0.16 (0.95,1.11)	0.06 (0.99,1.05)	0.01 (0.99,1.01)
Ti [mg/L]		0.87 (0.39,1.26)[15]				
Zn [mg/L]	1.06 (0.5,1.56)	0.18 (0.91,1.09)	1.25 (0.48,1.73)	0.35 (0.77,1.12)	1.17 (0.7,1.87)	0.61 (0.69,1.3)
E. coli [org/100 mL]	0.98 (0.49,1.47)	2.17 (0.45,2.62)	0.92 (0.35,1.28)	1.82 (0.38,2.2)	1.27 (0.52,1.79)	
Enterococci [org/100 mL]	1.28 (0.29,1.56)	1.16 (0.47,1.63)	1.56 (0.27,1.83)	0.9 (0.42,1.32)[19]	3.14 (0.44,3.58)	1.38 (0.34,1.72)17
TPHs [mg/L]				1.67 (0.32,1.99)[16]		

Values in parentheses indicate the 2.5 and the 97.5 percentile values for the 500 combinations tested. Superscript values indicate the number of samples used in the analysis which were above the detection limit. Missing pollutants and blanks indicate that the analysis could not be conducted due to too many non detections.

After further investigation, a general trend became apparent that for the pollutants in Table **3** that had high variability (i.e. their RSD value was high), the 95% confidence interval presented in Table 6 (representing the accuracy of using just one sample per week) becomes broader.

This means that as the variability of a pollutant in the dry weather samples increased, the accuracy in using one sample per week to estimate that pollutant's weekly load decreased.

This finding is logical, since the weekly load for a pollutant which has concentrations that do not vary (i.e. its RSD is close to zero) will be estimated well using any combination of pollutant concentrations.

Conversely, a pollutant that varies significantly throughout the day and week, will require more samples to be taken to achieve a similar level of accuracy.

These results are simply a product of the central limit theorem.

From the above findings, it was decided to determine whether there would be any quantifiable relationship between a pollutant's variability and the accuracy of the weekly load estimation using one sample per week.

The RSD of a pollutant (from Table **3**) was plotted against the 95% confidence intervals (from Table 6) and this plot is shown in Figure 15. This figure displays a clear positive linear relationship (very close to 1:1) between these two variables.

This type of information can be used to guide future sampling regimes by providing evidence that the sampling regime should be designed specifically based on the pollutant's variability.

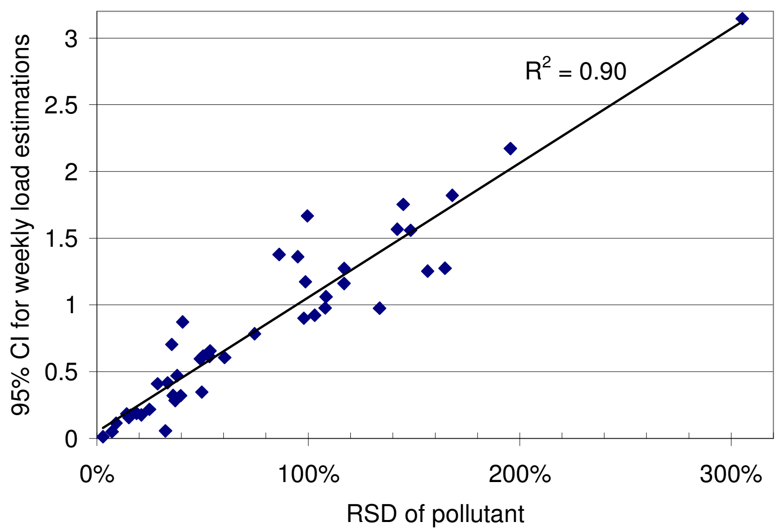

Figure 15. Relationship between the overall variability of the pollutant during dry weather (represented by Relative Standard Deviations from Table 3) and the accuracy of using one random sample per day to estimate weekly loads (represented by the 95% Confidence Interval of the pollutant, obtained from Table 6).

6.2 Wet weather data

In total, eight wet weather events were monitored from Hedgeley Dene and Nunawading (four from each site). Each event varied in the number of samples withdrawn, since sample spacing was flow-weighted.

In total, 43 samples were taken from Hedgeley Dene and 33 samples from Nunawading (Table 7). Summary statistics of each event for each site is provided in Table 7, including maximum flow rates, maximum rainfall intensities, total event volumes and total rainfall depths.

Comparing the flow rates leaving the two sites indicates that the Hedgeley Dene site had a much larger impervious area, with maximum run-off rates and total run-off volumes much larger than that observed at the Nunawading site. Impervious area was not the only factor controlling these flows, with an obvious difference in the magnitude and intensity of the rainfall events monitored at each site (Table 7).

It is interesting to note that the run-off coefficients presented in Table 7 (which represent the effective imperviousness of the catchment) varied quite considerably between the four events at the Hedgeley Dene site.

There are many reasons why these values vary between events, especially since the effective impervious area is often controlled by the intensity and size of the rainfall event. Tree canopy interception is also thought to be a factor in controlling the effective impervious area, with small events being largely affected by canopy interception and larger events being less impacted (especially after canopy saturation).

However, the two largest events at the Hedgeley Dene site had the lowest run-off coefficients, which does not follow that described above. A possible reason for this is related to the uncertainties in the measurements of rainfall and flow rates. For example, spatial errors in rainfall measurements using tipping bucket rainfall gauges could help explain this result.

Table 7. Summary of event data for the eight wet weather events collected at the Hedgeley Dene and Nunawading sites.

	Hedgeley Dene	Nunawading
Number of samples per event		
Event 1	10	4
Event 2	6	6
Event 3	11	6
Event 4	16	17
Total event rainfall depth (mm)		
Event 1	4.8	4.8
Event 2	4.4	2.6
Event 3	23.8	5.6
Event 4	23.6	17.8
Maximum event rainfall intensity (mm/6 min)		
Event 1	0.6	1.4
Event 2	0.6	0.4
Event 3	2.6	0.4
Event 4	3.6	0.8
Total event run-off (kL)		
Event 1	3346	191
Event 2	2038	114
Event 3	6165	209
Event 4	5523	689
Maximum run-off rate (L/s)		
Event 1	499	80
Event 2	316	24
Event 3	1297	29
Event 4	1645	72
Run-off coefficient		
Event 1	0.44	0.36
Event 2	0.29	0.40
Event 3	0.16	0.34
Event 4	0.15	0.35

The wet weather events are presented in Figure 16 and Figure 17 for Hedgeley Dene and Nunawading, respectively. These graphs indicate the run-off rate (L/s) and rainfall intensities (mm/6 min) for each of the four events collected at each site. The coverage of the samples over each event is also indicated, with sampling times included on these graphs.

The water quality characteristics of these samples are presented in the following sections, but all results are provided in

Appendix 4.

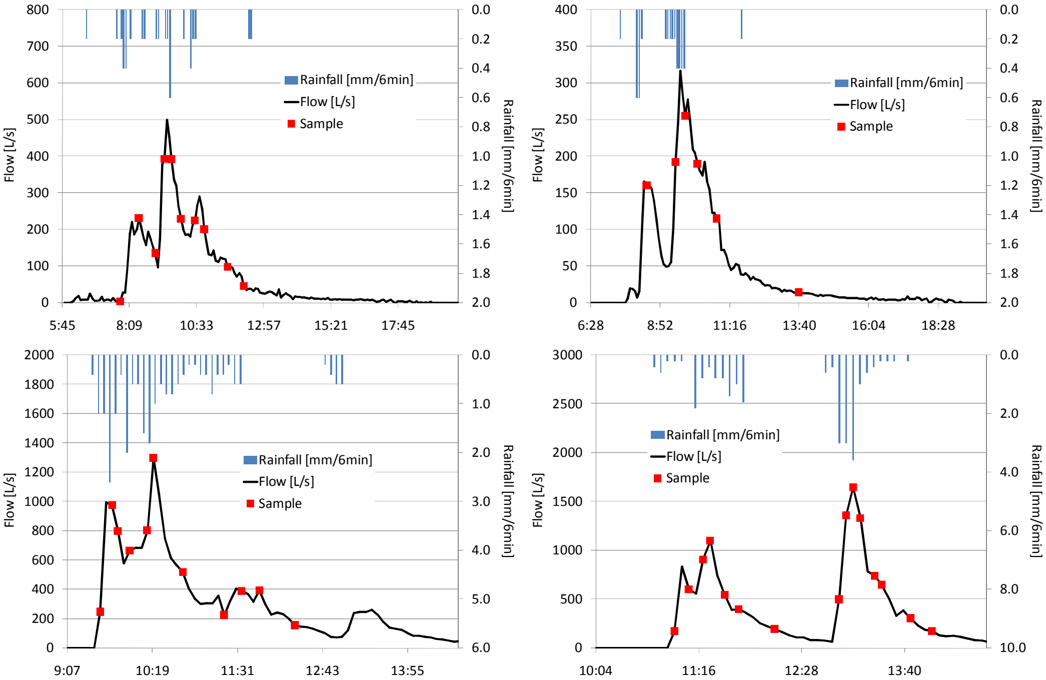

Figure 16. Flow rates, rainfall intensities and sampling times for the four rain events monitored at the Hedgeley Dene catchment. Top left – 5 March 2009, top right – 12 March 2009, bottom left – 14 March 2009, bottom right – 3 April 2009.

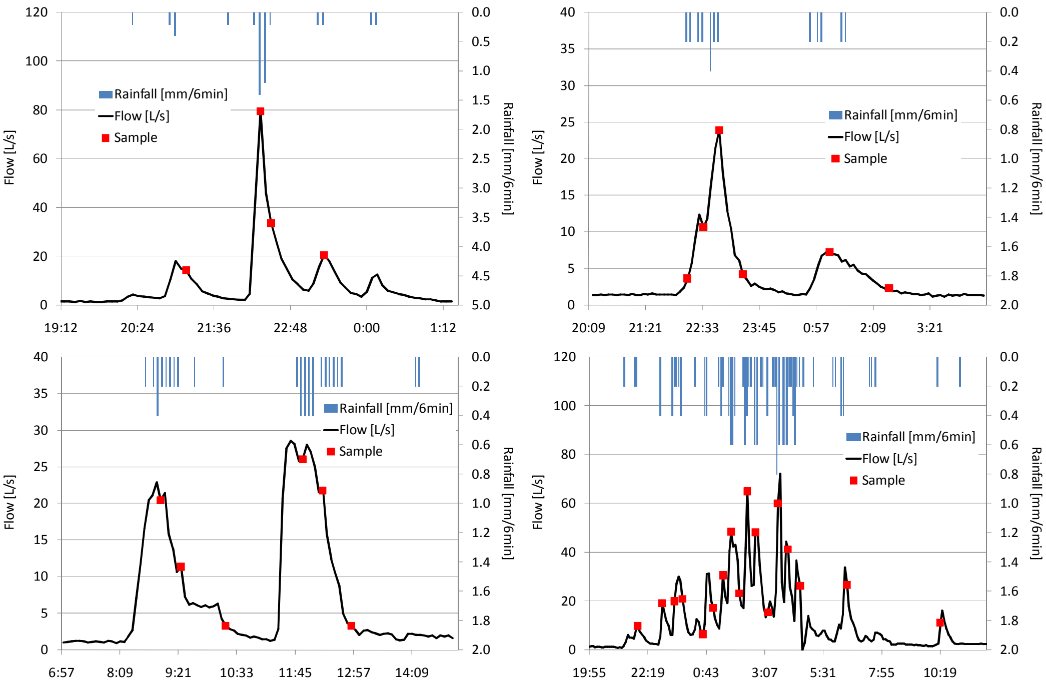

Figure 17. Flow rates, rainfall intensities and sampling times for the four rain events monitored at the Nunawading catchment. Top left – 27–28 May 2009, top right – 2–3 June 2009, bottom left – 9 June 2009, bottom right – 9–10 June 2009.

6.2.1 Between- and within-site variability

Table 8 provides a summary of the water quality constituents found in the wet weather samples taken from Hedgeley Dene and Nunawading. The mean and RSD for each pollutant was calculated using all 43 and 33 samples collected from these two sites, respectively. The boxplots in Figure **18** display how select pollutants vary both within each study site and between the two sites.

Table 8. Mean and Relative Standard Deviations (RSD = standard deviation divided by the mean, expressed as a percentage) of detected constituents in the four wet weather events monitored at each site (76 samples collected in total – 43 at Hedgeley Dene and 33 at Nunawading).

Pollutant	Hedgeley Dene	Nunawading
Aluminium	1.36 (88%)	0.28 (64%)
Barium	0.03 (73%)^{42}	0.02 (61%)^{32}
Copper	0.03 (51%)^{38}	0.02 (78%)^{5}
Iron	1.71 (88%)	0.52 (109%)^{21}
Lead	0.04 (92%)^{34}	0.02 (38%)^{4}
Manganese	0.05 (80%)	0.02 (56%)
Nickel	0.01 (0%)^{3}	ND
Strontium	0.04 (64%)	0.03 (46%)
Titanium	0.05 (73%)^{42}	0.01 (52%)^{9}
Zinc	0.30 (47%)	1.24 (49%)
E. coli	26688 (77%)	340 (118%)
Enterococci	20212 (52%)	668 (111%)
TPHs	0.34 (60%)^{17}	ND

A superscript indicates the number of samples used to calculate the mean and RSD, with all other samples not detected. Absent superscripts indicate all samples were above detection. Heavy metals and TPHs are measured in mg/L, *E. coli* and enterococci are both measured in MPN/100 mL.

- Antimony was not detected at any site.
- Arsenic was always under the detection limit.
- Beryllium was not detected at any site.
- Boron was always under the detection limit.
- Cadmium was not detected at any site.
- Chromium was only detected in three samples at Hedgeley Dene (0.01 mg/L).
- Cobalt was not detected at any site.
- Mercury was not detected at any site.
- Molybdenum was not detected at any site.
- Selenium was not detected at any site.
- Silver was not detected at any site.
- Thallium was not detected at any site.
- Tin was not detected at any site.
- Vanadium was only detected once at Hedgeley Dene (0.01 mg/L).

Many of the pollutants measured were either detected only in a select number of wet weather events, or were never detected during wet weather flows. Antimony, beryllium, boron, cadmium, cobalt, mercury, molybdenum, selenium, silver, thallium and tin were never detected at either Hedgeley Dene or Nunawading during wet weather flows. At the Nunawading site, the wet weather samples never contained detectable levels of TPHs or nickel.

Many other constituents were only present in a select number of samples (e.g. barium, copper, iron, lead and titanium). In general, detection of these pollutants was more common at the Hedgeley Dene site in preference to the industrial site (Nunawading). For all constituents except zinc, the average pollutant concentration found at the Hedgeley Dene site was higher than that for the Nunawading site.

This is an interesting finding, considering that the industrial site was hypothesised to have higher, more consistent, heavy metal and hydrocarbon levels than the residential site.

The higher zinc levels in the industrial catchment are not surprising since the proportion of rooves (often comprised of zinc components) that make up the impervious area in this catchment is likely to be much higher than that of the residential catchment.

Of the heavy metals analysed, iron seemed to vary the most (with RSD of 88% and 109%, for Hedgeley Dene and Nunawading, respectively) while zinc varied the least and had RSD of less than 50% for both sites (Table 8 and Figure **18**).

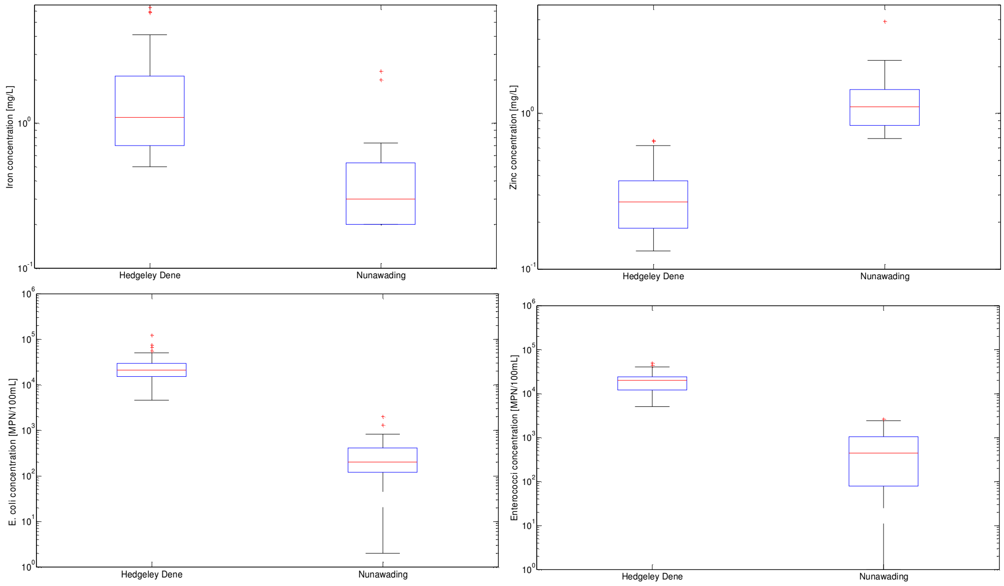

Figure 18. Boxplots showing the distribution of iron (top left), zinc (top right), *E. coli* (bottom left) and enterococci (bottom right) concentrations found during the four wet weather events at Hedgeley Dene and Nunawading.

6.2.2 Within-event variability

The first flush phenomenon has been noted in urban stormwater run-off for many years. However, while the first flush does occur for many stormwater quality pollutants, its presence is not consistent between wet weather events, between different pollutants and between different sites. It is often interesting to investigate whether there is a general trend for pollutant concentrations to decrease as the event progresses.

As a result, Figure **19** is shown to help identify trends between cumulative run-off depth of wet weather events (x-axis) and pollutant concentrations.

It is evident that for zinc, and to a lesser extent iron, the concentrations decreased as the event progressed. To determine whether or not concentrations for other pollutants follow a similar trend, a correlation analysis was conducted for each pollutant's concentrations and the cumulative runoff depth (see Table 9).

The results indicate that there are a number of significant correlations present at the Hedgeley Dene site, with eight heavy metals' concentrations decreasing as wet weather events progress. Only two metals followed that trend at the Nunawading site, possibly because many more of the samples contained levels below detection, making it impossible to conduct these correlation analyses (i.e. correlations could have been seen, but because of the low levels, could not be identified due to non detection). This was especially true for copper, lead and titanium.

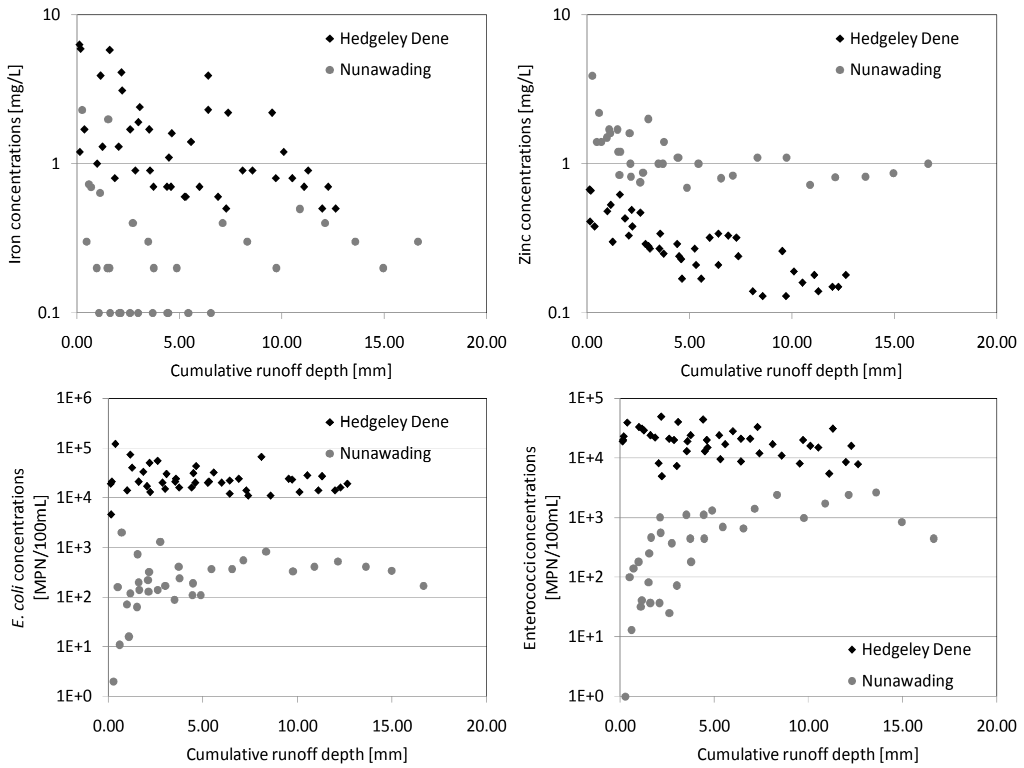

Figure 19. Pollutant concentrations found in the four wet weather events at the Hedgeley Dene and Nunawading sites plotted against cumulative run-off depth [mm] for iron (top left), zinc (top right), *E. coli* (bottom left) and enterococci (bottom right).

These results indicate that a slight first flush might be present for heavy metals and the sources of these pollutants are depleted during wet weather events (whether by rainfall drop impact or run-off shear forces).

For copper, this finding is especially prevalent at the residential site, with a strong negative trend. The main source of copper in urban stormwater is thought to be from the wearing of tyres and brake linings (Makepeace et al. 1995). Copper deposited on the roads in the catchment could be effectively conveyed to the catchment's outlet during rainfall/run-off events. If these events are large enough (in intensity and volume) the deposited copper could be effectively depleted, thus causing a first flush effect.

As mentioned above, a similar correlation was not detected at the Nunawading site because there were insufficient samples above detection to perform statistical testing.

For the microbial indicators, different trends were observed. Figure 19 shows that for the Hedgeley Dene site, the concentrations of *E. coli* generally stayed constant and high throughout the events. However, for enterococci at this site, there was a slight decrease in concentrations with cumulative run-off depth. This trend is also reported in Table 9 as being significant at the 95% level.

Whilst this is in line with other studies that have shown little first flush effects for microorganisms, it should be noted the presence of a first flush for microorganisms in urban stormwater is still subject to debate (Makepeace et al. 1995; McCarthy et al. in press).

Table 9. Linear correlation coefficients between cumulative run-off depths [mm] and pollutant concentrations taken from the four wet weather events at each study site.

	Hedgeley Dene	Nunawading
Al [mg/L]	-0.43	
Ba [mg/L]	-0.57	
Cu [mg/L]	-0.73	
Fe [mg/L]	-0.48	
Pb [mg/L]	-0.36	
Mn [mg/L]	-0.55	-0.39
Ti [mg/L]	-0.45	
Zn [mg/L]	-0.76	-0.45
Enterococci [MPN/100 mL]	-0.38	0.67

Only correlations which were significant at the 95% level were reported.

6.2.3 Correlations between water quality pollutants and flow rates

Many of the heavy metals found at the Hedgeley Dene site, and to a lesser degree at the Nunawading site, were positively correlated with one another (Table 10). Most of these relationships were very strong, with correlation coefficients of greater than 0.90 (these trends were plotted to ensure they were not being skewed by one outlier).

These strong correlations indicate that the majority of these metals most probably originate from similar sources at both study sites and that their behaviour in urban stormwater wet weather flows are similar.

Again, the lack of correlation for the Nunawading site can partly be explained by the low level of heavy metals found at this site, which resulted in a number of samples having metal concentrations less than the detection limit (Table 8), making it difficult to perform a correlation analysis.

Few heavy metals were significantly correlated with flow rates, with aluminium being the only metal increasing in concentration with increasing flow rate. Strontium concentrations decreased significantly with flow rate at both sites, possibly indicating that this pollutant is being diluted in stormwater flows.

The negative correlation between flow rates and zinc concentrations at the Nunawading site also indicates a dilution effect for zinc at this site. However, in such an industrial estate it was hypothesised that there should be a positive correlation with flow rates. This is because shear forces associated with run-off would increase with increasing flow rates, thus allowing more of the catchment's zinc load to be transported to the outlet.

Inspecting these trends further showed that, unlike the other correlations presented in Table 10, this correlation was being skewed by one outlier. While the trend is still generally negative, the removal of this point reduced the correlation coefficient to less than -0.33, which is no longer significant at the 95% level.

Only one correlation was found that significantly explained the TPH concentrations, maybe as a result of the non detects observed for the majority of wet weather TPH samples. The positive correlation found with copper indicates that these two pollutants may share a similar source of contamination.

Copper in stormwater has often been highly correlated to vehicular traffic (Dannecker et al. 1990) because it is sourced from the wear of brake linings, tyres and other moving parts located in cars. TPHs are also often associated with vehicular traffic because of the use of petroleum and diesel products for combustion engines (Fam et al. 1987). It is therefore logical that these pollutants are positively correlated.

Table 10. Correlation coefficients between wet weather pollutant concentrations and flow rates measured at Hedgeley Dene and Nunawading (presented in that order, separated by a solidus).

	Ba [mg/L]	Cu [mg/L]	Fe [mg/L]	Pb [mg/L]	Mn [mg/L]	Sr [mg/L]	Ti [mg/L]	Zn [mg/L]	*E. coli* [MPN/100mL]	Flow rate [L/s]
Al [mg/L]	0.93 / 0.47	0.77 / --	0.99 / 0.69	0.96 / --	0.97 / 0.38		0.98 / 0.86	0.73 / --	-- / 0.43	-- / 0.47
Ba [mg/L]		0.86 / --	0.95 / 0.64	0.93 / --	0.96 / 0.47		0.94 / --	0.85 / 0.44		
Cu [mg/L]			0.80 / --	0.72 / --	0.85 / --		0.78 / --	0.92 / --		
Fe [mg/L]				0.97 / --	0.97 / 0.90		0.98 / --	0.76 / 0.68		
Pb [mg/L]					0.95 / --		0.95 / --	0.70 / --		
Mn [mg/L]						-- / 0.68	0.96 / --	0.85 / 0.60		
Sr [mg/L]								0.30 / 0.40		-0.50/-0.73
Ti [mg/L]								0.73 / --		
Zn [mg/L]										-- / -0.39
TPHs [mg/L]		0.61 / --								
Ent. [MPN/100 mL]						-- / -0.48		0.35/ -0.46	0.40 / --	-- / 0.47

Only statistically significant correlation coefficients are reported (i.e. $p < 0.05$). Dashes or empty cells indicate non significant or absent correlations (due to detection limit problems).

Correlations between heavy metals and indicator organisms occur on three occasions, with *E. coli* and aluminium positively correlated (Nunawading), strontium and enterococci negatively correlated (Nunawading) and enterococci and zinc being positively correlated at Hedgeley Dene and negatively correlated at Nunawading.

The correlation between strontium and enterococci could have been a product of the strong negative correlation between flow and strontium, and the positive correlation between enterococci and flow at this site (i.e. because strontium is negatively correlated with flow rates and enterococci is positively correlated with flow rates, strontium and enterococci are hence positively correlated).

A similar explanation could be made for the negative correlation between zinc and enterococci at the Nunawading site.

The positive correlation between *E. coli* and enterococci at the Hedgeley Dene site means that these two indicators are likely to have very similar sources, and behave similarly in wet weather flows. This is similar to what was found for the dry weather data, with positive correlations between *E. coli* and enterococci at this site. As with the dry weather data, there was no correlation between *E. coli* and enterococci at the industrial site, again iterating that the sources and behaviour of these indicator organisms at industrial sites may not be related.

6.2.4 Errors in loads using a small number of samples per event

To understand the impact of taking just one, two, three or four grab samples from a wet weather event to estimate downstream loads, a boot strapping methodology was adopted. **Figure** 20 shows the results, and indicates that as the number of samples used per event to estimate wet weather loads increases from one to four, the spread of the boxplots tends to decrease. This is logical since more samples are being used to estimate the load, hence capturing more of the likely variability in the pollutant.

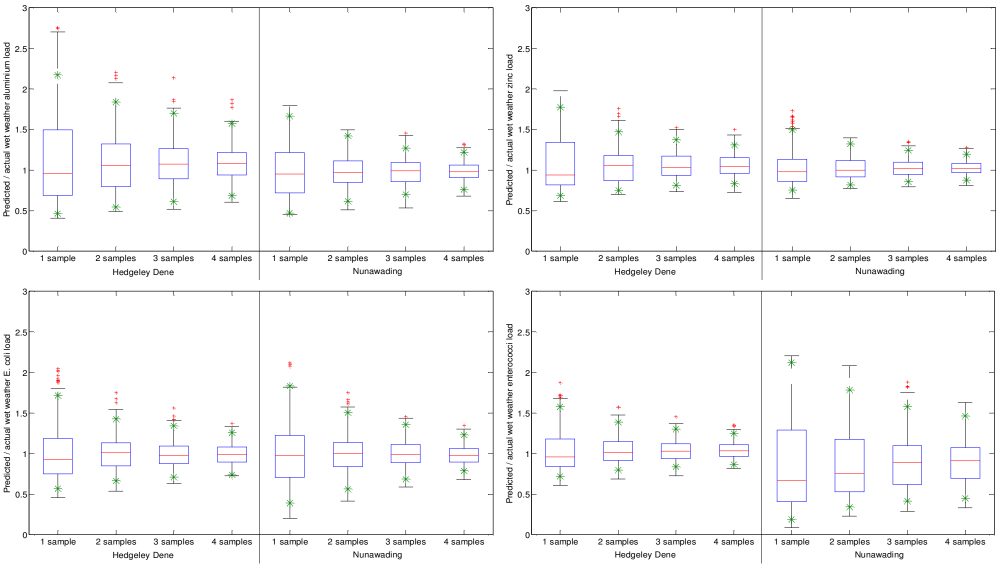

Figure 20. Boxplots showing the accuracy of using one, two, three and four samples randomly selected from each wet weather event to estimate total wet weather loads at each site. Green stars indicate 95% confidence interval.

Figure **20** shows that for some pollutants, taking just one or two samples during an event produces reasonable estimates of the total wet weather load (to within 50% of the actual value, e.g. zinc at Nunawading). For other pollutants, however, even taking four samples from each event does not produce accurate wet weather event load estimates (e.g. enterococci at Nunawading).

Table 11 shows the 95% confidence intervals for estimating the total wet weather event load for each site and each pollutant using one, two, three and four samples from each of the available events. There is an amount of variability in these 95% confidence intervals. The intervals were always greater at the Hedgeley Dene site for heavy metals, but the opposite was true for microbial indicators (with Nunawading producing the larger confidence intervals).

As explained in section 6.1.4, it was expected that the accuracy of using a few samples from each event to estimate wet weather loads was related to the variability of the pollutant at each site.

A plot of the confidence intervals obtained from Table 11 and the relative standard deviations from Table 8 is provided in Figure 21. Four plots are presented in this figure, each representing a different number of samples used to estimate the wet weather load.

Although not as significant as that shown in Figure 15, the trends in this graph still indicate the direct relationship between a pollutant's variability and the accuracy of using, for example, just one sample from each event to estimate pollutant loads.

Table 11. 95% confidence intervals for estimating a pollutant's wet weather load using just one, two, three or four samples randomly selected from each event.

	Hedgeley Dene				Nunawading			
	1 sample	2 samples	3 samples	4 samples	1 sample	2 samples	3 samples	4 samples
Al [mg/L]	1.70	1.29	1.09	0.88	1.20	0.80	0.57	0.46
Ba [mg/L]	1.63^{42}	1.14^{42}	1.02^{42}	0.83^{42}	1.18^{32}	0.67^{32}	0.48^{32}	0.36^{32}
Cu [mg/L]	1.34^{38}	0.96^{38}	0.82^{38}	0.70^{38}				
Fe [mg/L]	1.83	1.33	1.04	0.83				
Pb [mg/L]	2.23^{34}	1.62^{34}	1.30^{34}	1.02^{34}				
Mn [mg/L]	1.66	1.26	0.99	0.79	0.78	0.51	0.36	0.26
Sr [mg/L]	0.89	0.64	0.49	0.39	0.87	0.57	0.41	0.36
Ti [mg/L]	1.54^{42}	1.14^{42}	0.88^{42}	0.72^{42}				
Zn [mg/L]	1.09	0.72	0.56	0.48	0.74	0.51	0.39	0.32
E. coli [MPN/100 mL]	1.15	0.76	0.63	0.52	1.44	0.94	0.67	0.44
Enterococci [MPN/100 mL]	0.86	0.59	0.47	0.38	1.93	1.44	1.16	1.02

Superscript values indicate the number of samples used in the analysis which were above the detection limit. Missing pollutants and blanks indicate that the analysis could not be conducted due to too many non detections.

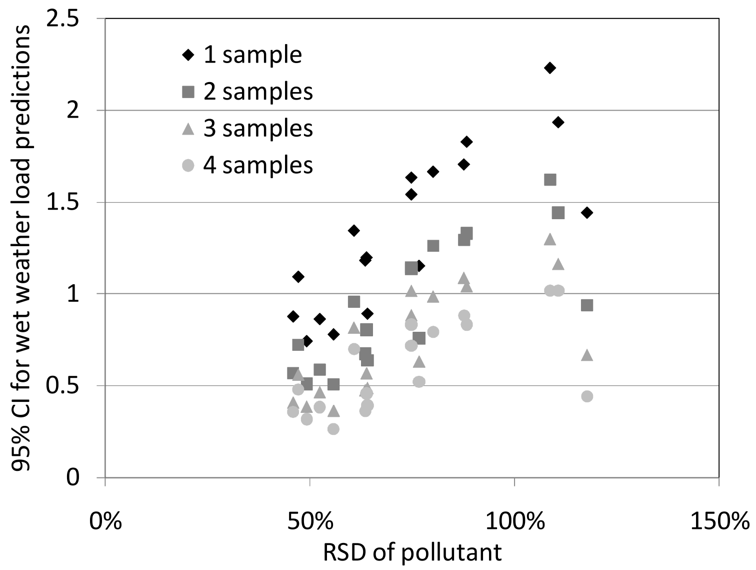

Figure 21. Relationship between the overall variability of a pollutant during wet weather (represented by Relative Standard Deviations given in Table 8) and the accuracy of using just one, two, three or four random samples per event to estimate total wet weather loads (represented by the 95% confidence interval (CI) of the pollutant, obtained from Table 11).

This section has presented information which can be used to help identify the number of samples required to be collected during events to accurately estimate wet weather loads.

It clearly demonstrates that it is possible to obtain accurate total wet weather loads from taking just one random sample from each event. It also illustrates, however, that there are definitely different wet weather sampling regime requirements for different pollutants at different sites.

While many of the heavy metals at a site could be assumed to share similar sampling requirements, some heavy metals are clear outliers (e.g. strontium at Hedgeley Dene). This is similar for indicator organisms.

While these general within-site assumptions of equality may be sufficient enough for load estimations, from the results presented here it is not possible to assume that the sampling requirements of a pollutant at one site is the same as for the same pollutant at a different site.

In any case, further collection and subsequent analysis of the data will help us understand the true underlying distributions (i.e. true population variability) for different pollutants. This could then be used to obtain 'minimum' sampling requirements to meet the likely maximum variability of a pollutant.

6.3 Comparison between wet weather and dry weather concentrations and loads

Comparison of concentrations

Comparing the concentrations of the pollutants measured during dry and wet weather periods can help explain sources and the behaviour of pollutants in stormwater.

It can also help determine whether efforts should concentrate on treating rainfall events, or whether treatment of dry weather flows is more important.**Figure** 22 provides boxplots that allow a comparison between dry weather and wet weather concentrations of select pollutants. While iron concentrations were relatively similar during dry and wet weather periods, zinc concentrations at both sites were generally higher during wet weather periods.

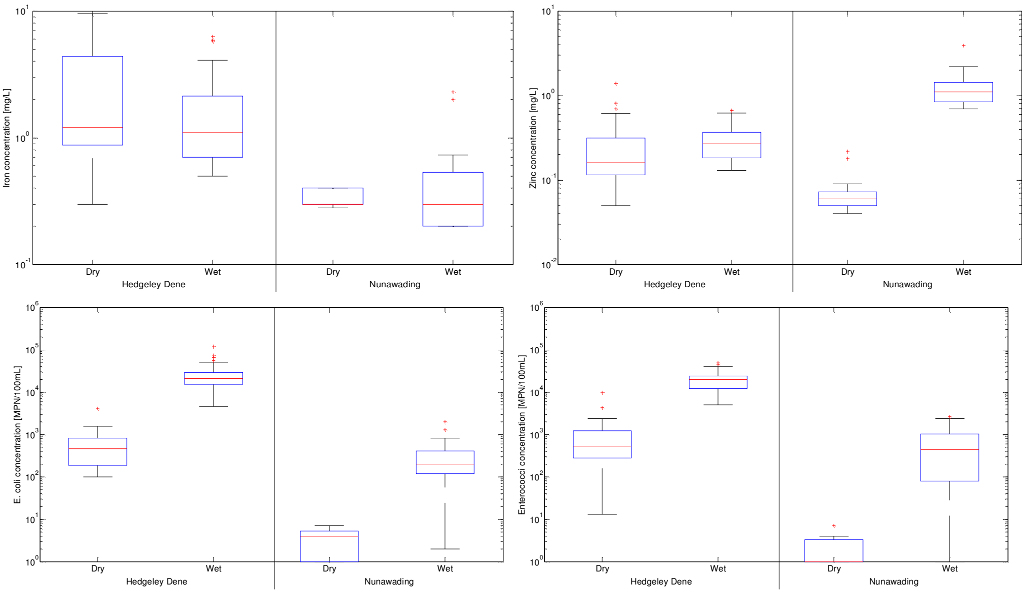

Figure 22. Boxplots comparing the concentrations of iron, zinc, *E. coli* and enterococci during dry weather and wet weather at Hedgeley Dene and Nunawading.

Table 12 summarises Table 3 and Table 8 to provide easy comparisons between pollutant concentrations during dry and wet weather periods.

Heavy metal concentrations at the Hedgeley Dene site were generally higher during dry weather periods, with the exception of aluminium and zinc. There is no such trend at the Nunawading site, with some pollutants having higher concentrations in wet weather, and others vice-versa. Variability of these heavy metals also changed between dry and wet weather, but no general trends are obvious.

Comparing the mean values obtained during wet and dry weather periods can help identify the sources of these heavy metals. For instance, average zinc concentrations increased during wet weather events at both sites (more significantly at the Nunawading site), clearly indicating the presence of zinc sources during rainfall periods.

On the other hand, the significant reduction in strontium levels during wet weather at Hedgeley Dene (i.e. Table 12 shows the wet weather levels are almost six times lower than in dry weather) indicates that this heavy metal might not have significant sources during rainfall events, and is really only being diluted during high flow rates.

This is exactly what is shown in Table 5 and Table 10, where strontium concentrations were negatively correlated with flow rates, verifying that as flow rates increase, the concentration of strontium decreases.

Table 12. Average and relative standard deviations (shown in parentheses) of pollutants in dry weather and wet weather flows at the Hedgeley Dene and Nunawading sites.

	Hedgeley Dene		Nunawading	
Pollutant	Dry weather	Wet weather	Dry weather	Wet weather
Aluminium	1.09 (142%)[16]	1.36 (88%)	0.17 (25%)	0.28 (64%)
Barium	0.06 (50%)	0.03 (73%)[42]	0.03 (7%)	0.02 (61%)[32]
Copper	0.03 (74%)[14]	0.03 (51%)[38]	ND	0.02 (78%)[5]
Iron	2.65 (108%)[11]	1.71 (88%)	0.33 (14%)	0.52 (109%)[21]
Lead	0.05 (90%)[7]	0.04 (92%)[34]	0.01 (0%)[1]	0.02 (38%)[4]
Manganese	0.16 (129%)[11]	0.05 (80%)	0.06 (9%)	0.02 (56%)

Nickel	0.01 (43%)[3]	0.01 (0%)[3]	ND	ND
Strontium	0.22 (33%)	0.04 (64%)	0.08 (3%)	0.03 (46%)
Titanium	0.04 (106%)[10]	0.05 (73%)[42]	ND	0.01 (52%)[9]
Zinc	0.30 (108%)	0.30 (47%)	0.07 (60%)	1.24 (49%)
E. coli	655 (134%)	26688 (77%)	3 (71%)[9]	340 (118%)
Enterococci	1331 (165%)	20212 (52%)	2 (86%)[17]	668 (111%)
TPHs	0.15 (0%)[1]	0.34 (60%)[17]	ND	ND

ND indicates the pollutant was not detected, superscript numbers indicate the number of samples which were above detection, absent superscripts indicates all samples were used.

For TPHs, the number of detections at the Hedgeley Dene site grew from just one in dry weather flows to 17 in wet weather flows, truly indicating that the main source of hydrocarbons in this catchment is only prevalent during rainfall events.

This is logical since sources of hydrocarbons during dry weather flows should not be high in residential areas, and if present would be highly intermittent (e.g. someone washing their engine over a stormwater grate may create detectable levels). However, oil and petroleum products which are deposited onto the surfaces of the catchment during dry weather periods are effectively washed to the catchment's outlet by the kinetic energy of rainfall and the shear forces of run-off.

It is very interesting that Nunawading's samples never had detectable levels of TPHs, especially since many of the businesses in this catchment are focused on motor repairs. Dry weather levels could have been diluted in this site's high flow rates, but non detectable levels in wet weather flows is difficult to explain.

Referring to Table 12 and Figure **22**, *E. coli* and enterococci concentrations tended to increase in wet weather events, generally by several orders of magnitude at each site. The Hedgeley Dene site saw a decrease in the variability of these microbes in wet weather periods, while the Nunawading site had a large increase in variability during wet weather.

This indicates that the sources of *E. coli* and enterococci at the Hedgeley Dene site were more constant during wet weather than during dry weather. The opposite can be said for the Nunawading site.

Comparison of loads

Table 13 provides an overview of the dry weather and wet weather annual loads for each pollutant at Hedgeley Dene and Nunawading.

It is interesting to note the large amount of aluminium, iron and zinc which were delivered to downstream systems from both sites, but more notably from the residential site. Over 4.3 x 10^{13} *E. coli* also came from the residential catchment each year, which is equivalent to that found in around 1200 kg of human faeces (calculated using a human faecal concentration of 3.6 x 10^7/g; Leeming et al. 1998).

The total loads from the industrial catchment were always much lower than that from the residential catchment, mainly due to its smaller size and therefore lower run-off volumes.

However, Nunawading's heavy metal dry weather loads were always greater than those of Hedgeley Dene, even though the concentrations at the industrial site during dry weather were generally much lower than those found at the residential site (Table 12).

A logical reason for these higher loads is the high dry weather flows at the Nunawading site, with average flow rates exceeding 1 L/s during dry weather (compared to less than 0.2 L/s for Hedgeley Dene).

This is an interesting finding considering the sizes of each catchment. If only stormwater run-off was being discharged to the stormwater pipe system, then baseflow rates should be relative to the catchment's area (or more specifically to its pervious area, assuming groundwater infiltration is negligible in these areas). This data clearly shows that dry weather flows, and hence a certain portion of wet weather flows, are comprised of anthropogenic sources of water.

Table 13. Total annual loads sourced from wet and dry weather periods for select pollutants at Hedgeley Dene and Nunawading.

	Hedgeley Dene			Nunawading		
	Wet weather load	Dry weather load	% wet weather	Wet weather load	Dry weather load	% wet weather
Al [kg/yr]	197.2	5.0	98%	7.2	8.1	47%

Ba [kg/yr]	4.6	0.4	93%	0.6	1.4	29%
Cu [kg/yr]	3.4	0.1	96%			
Fe [kg/yr]	247.0	8.7	97%	8.5	15.4	36%
Mn [kg/yr]	7.0	0.5	93%	0.5	3.0	15%
Sr [kg/yr]	6.4	1.5	81%	0.6	3.6	14%
Zn [kg/yr]	43.4	1.7	96%	28.5	3.5	89%
E. coli [MPN x 10^8/yr]	430000	490	100%	960	6.0	99%
Enterococci [MPN x 10^8 /yr]	310000	900	100%	2000	8.7	100%

Blank cells indicate the pollutant has too many non detects for the analysis.

At Hedgeley Dene the loads contributed to by wet weather events dominated the total load being delivered to downstream systems from this catchment. This holds true for all pollutants, with 90% of most pollutant loads being sourced from wet weather. This is partially due to the very low flows found at this catchment during the dry weather monitoring period.

At the Nunawading site a different trend was observed for the heavy metals. Again, this is partially due to the quite high and consistent flows found at the Nunawading site during the dry weather monitoring periods.

These results demonstrate the differences which can occur between different catchments, and that management decisions need to take into account all variables when deciding to implement certain mitigation options.

The results suggest that the treatment of Hedgeley Dene's dry weather flows is not going to drastically reduce loads going to downstream systems. In fact, in order to reduce a large percentage of the total pollutant load, wet weather flows need to be mitigated. This may require large amounts of money and infrastructure to achieve, since the volume of water would require a large treatment system.

On the other hand, treatment of Nunawading's dry weather flows has the potential to remove a large proportion of the annual pollutant load being delivered to downstream systems. The treatment of this water would be relatively straightforward since treating 1 L/s is easily achievable using a small Water Sensitive Urban Design system.

6.4 Analytical uncertainty of laboratory methodologies

During the dry weather period, triplicate samples were taken on one occasion at each site to help assess the analytical uncertainty of the laboratory methods.

Some heavy metals were never detected in these triplicate samples, making it impossible to assess this uncertainty for the following: antimony, arsenic, beryllium, boron, cadmium, chromium, cobalt, lead, mercury, molybdenum, selenium, silver, thallium, tin, titanium and vanadium.

For the other heavy metals, the triplicate results were all very close, indicating that the analytical uncertainty of heavy metals was generally very low, with most heavy metals being identical in all three replicate samples. One large difference was observed at the Box Hill site for nickel concentrations, which varied by more than 50% between replicates (0.14 mg/L, 0.07 mg/L, 0.07 mg/L).

The analytical uncertainty for microbes was much more substantial than that of heavy metals, with samples often varying by over 50% within triplicates (Figure 23). For example, the concentrations in the triplicate samples obtained from the Box Hill site were: 1400, 1900 and 3000 MPN/100 mL.

This shows that while the error in the laboratory method was far less than an order of magnitude (which is often considered to be the accuracy of microbial measurements), the uncertainty was still considerable.

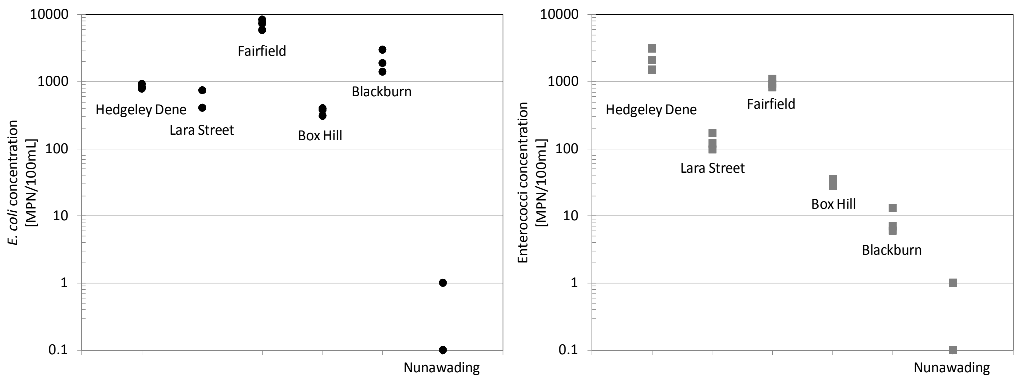

Figure 23. Triplicate results for *E. coli* (left) and enterococci (right). Each point on these graphs indicates the concentration of one of the triplicate samples. At Nunawading, two of the triplicate samples had non detectable *E. coli* and enterococci concentrations, while one had a concentration of 1 MPN/100 mL for both indicators.

TPHs were only detected in the triplicate samples collected from the Box Hill site. However, only one of the three samples had detectable levels of TPHs (0.36 mg/L), with the other two samples having non detectable TPH concentrations.

This translates into a very high level of uncertainty, considering the detection limit for TPH analysis is around 0.01 mg/L (over 36 times lower than that detected in one of the samples). This could have been caused by a number of different uncertainty sources, including sampling, laboratory, and transportation.

For the majority of pollutants measured during the sampling regime, there were only a few which had high associated analytical uncertainties. It is unlikely that the analytical uncertainties in the pollutants investigated caused all of the variability seen between or within each of the study sites.

Actual biophysical processes (e.g. rainfall kinetic energy, flow shear stress, human behaviour, etc) are therefore controlling these variations (i.e. not just random/systematic uncertainties in their measurements causing these variations).

However, these uncertainties definitely contributed to the observed variability, and should not be ignored, especially for the indicator organisms.

For example, while the RSD of *E. coli* at the Blackburn site was high during dry weather (at 117%), the RSD of the triplicate samples taken from the same site was over 38%, indicating that a significant proportion of the variability in *E. coli* observed at this site could have been caused by analytical uncertainties, and not the actual variation in pollutant levels.

7 Conclusions

The results of this research revealed the intermittent and variable nature of urban stormwater systems, with flow rates and pollutant concentrations varying by a large degree in both dry weather and wet weather events.

The magnitude and variability of a pollutant load was rarely consistent between study sites, and rarely consistent among land use types.

It was also determined that the variability for some pollutants between catchments and within sites is not just caused by the actual fluctuation of the pollutant's concentrations, but is also due to the inherent analytical uncertainty in the laboratory method used to quantify the pollutant. This was especially the case for *E. coli* and enterococci, which had large analytical uncertainties, but was generally not the case for heavy metals.

The variability of the pollutants has a large influence on the accuracy of certain sampling strategies on pollutant load estimations. For example, a pollutant which has concentrations that vary quite considerably during dry weather flows cannot have its weekly loading accurately estimated by one random sample per day.

On the other hand, a pollutant load which is fairly constant during dry weather periods could have its load accurately estimated using the same sampling regime. This argument holds true for wet weather as well, with the variability in the pollutant's concentrations governing how many samples are required to be taken during each event for accurate wet weather pollutant load estimations.

While this dataset has helped us understand the variability of these pollutants between and within each study site, there is insufficient data to extrapolate these findings directly to other catchments.

More data collection is required to understand the underlying population distribution of each pollutant at a range of different sites. This population distribution can then be used to estimate the likely pollutant load coming from an unmonitored catchment.

Until this is completed, it will be necessary to monitor catchments to understand their pollutant levels and their associated variability.

8 Recommendations

This dataset can help future studies to develop these sampling strategies. For example, if a pollutant's variability at a site can somehow be estimated accurately, then the information presented within this report can help estimate the likely sampling regime requirements to adequately assess this pollutant's loads.

However, without an accurate estimate of the pollutant's variability, it is very hard to specify an adequate sampling strategy which is both cost effective and produces accurate results.

Estimating this variability is a difficult task, mainly because it is so pollutant- and site-dependent.

There are several solutions that could be employed to obtain the required sampling regime for a pollutant. Firstly, a 'safe' sampling regime could be adopted, where it is assumed that the variability of the pollutant is in the upper range identified within this report. From this variability, it would be possible to estimate the required number of samples needed for accurate load estimates using a boot strapping methodology, as presented in this report.

This first method has the advantage of likely producing very accurate load estimations, but is associated with increased sampling costs because of the high variability assumption.

The second option would be to employ a dynamic sampling strategy, where the number of samples taken is adapted based on previous sample information. For instance, a sampling method may start out similar to that of the 'safe' method presented above, but after a certain number of days, weeks or months, this sampling strategy is adapted to suit the variability which has been seen in the previously collected data.

This type of sampling method has the advantage of reducing costs quite considerably, whilst still ensuring accurate load estimates are obtained – although the demand on management and the alteration of sampling strategies during a sampling regime may introduce a number of barriers for implementation of this strategy.

This method could be employed for both dry and wet weather load estimations. In either case, if the monitoring regime is required to characterise a number of pollutants, it is more than probable that one of these pollutants is going to govern the sampling regime.

For example, if strontium and *E. coli* are to be monitored, then it is likely that the variability of these pollutants is such that the number of samples required for accurate *E. coli* load estimations are much higher than that for strontium. Since sampling has to occur more regularly for *E. coli*, and considering that sending sampling teams out to each catchment is often the major cost, it would make little difference to the overall budget to analyse all samples for strontium as well.

In any case, more data collection will help us to fully understand the variability of these pollutants in urban stormwater, and thus provide us with appropriate datasets on which to base these future sampling designs.

In fact, more data could start to help us understand the behaviour of these pollutants at a physical level, so that accurate water quality models could be developed. These models (which would have to be partly stochastic) could use certain inputs to identify the likely magnitude and variability of each pollutant, and hence could help with designing sampling strategies in the future.

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