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Understanding the role of land use for urban stormwater management in coastal waterways

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Abstract

A holistic understanding of the quality and quantity of stormwater in the context of catchment land use plays a crucial role in stormwater management. This study investigated the quality and quantity of stormwater from forested, residential, industrial, and mixed land use areas. Water samples were collected from seven sites over two years at different stages of the runoff hydrograph using fixed sampling stations. Analysis of physicochemical and hydrological variables showed different patterns across the four land use types at various flow conditions highlighting the complex nature of stormwater quality influenced by catchment and rainfall characteristics. Mean concentrations of dissolved organic and oxidised nitrogen (DON and NO_x-N) and dissolved organic and filterable reactive phosphorus (DOP and FRP) in stormwater from industrial, mixed-use and residential catchment types were statistically different from stormwater originating from a forested catchment. On average, residential, mixed-use and industrial catchments transported over 50 times more NO_x-N to the receiving waters compared to forested catchments. Under high flow conditions, total phosphorus, FRP and total suspended solids (TSS) were mobilised, indicating that phosphorous export is directly related to sediment export regardless of the land use. The study outcomes contribute to the formulation of more effective stormwater management strategies to deal with the drivers of nutrients and TSS inputs resulting from modified land use types to minimise the urbanisation impacts on aquatic biota. In particular, the elevated dissolved nitrogen fractions from all the catchment types other than the forested catchment is a concern for receiving waters, as these can potentially impair water quality and impact the ecosystem health of downstream water bodies such as Intermittently Closed and Open Lakes or Lagoons (ICOLL). The stochastic nature of hydrology and corresponding nutrient loads should be prioritised in stormwater management action plans. However, as space limitations hinder the expansion of vegetation cover and retrofitting stormwater management devices, a paradigm shift in stormwater management is required to achieve the desired outcomes. The study outcomes further indicate that a one-size-fits-all approach to stormwater management may not deliver the desired outcomes, and a suite of tailor-made approaches targeting various flow conditions and catchment surface types is needed.

Keywords: Stormwater quality, water quality monitoring, stormwater pollutant processes, nutrients, land use

1. Introduction

Overland runoff from storm events and dry weather baseflow is among the most significant sources of anthropogenic pollutants in receiving water bodies (Kong et al., 2021, Francey et al., 2010, Fletcher and Fisk, 2017). Presently, about 40% of the world's population lives within 100 km of the coast meaning that anthropogenic activities have a profound influence on the quality and quantity of stormwater inputs to coastal waterways (Commonwealth of Australia, 2002, Walsh et al., 2004, Ferreira et al., 2016). Numerous studies agree that the quality and quantity of runoff are influenced by land use intensification (Jennings and Jarnagin, 2002, Goonetilleke et al., 2005; Liu et al., 2013). As cities expand, vegetation cover is cleared, and the land surface is converted from pervious to impervious surfaces. Past research has highlighted that as little as 10% of imperviousness in a catchment can trigger degradation effects in the receiving aquatic environment (Brun and Band, 2000, Wang et al., 2001). Similarly, the impacts on stormwater quality and quantity due to the increase in impervious area and associated anthropogenic activities on aquatic fauna and waterway geomorphology have been well documented (Wang et al., 2001, Booth et al., 2002, Settacharnwit et al., 2003). Consequently, a holistic understanding of the impacts on the quality and quantity of stormwater in the context of catchment land use changes is necessary for formulating effective urban stormwater management strategies.

Past studies have identified the relationships between stormwater quality, land use and impervious area characteristics. For example, stormwater flowing over roofs is commonly associated with zinc contamination, lawns and driveways are associated with phosphorus loading (Bannerman et al., 1993), and parking lots and roads are associated with organic and inorganic toxicants (Gbeddy et al., 2022, Ma et al., 2021, Brattebo and Booth, 2003, Perera et al., 2021). On the other hand, stormwater quantity is determined by rainfall intensity, soil characteristics, and landscape and land use characteristics (WHO, 1991). Consequently, place-based heterogeneity of stormwater quality and quantity makes the cross-jurisdiction comparison of its spatiotemporal patterns challenging. The knowledge gaps in stormwater management area are largely due to the lack of understanding of how different land use types contribute to both, the quality and quantity of stormwater, as well as the pollutant budget in the receiving environment, the need for management interventions, and how to prioritise and mitigate stormwater risks (Al Bakri et al., 2008, Liu et al., 2012, Wijesiri et al., 2018).

Urban stormwater management is a complex task governed by multiple factors that often extend beyond mathematical modelling and current treatment technologies recommended for this purpose (Boogaard et al., 2014, Barbé et al., 1996). The generation of large quantities of stormwater is inevitable as the catchment surface characteristics are altered for human needs. As a result of storm events that can generate a large volume of stormwater and the inherent complexity of changes in water quality, several technologies and approaches have emerged that can help achieve urban water sustainability goals by capturing stormwater for treatment and reuse before discharging it to the receiving environment. For example, technologies grouped under Best Management Practices (US), Low Impact Development (China), Water Sensitive Urban Design (Australia), and Sustainable Urban Drainage Systems (UK) which have emerged over the past decades include various technologies aimed at detaining, treating and harvesting stormwater and rainwater as core elements in conjunction with climate-resilient adaptation strategies for urban planning and integrated urban water cycle management (Hart et al., 2022). Most of these management strategies focus on mitigating hydrological and ecological issues associated with stormwater, replicating the pre-urbanised runoff hydrograph and minimising environmental damage and risk. Another approach to stormwater management is source tracking of pollutants and implementing best practice management strategies at hotspot locations to minimise downstream pollution (Bannerman et al., 1993, Al Bakri et al., 2008).

For these strategies to succeed, understanding place-based temporal patterns of stormwater quality and quantity are essential. In this context, place-based characteristics of stormwater

are defined as quality and quantity differences due to unique catchment characteristics and weather patterns. Past studies of this nature are limited, particularly those that have investigated the quality and quantity of coastal stormwater networks terminating at Intermittently Closed and Open Lakes or Lagoons (ICOLL). ICOLLs provide habitat for a wide range of aquatic species and are intermittently closed to the ocean. In Australia, there are over 100 ecologically sensitive and important ICOLLs where the quality and quantity of stormwater affect nutrient dynamics and aquatic health (McSweeney et al., 2017, Scanes et al., 2020). The present study was formulated to bridge this knowledge gap and to understand the characteristics of the quality and quantity of stormwater originating from different land use types, namely, urban, industrial, residential and forested, and their environmental impacts on ICOLLs.

It is expected that the knowledge gained from this study will assist catchment managers in prioritising stormwater management efforts through control target setting and best practice management planning. The research investigations were undertaken in the context of an integrated approach to stormwater management aiming to deliver improved environmental outcomes by considering variable flow conditions and catchment surface types.

2. Materials and methods

2.1 Case study locations and catchment characteristics

Stormwater quality and quantity were monitored at seven sites across the Northern Beaches region of greater Sydney, New South Wales, Australia. The sites included: stormwater drains receiving runoff from residential (n=3), industrial (n=1) and mixed land use (n=3) areas, and one site was a natural stream channel receiving runoff from forested land use (n=1) (**Figure 1**) to obtain baseline data. The study sites occur in the Australian climatic zone 5 (Warm temperate). The annual total rainfall reported for 2019 and 2020 were 824mm and 1258mm, respectively (Collaroy weather station-33.74 °S, 151.31 °E) (Australian Government, 2022, BOM, 2022b). The mean annual temperature varies between 16 °C to 29 °C, depending on the season (BOM, 2022a).

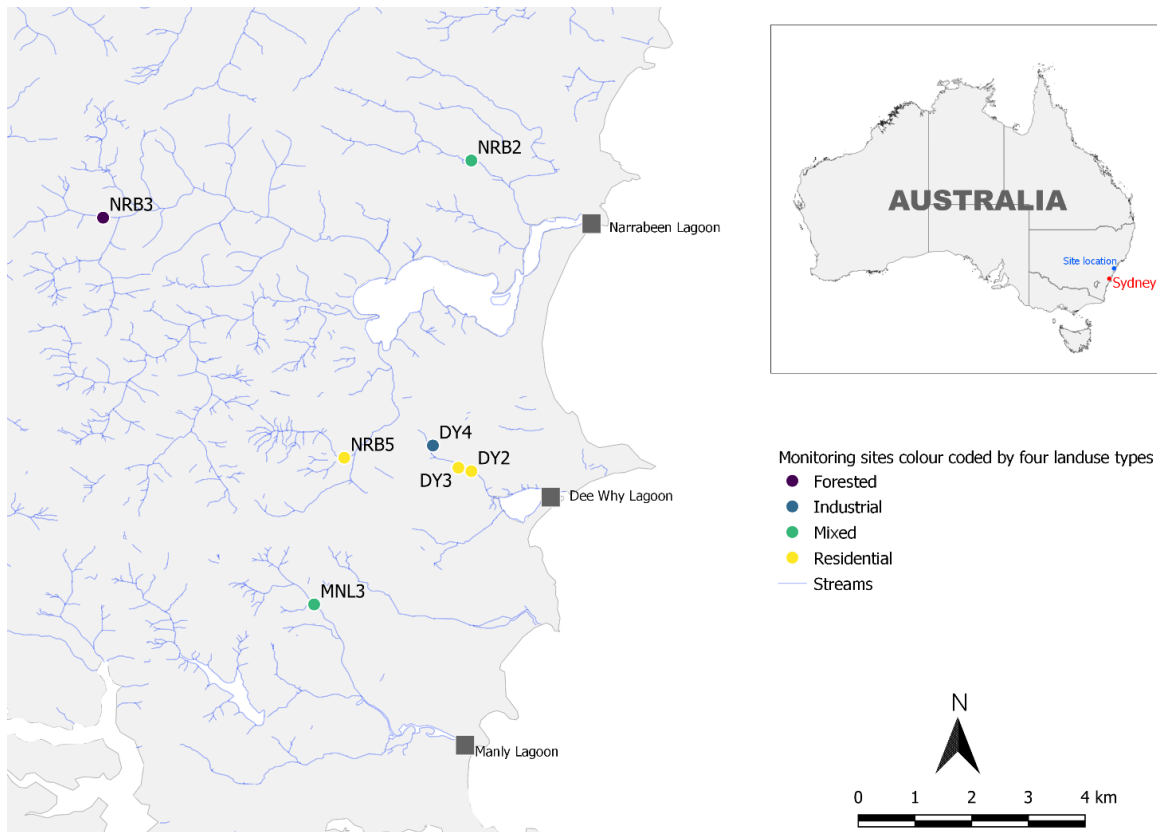


Figure 1. Location of sampling sites.

2.2 Sample collection

Above-baseflow conditions were sampled at different stage heights across the event hydrograph to assess the changes in the flow characteristics. Water quality and quantity values derived from the sampling are referred to as 'above-baseflow' conditions in this study. Baseflow sampling was undertaken at least once a month over two years when there had been no rainfall for at least 48 hrs before sampling.

The flow discharge values were estimated by multiplying the channel cross-sectional area by the stormwater flow velocity (m/s) during each field sampling trip (**Figure 2**). Corresponding total rainfall received in each study area between 24 and 48 hrs before sampling and the shape of the discharge curve was then used in conjunction with field notes on the water level to determine a site-specific cut-off threshold for baseflow and above-baseflow. The stormwater drains had varied cross-sectional shapes such as semi-curved, rectangular, circular, trapezoidal and irregular.

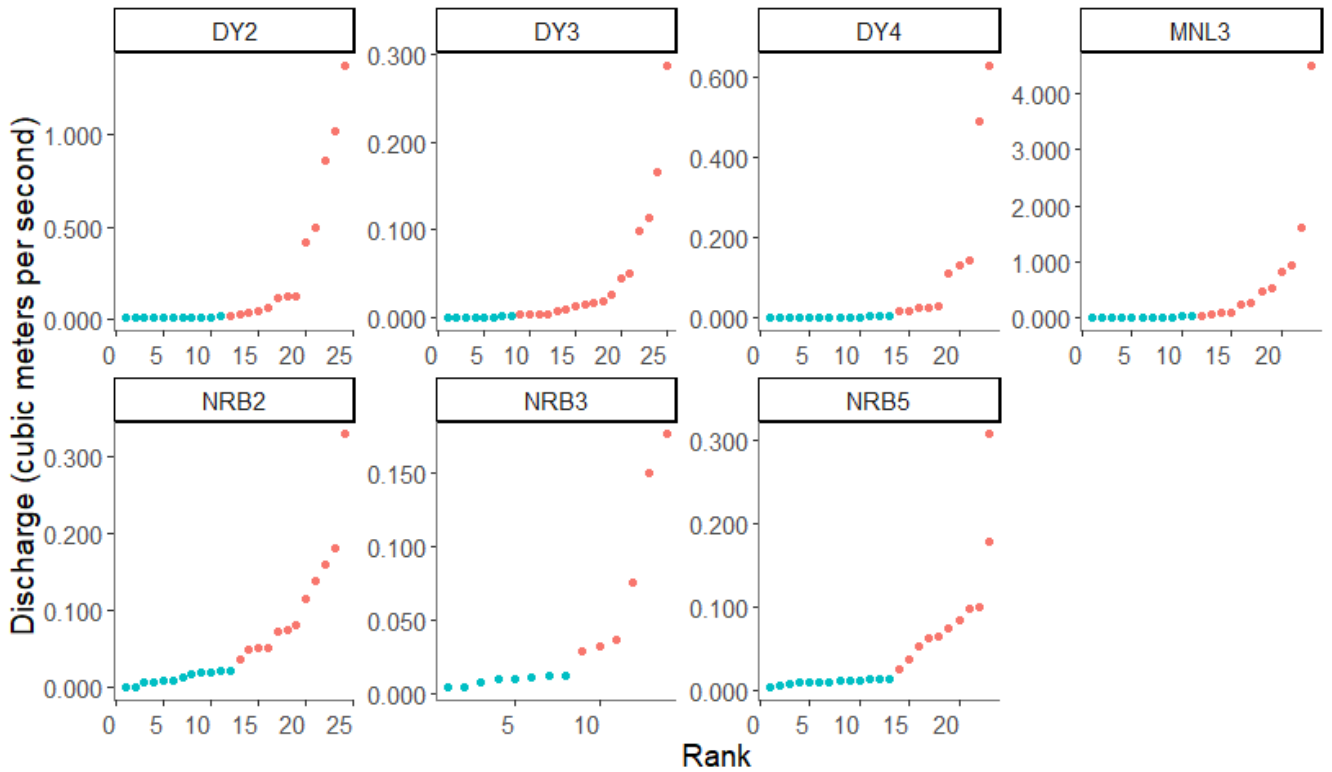


Figure 2. Discharge curves at the study sites in ascending order (Rank). Base discharge and above base-discharge levels determined for DY2 = 0.0154, DY3 = 0.0021, DY4 = 0.0069, NRB2 = 0.021, NRB3 = 0.012, NRB5 = 0.014 and MNL3 = 0.036 m³/sec. Red= above-baseflow discharge values. The channel shapes and catchment sizes varied considerably and different scales for the Y-axis are used to show the patterns of the discharges.

Continuous stage height at 15 min intervals was measured by barometric compensation using pressure sensors (HOBOWARE™, USA) installed at fixed cross-sections in the drainage channel at each site. The loggers were deployed from February 2019 to February 2021, covering two years. This period included baseflow and above-baseflow events that represented the expected flow types for each site. Flow velocity (Xylem Flo-Pro 2, USA) and water depth were measured at each site concurrent with water quality sampling. The water level logger data were reviewed, and quality was assessed before analysis. As part of the quality control process, the negative water heights were removed, negative water heights close to the zero level (under 0.02 m) were reset as zero, and flow heights above the depth of the channels were removed. Following this step, the calibration curves were used in conjunction with logged water height time series to correct the stage height. Discharge (Q) was calculated using the velocity (V) area (A) equation ($Q = AV$) to establish site-specific stage-discharge rating tables for each sampling site (**Figure 3**). Rating curves were derived using quadratic curve fitting in MATLAB® which showed high confidence and correlation for all sites except NRB3. The confidence limits and curve equations were also derived for each site. Unlike the other sites, NRB3 is a natural stream in a forested catchment with variable slope and bed, bank and channel shapes, giving irregular flow patterns, meaning the relationship between stage height and discharge at higher flows indicated low confidence and correlation.

Water pH, salinity (psu), total dissolved solids (mg/L), conductivity (μS/cm), turbidity (NTU) and dissolved oxygen (DO, mg/L) were logged in-situ using a ProDSS™ (USA) water quality meter. Water samples were collected by manually filling prewashed stainless-steel containers with site water and then homogenising by swirling. A 60 mL disposable syringe was used to transfer 28 mL of unfiltered site water into a clean vial for total nutrient analysis. Two additional 28 mL samples were filtered through a 0.45 μm cellulose acetate filter

(Minisart[®], Germany) into vials for dissolved nutrient (dissolved inorganic, total dissolved) analysis. All samples were frozen immediately until analysed. Samples were analysed for oxidised-N ($\text{NO}_x\text{-N}$), ammonium-N (NH_4^+), filterable reactive phosphorous (FRP/ $\text{PO}_4^{3-}\text{-P}$), total dissolved-P (TDP), total-P (TP), total dissolved-N (TDN), and total-N (TN). Nutrient concentrations were determined by flow injection analysis (Lachat[™] QuikChem 8500 Flow Injection Analyser) using standard methods: nitrate and nitrite ($\text{NO}_x\text{-N}$) (APHA 4500-NO3-I - Cadmium reduction method), $\text{NH}_3\text{-N}$ (APHA 4500-NH3-H:phenate method), FRP (APHA 4500-P-E-Ascorbic acid method), TN, TP, TDN, TDP (APHA 4500-P-J: persulfate digestion method) (Eaton and Franson, 2005). A separate water sample (500 mL) was collected into a clean plastic bottle and analysed for total suspended solids using modified APHA Method 2540-D (Eaton and Franson, 2005).

The weekly total rainfall (North Beach Manly Hydraulics weather station, -33.7121 S, 151.2967 E) was compared with the above weekly total discharge to derive a possible correlation. This weather station was chosen due to its proximity to the stormwater monitoring sites. The confidence limits, Pearson correlation coefficients and relationship equations were derived for each site.

The annual nutrient loads were estimated by summation of the product of the discharge time series and the mean of the monthly water quality grab samples over the two years. The annual loads were separated into three flow classes: baseflow (derived from **Figure 1**), above-baseflow and total flow. Due to limitations in field sampling, the water quality grab samples had a coarser temporal resolution compared to the flow, but their product is the best available estimate of the loads for this period. The loads were standardised (i.e., loads at each site/loads at the forested site) using the forested site as the baseline.

2.3 Statistical analysis

There were ten physicochemical variables (dissolved oxygen concentration and saturation percentage, pH, turbidity (Turb), conductivity, specific conductivity (SpCond), total dissolved solids, temperature (Temp), salinity and total suspended solids), seven nutrient variables ($\text{NH}_4^+\text{-N}$, FRP, $\text{NO}_x\text{-N}$, TDN, TDP, TP and TN) and three estimated dissolved nutrients from the initial data set: dissolved inorganic nitrogen (DIN), dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP). Descriptive statistics of these variables are presented in **Table 1**.

Seven variables, DIN, TDN, TDP, salinity, conductivity, TDS and DO concentration were removed from further analysis as significant relationships between the physicochemical variables were found which were attributed to their inherent association between total dissolved ionic particles and electrical conductivity. $\text{NO}_x\text{-N}$ was retained as it is a commonly monitored nutrient variable in stormwater quality studies (Wright et al., 2022; Francey et al., 2010).

Log transformed monthly mean concentrations of nutrients were subjected to one-way ANOVA with Tukey's post-hoc test. The homogeneity of variance and normality of the data was tested using Levene's and Shapiro-Wilk tests and visually, the QQ plots. The association between variable concentration values were assessed using Pearson Correlation coefficient and Principal Component Analysis (PCA). Both methods help understand the structure of the stormwater data set and how the variables relate to each other during different flow conditions. PCA has been widely used in stormwater studies as it transmutes a large number of interrelated variables into a small number of uncorrelated variables that are represented as 'latent variables'. These comprise the most meaningful sets of variables that describe most of the variance in the stormwater quality data set (Ekanayake et al., 2019, Miguntanna et al., 2013). The principal components (PC) are the linear combinations of initially measured water quality variables and are given as eigenvalues (indicating the variances accounted for by the component) and eigenvectors

(indicating the directions of the PCA axis) (Chapman, 1992). PCA was performed on the standardised data (σ quality = 1, μ = 0). The data set was separated into baseflow and above-baseflow conditions before analysis. In the PCA ordination plot, variables were k - means clustered into seven groups for interpretation. The number of clusters was determined by evaluating the Euclidian distances of variables using group linkage (Jarman, 2020). Pearson's correlation coefficients were derived and plotted using *psych* package (Revelle and Revelle, 2015). PCA was undertaken using FactoMineR and *factoextra* packages in R statistical program (Husson et al., 2016, Kassambara and Mundt, 2017).

ANZECC/ARMCANZ (2000) trigger values were used to assess the risk to aquatic health from stormwater. The trigger value is the 80th percentile value of reference site data and assesses the physicochemical-biological condition of the water for aquatic ecosystem health in south-eastern lowland rivers in Australia (ANZECC/ARMCANZ, 2000). The water quality variables with relevant ANZECC/ARMCANZ (2000) guidelines were compared to data from this study to identify exceedances.

3. Results

3.1 Descriptive statistics of the physicochemical data

Nutrient concentrations (empirical measures) and annual loads (estimated) at baseflow and above-baseflow levels were used in the analysis. For each variable, multiple samples were tested at different stages of the hydrograph. Turbidity showed the highest variability among the physical variables (**Table 1**) and pH varied between acidic and alkaline conditions. Among nutrient variables, TN recorded the maximum value of 3.8 mg/L followed by NO_x-N (2.9 mg/L). TSS varied in the range of 0.3 to 1197 mg/L depending on the flow condition.

Table 1. Descriptive statistics of stormwater quality data (means with \pm Standard deviation in parentheses).

	N	Minimum	Maximum	Mean for the current study	Median	Overseas Medians	Overseas Means
DO (% Sat)	158	9.04	108.45	94.41 (\pm 21.8)	94.22		
pH	158	4.69	11.14	7.23 (\pm 1.0)	7.14		
Turbidity (NTU)	157	0.01	183.93	13.68 (\pm 23.1)	6.75		
Specific Conductivity (μ S/cm)	155	3.85	608.63	291.07 (\pm 130.19)	293.92		
Temperature ($^{\circ}$ C)	157	6.95	23.2	16.61 (\pm 3.7)	17.1		
TSS (mg/L)	152	0.28	1196.72	24.89 (\pm 101.3)	6.56	141**, 48*	17 [#]
FRP (mg/L)	181	0.001	0.201	0.024 (\pm 0.03)	0.01		
NO _x -N (mg/L)	190	0.001	2.900	0.397 (\pm 0.482)	0.24		
TP (mg/L)	188	0.002	0.860	0.068 (\pm 0.085)	0.04	0.42**, 0.30*	0.4 [#]
TN (mg/L)	186	0.100	3.800	0.874 (\pm 0.688)	0.66	2.36**	
DON-Estimated	183	0.023	1.074	0.293 (\pm 0.197)	0.24		
DOP-Estimated	184	0.0002	0.063	0.0091 (\pm 0.010)	0.01		

N = number of samples, ** (Fuchs et al., 2004), * Pitt et al. (2004), # Boogaard et al. (2014)

3.2 Discharge and velocity

The stage and the discharge associated well for all sites except for the NRB3 site (**Figure 3**). NRB3 is the only site with a relatively low R² value (<0.30) compared to other sites (>0.90). This site is inside a national park with undefined boundaries and an irregular-shaped stream bed. At greater than baseflow conditions, flow tends to spread laterally (not monitored), thus adversely affecting the stage-discharge relationship. Overall, the relatively

higher R^2 values confirm the quality of the measurements and suitability for further analysis. Two curve fitting functions were applied to the stage-discharge observations (quadratic-curve fit and power-curve fit) as shown in **Figure 3**. The quadratic fit was found to give a much better fit compared to the power curve fits (R^2) for all the sites and was used for all further analyses.

The weekly rainfall total as a percentage of the maximum weekly total observed rainfall in the assessed period and the weekly total volume flux derived from the stage height and the calibration curve coefficients were also significantly correlated for all sites except for NRB3 and NRB5 sites (**Figure 4**). All sites other than the forested site (NRB3) had low baseflow discharge and sharp peaks corresponding to the weekly total rainfall and other potential input sources.

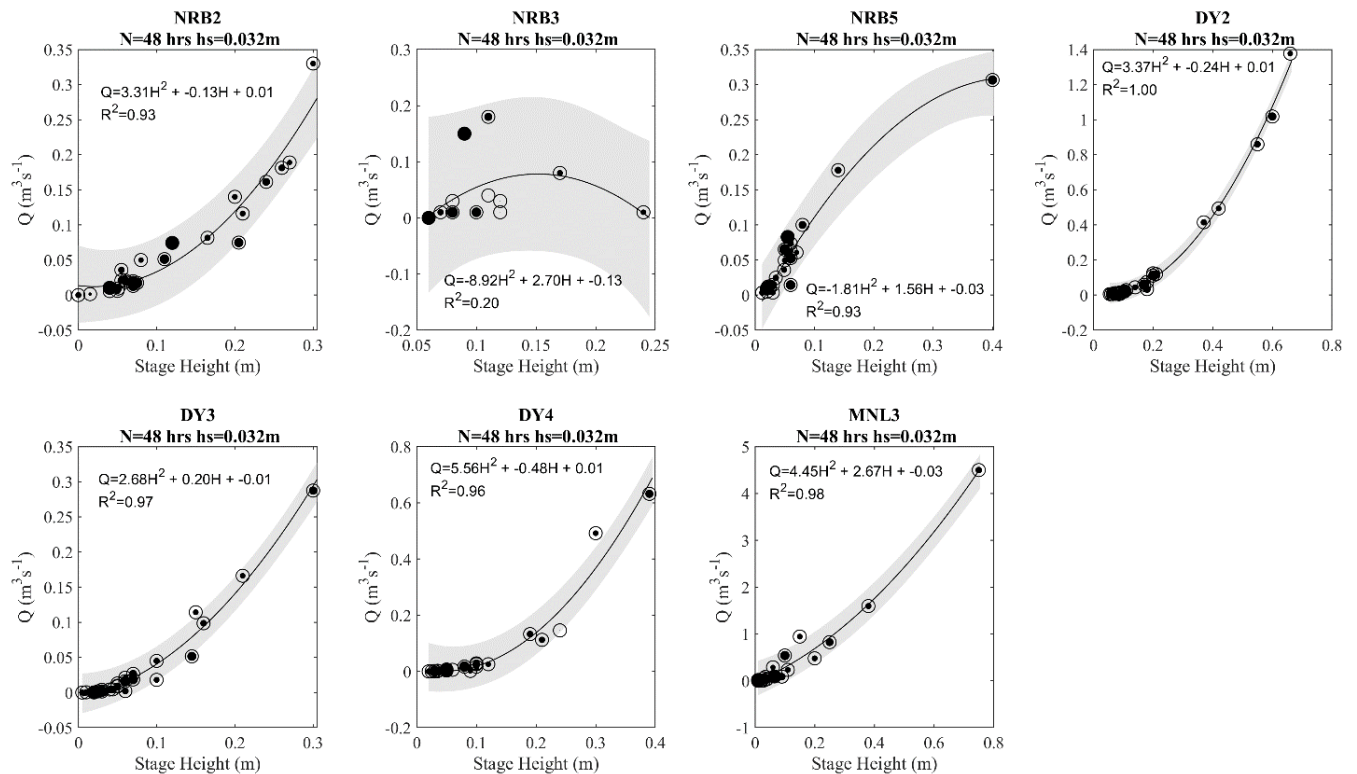


Figure 3. Rating curves for each monitoring site. Circles = events when the water height and discharge were measured; level of solid fill in each circle = the intensity of the rainfall (last 48 hrs) relative to the largest event observed in the two years; empty circles = no rainfall was recorded in previous 48 hrs; solid line = best quadratic fit to the data (equation and R^2 displayed in each subplot); grey bands = 95% confidence interval.

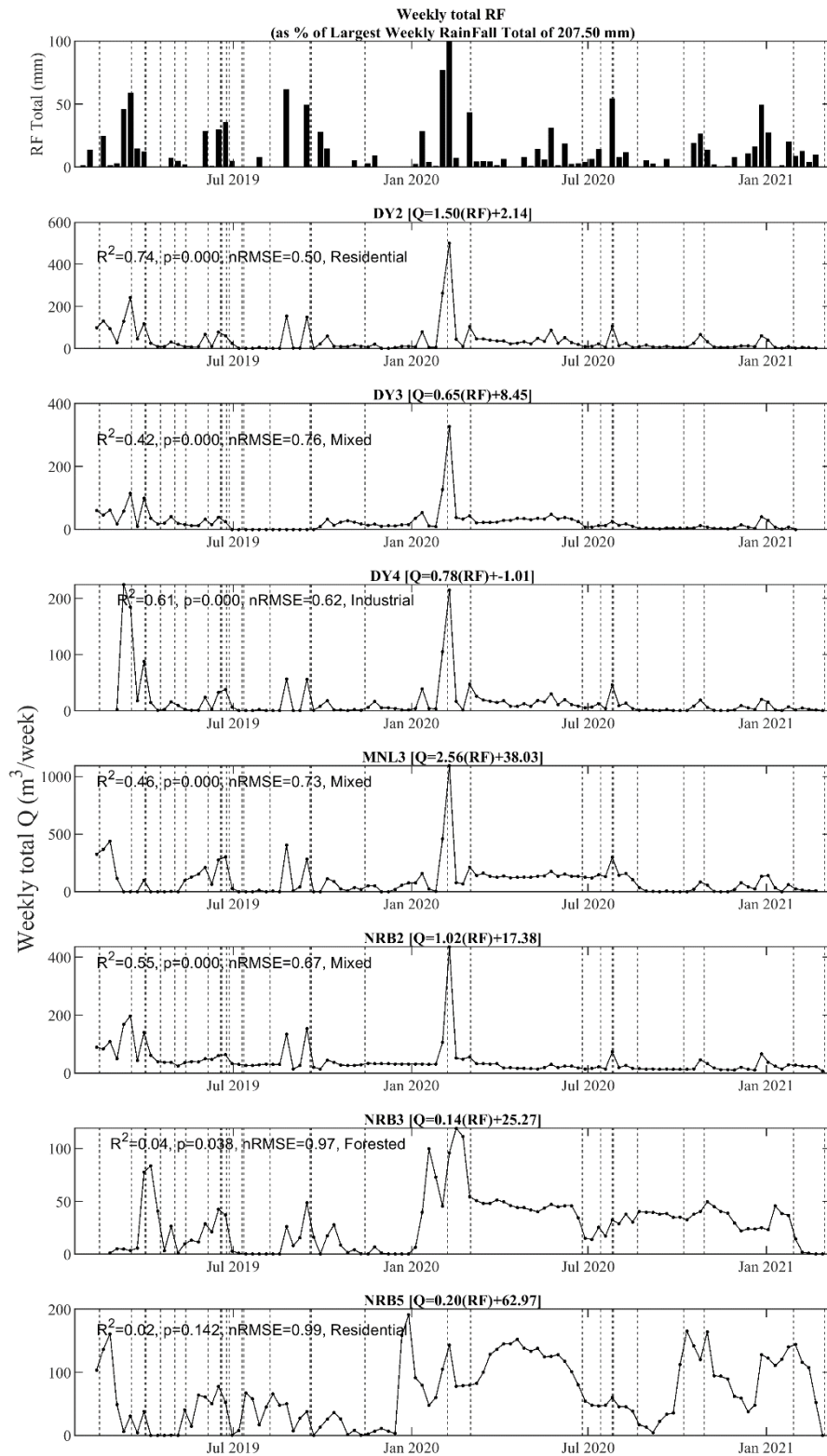


Figure 4. The rainfall and discharge time series for Feb 2019- Feb 2021. **A:** The weekly total rainfall as a percentage of the largest total weekly rainfall observed in the period. **B-H:** The discharge time series derived from the water level logger and the site calibration curve. Each panel shows the site type, the correlation coefficient, the normalised RMSE relative to the standard deviation and the relationship between the weekly discharge and rainfall. The dashed vertical lines indicate the dates when field water quality samples and flow rates were collected.

3.3 Relationships between variables

The correlation coefficients are important in understanding nutrients and physicochemical variables that follow a similar pattern and ensuring that highly correlated variables are made redundant in future monitoring due to surrogate predictions that can be made using correlated variables. TN showed significant positive correlations with dissolved nutrients, DOP ($r = 0.29$), FRP ($r = 0.46$), TP ($r = 0.53$), DON ($r = 0.61$) and NO_x ($r = 0.77$) indicating that the total and dissolved nutrients varied following a similar pattern (**Figure 5**).

Flow velocity correlated positively and significantly with TSS ($r = 0.18$). Velocity and discharge correlated positively and significantly with TP ($r = 0.3$ and 0.2 , respectively). Velocity also correlated positively with FRP ($r = 0.21$) explaining the movement of dissolved and total phosphorus is elevated with velocity. The likely result of mobilised fine soil particles associated with the flow or dissolved phosphorus in overland runoff entering the stormwater channels. The negative correlation coefficients between the hydrological variables (discharge and velocity) with dissolved salts (assessed through Specific conductivity) indicate the dilution effects of salts in stormwater. Specific conductivity also correlated positively and significantly with DON ($r = 0.36$), NO_x ($r = 0.61$) and TN ($r = 0.48$), but negatively with velocity ($r = -0.28$) and discharge ($r = -0.31$).

TSS and turbidity were significantly correlated for all land use types ($r = 0.80$, $p < 0.005$), with industrial and residential sites showing the strongest association ($r = 0.92$ and 0.78 , $p < 0.05$, respectively) (**Supplementary material S1**). This indicates that suspended particulate matter (and not organic dissolved substances) is responsible for causing turbidity in stormwater for all land use types. Regardless of land use type, sediment and phosphorous are mobilised in response to flow.

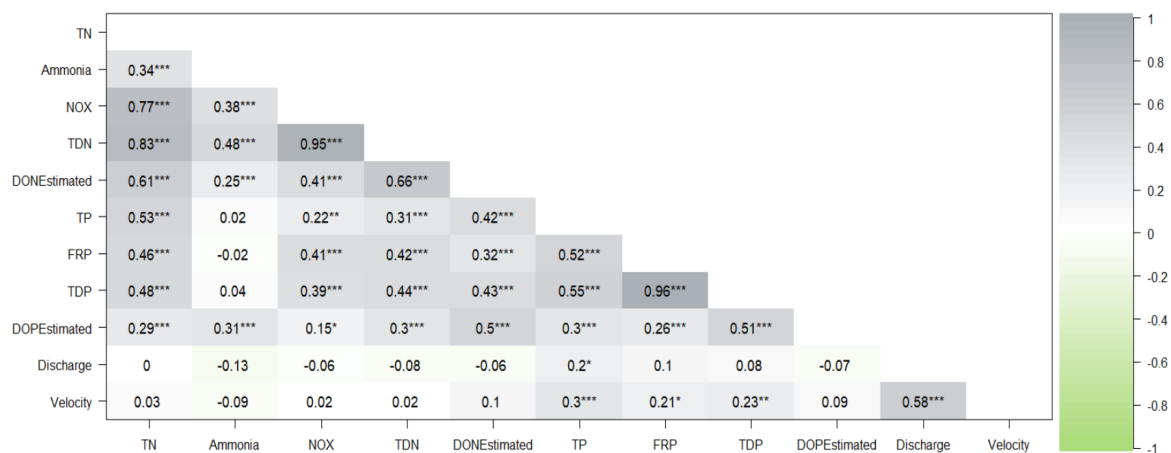


Figure 5. Matrix of Pearson's correlation coefficients for the measured physicochemical, nutrient and hydrological variables. Asterisks indicate significance level: * at $p < 0.1$, ** at $p < 0.01$, * at $p < 0.001$.**

The PCA revealed the interrelationships between water quality variables during baseflow and above-baseflow conditions (**Figures 6A and 6B**). The vectors in each plot characterised a unique pattern indicating that the physicochemical (i.e., Turbidity, DO, pH, SpCond and Temperature), nutrient, and flow variables behave differently as the flow conditions change. The percentage of variance explained by each PC was assessed using a scree plot to determine the number of PCs to retain. During both flow conditions, six PCs captured over 75% of the variance in the data set. However, PC1-3 accounted for the largest variability in the data with PC1-3 accounting for 53% of baseflow and 58% for above-baseflow conditions. The vector lengths indicate the relative contribution of each variable to PC1 and PC2, and

the angles between the two vectors show the strength of the correlation. Below are the key findings for baseflow and above-baseflow conditions.

Baseflow (**Figure 6A**)

- At baseflow conditions, the seven k-means clusters were related to water depth and discharge, rainfall, dissolved organic nutrients (DON and DOP), phosphorus (FRP and TP), nitrogen species (TN, NOX and SpCond) and physicochemical characteristics (Turbidity, TSS, Temperature, DO saturation and pH) in the dataset.
- Vector directions and lengths for FRP, TP, DON and DOP were the same, and the loadings increased on PC1, indicating their similar patterns in the water column. The vector loadings for velocity and rainfall 24 hrs before sampling also increased on PC1 and followed a similar direction to nutrients indicating that their concentrations were influenced by rainfall and flow velocity. In particular, the two dissolved organic nutrients, DON and DOP were highly correlated and followed a similar pattern.
- NOx and SpCond behaved the same way as TSS, indicating the correlations between suspended ionic particulate matter, oxides of nitrogen and various dissolved salts.
- Velocity and DO saturation vector loadings were in opposite directions indicating that at baseflow conditions, slow-moving water was related to an increase in oxygen saturation in the stormwater.

Above-baseflow conditions (**Figure 6B**)

- At the above-baseflow conditions, the seven clusters were related to water depth, velocity and discharge, rainfall, nitrogen species (TN, NOX, DON, SpCond), phosphorus (FRP and TP), water clarity (Turbidity and TSS) and physicochemical quality of the stormwater (DO saturation, pH).
- Total phosphorus and FRP showed a similar pattern and correlated highly with flow velocity, turbidity and TSS, indicating the mobilisation of total and dissolved phosphorus at high flow levels in the form of particulate matter.
- At the above-baseflow conditions, TN, NOx and DON vectors had similar directions and increasing loadings on PC1, indicating their presence in stormwater at similar times and concentrations. The vector length and direction of the total rainfall within 24 hrs of the sampling were also closely associated with these variables and further, confirm this pattern.
- DOP was highly correlated with NOx and DON and also with total rainfall at 24 hrs indicating the mobilisation of dissolved nutrients as rainfall increased.

Overall, the water quality characteristics, specifically total and dissolved nitrogen and organic phosphorus in stormwater were more prominent at above-baseflow conditions in all land use types. The high correlations with nitrogen variables and specific conductivity were more substantial at baseflow conditions than in the above-baseflow conditions indicating the ongoing nutrient presence in the stormwater channels (**Figures 6A and 6B**).

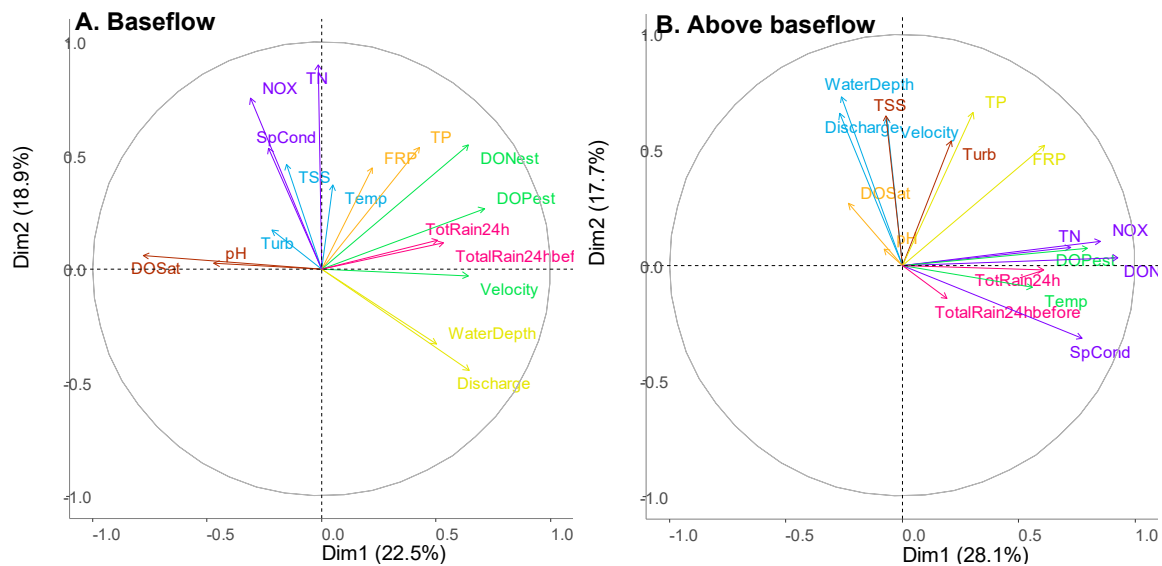


Figure 6. PCA ordination plots for A: Baseflow and B: Freshes or higher flow conditions. Vector lines in similar colours represent clusters derived from the k-means algorithm. Dim1 and Dim2 indicate Principal components 1 and 2.

The physicochemical, nitrogen and hydrological variables showed different patterns across four land use types indicating the complex nature of the stormwater quality influenced by catchment and rainfall characteristics (**Figure 7**). Turbidity in the forested and mixed land use catchments correlated well with discharge. In the residential catchments, TSS correlated highly with velocity and at the industrial sites, TSS correlated highly with total rainfall 24 hrs before sampling. On the other hand, the second water clarity-related variable, TSS highly correlated with discharge only in the residential and mixed land use sites. In the forested site, TSS followed a very similar pattern to rainfall received in the catchment 24 hrs before sampling. These results indicate that TSS input is not only driven by increased rain events but also strongly influenced by the range of catchment surface characteristics. To manage TSS input into stormwater drainage channels, land use-specific measures will be required.

Specific conductivity is a measure of dissolved salts in stormwater and showed a negative correlation to the three flow-related variables, namely, velocity, water depth and discharge in all the land use types indicating the dilution effects in both flow conditions (Figure 7A-D). The similar vector lengths and acute angles for NO_x and TN vectors in the PCA ordination plot for the residential sites indicated that both forms behaved the same way. In industrial and mixed-use sites, both forms showed some correlation. However, in the forested site, these two vectors were at an obtuse angle, indicating low or no correlation. Across all sites, DOP and FRP showed opposite vector directions indicating their negative correlations, possibly due to multiple sources. However, TP and FRP both followed a similar pattern. Total phosphorus was highly correlated with TSS in industrial and forested sites. However, correlations were weaker in residential sites and mixed-use sites. These results highlight the complexity of nutrient inputs into stormwater drainage channels from different land use types and the need to implement tailor-made catchment management solutions to minimise such inputs.

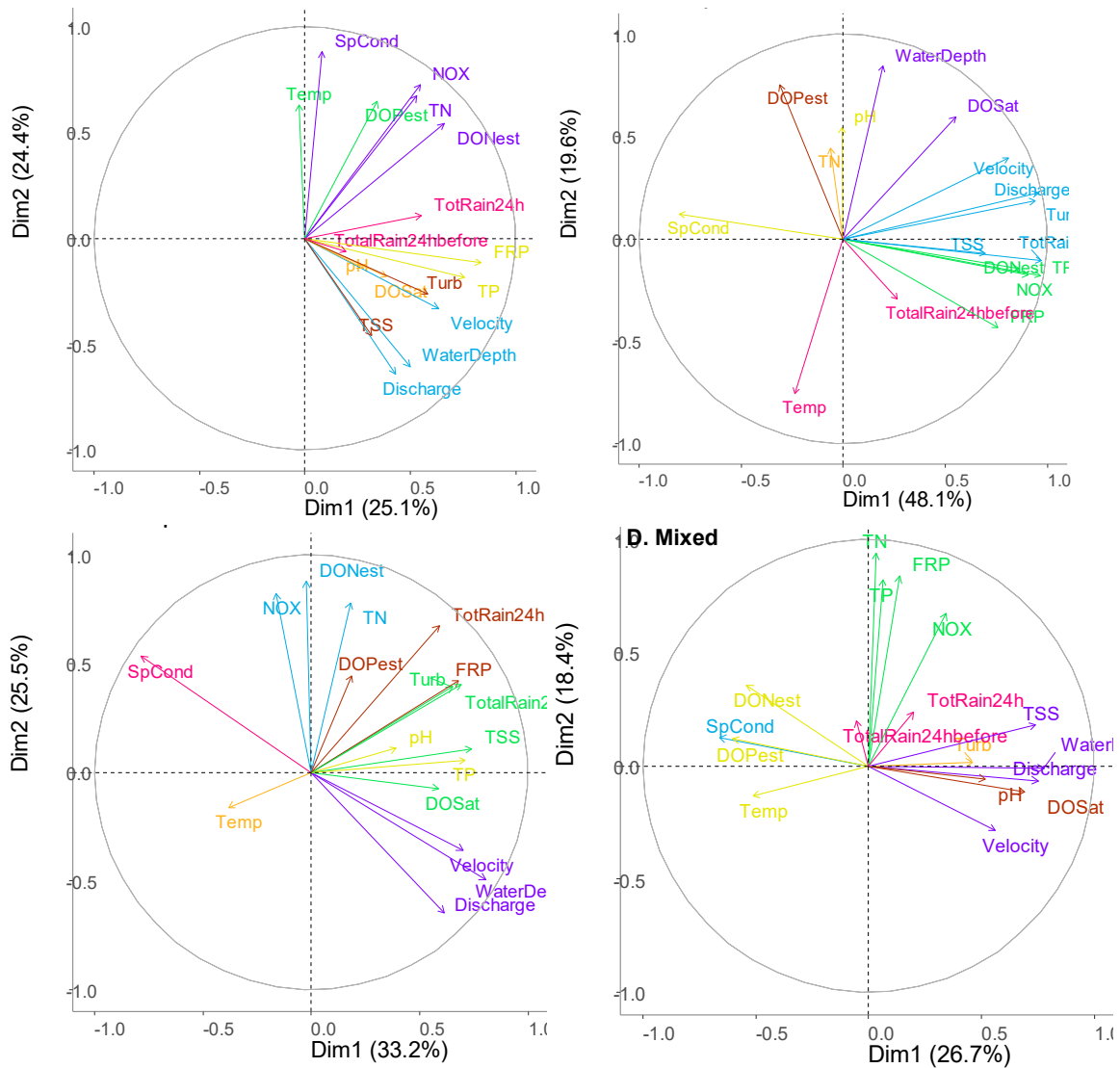


Figure 7. PCA ordination plots for A: Residential, B: Forested, C: Industrial, D: Mixed catchment land use. Vector line colours represent seven clusters derived from the k-means algorithm. Dim1 and Dim2 indicate Principal components 1 and 2.

3.4 Variability in total and dissolved nutrients

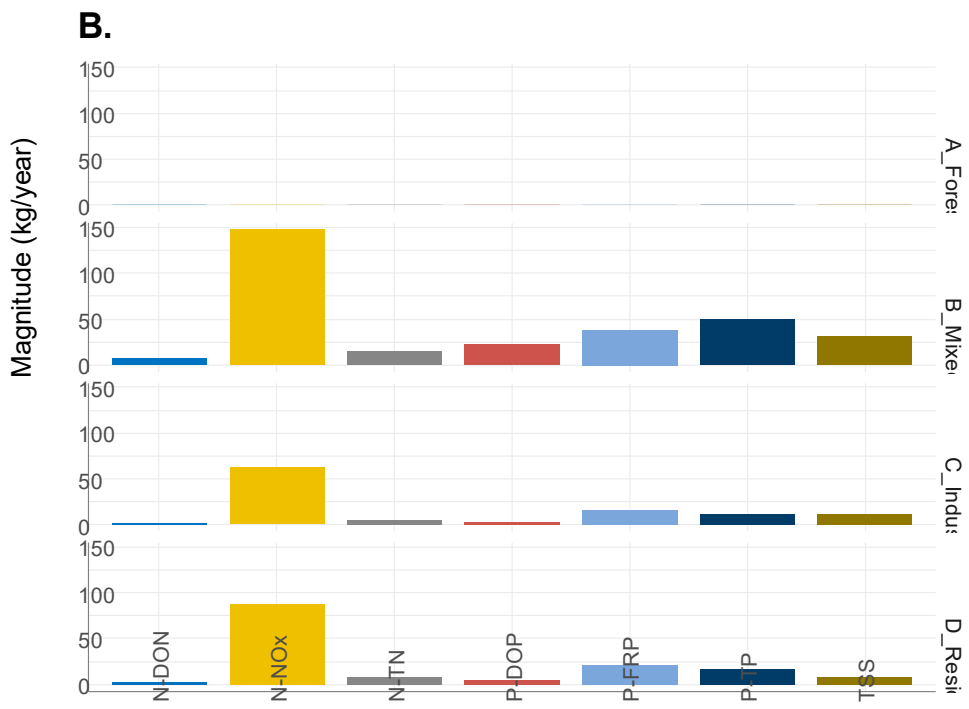
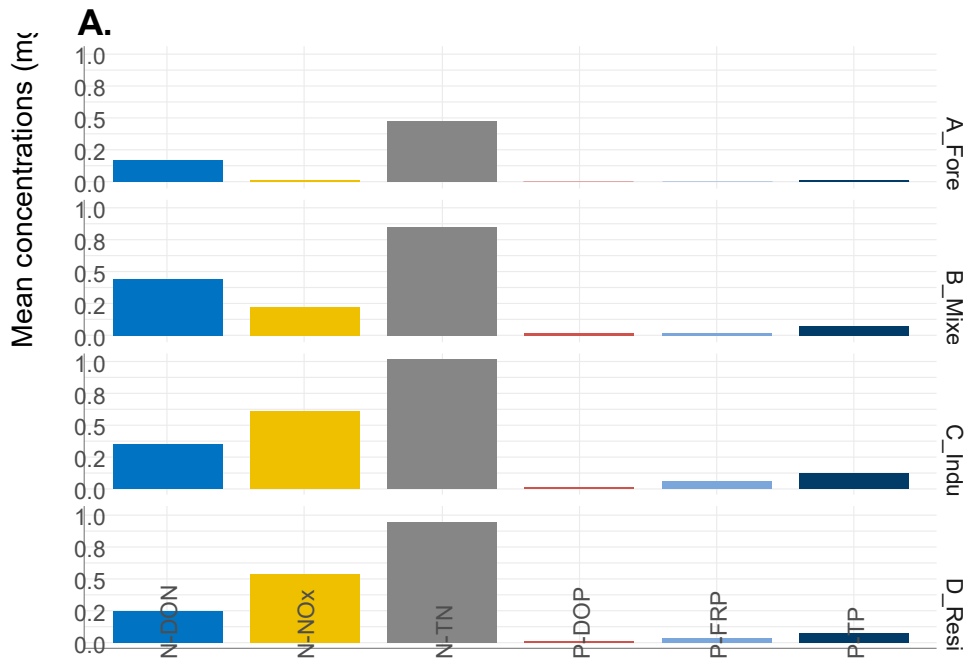
Across all sites, total nitrogen concentrations were greater than total phosphorous (**Figure 8A**). In general, NO_x export from the different urban land use types was greater compared to the forested site (**Figure 8B**). At the mixed-use, urban residential and industrial sites, the greatest proportion of nitrogen species was NO_x. NO_x was also significantly different between sites ($F[3,36], 87.18, p = 0.00$) (**Figure 8A**). Tukey's HSD Test for multiple comparisons found that the mean NO_x was significantly different between the forested and industrial ($p = 0.00, 95\% \text{ C.I.} = [-2.32, -0.35]$), mixed-use ($p = 0.00, 95\% \text{ C.I.} = [-2.32, -0.73]$) and residential sites ($p = 0.00, 95\% \text{ C.I.} = [-2.32, -0.32]$), between industrial and mixed-use sites ($p = 0.03, 95\% \text{ C.I.} = [-0.35, -0.73]$) and mixed-use and residential sites ($p = 0.00, 95\% \text{ C.I.} = [-0.73, -0.32]$).

Mean DON differences between catchment types were significantly different ($F(3,36), 10.24, p = 0.00$). Tukey's HSD Test for multiple comparisons found that the mean DON were significantly different between forested and industrial sites ($p = 0.00, 95\% \text{ C.I.} = [-0.89, -$

0.51]), mixed-use ($p = 0.00$, 95% C.I. = [-0.89, -0.44]) and residential sites ($p = 0.01$, 95% C.I. = [-0.89, -0.63]). Mean DOP ($F(3,35)$, 15.94, $p=0.00$) and FRP ($F(3,36)$, 20.9, $p=0.00$) concentrations were also significantly different between the different catchment types. All dissolved nutrient species in industrial, mixed-use and residential catchment types were statistically different from the forested catchment.

The mixed-use sites overall indicated the highest magnitudes for all variables (**Figure 8B**). On average, NO_x annual loads in the mixed-use catchments were 50 times or more than the reported values for the forested catchment (**Figure 8B**). FRP, TP and TSS loads were also approximately 20 times higher in the mixed-use areas (**Figure 8B**). The magnitude of NO_x load was comparatively high across all land use types. On average, all land use types showed TSS loads 10 times higher than the forested catchment. Nutrient loads were generally higher at above-baseflow conditions across all land use types (**Figure 8C**). TN:TP molar ratios were estimated to understand the nutrient-limiting effects of the stormwater as this exerts impacts on the receiving ICOLLs. The estimated ratios varied between 12 to 53, with forested land use indicating the highest ratio of 53 for baseflow and 42 for above-baseflow. For all land use types, the baseflow ratio is higher than the above-baseflow ratio (**Figure 8D**).

Overall, stormwater quality was influenced greatly by nitrogen compounds. Mixed-use catchments contributed the highest loads of nutrients and TSS to stormwater drainage channels for above-baseflow conditions.



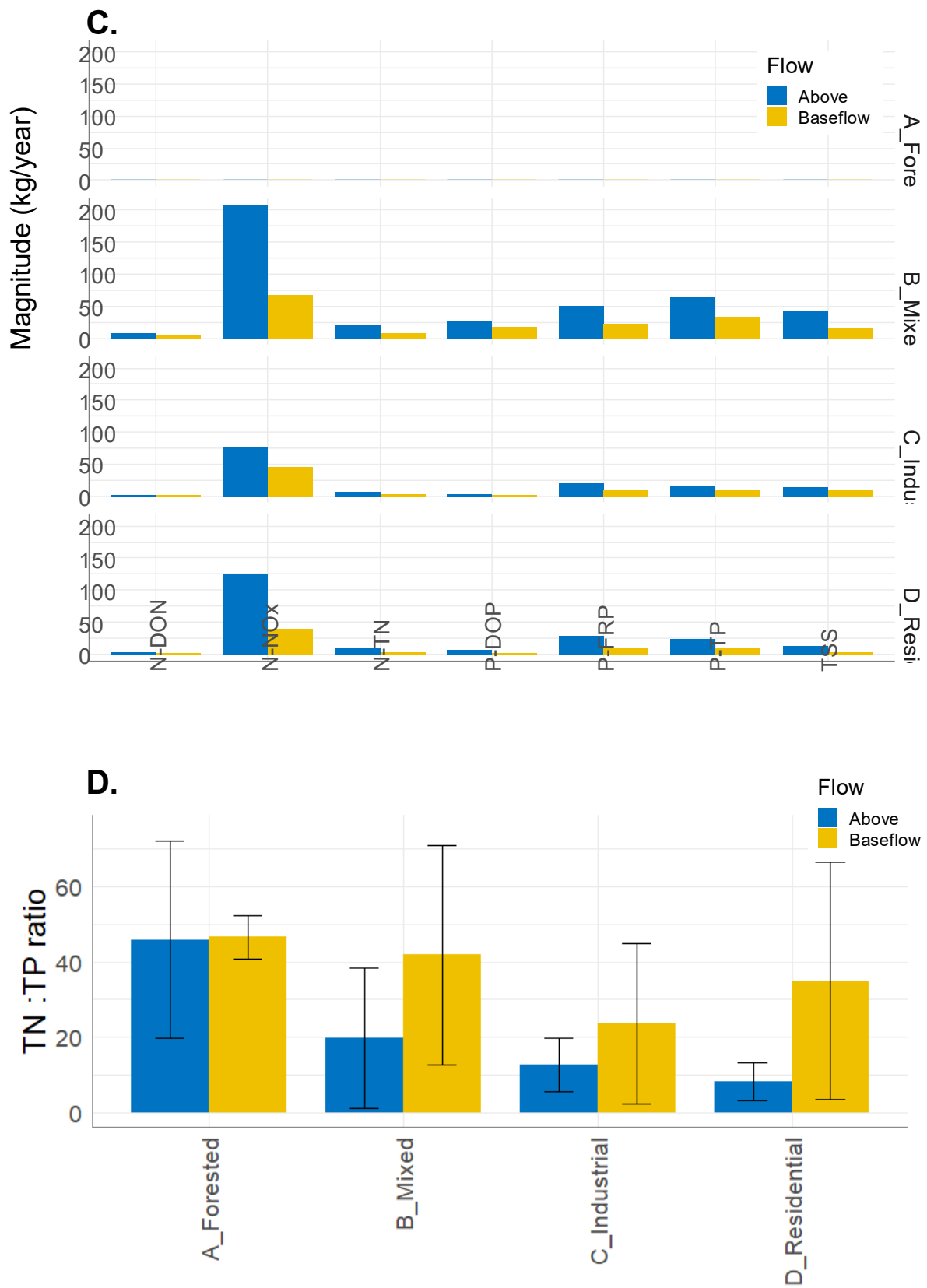


Figure 8. Variability in nutrients and TSS in stormwater collected at forested, mixed, industrial and residential land use types. A. Mean concentrations of total and dissolved nutrients, B: Load magnitudes after standardising against the forested site, C: Load magnitudes compared to the forested site at baseflow and above-baseflow level, D: TN to TP ratios.

3.5 Comparison with trigger values

The physicochemical variables, DO saturation, pH and turbidity were within the ANZECC/ARMCANZ (2000) trigger values for all land use types. At both flow conditions, industrial, mixed-use and residential sites showed large exceedances for TP, TN, FRP and NOx. Turbidity in the case of all land use types was relatively low during low flow. However, at above-baseflow levels, turbidity in all land use types was considerably high due to increased overland flow. Interestingly, TN exceeded in the forested site at above-baseflow levels. Stormwater originating from industrial land use areas exceeded all nutrient trigger values during above-baseflow conditions (**Table 3**). Overall, stormwater originating from any land use type other than the forested area showed high nutrients and TSS concentrations, which were considerably high at high flow events. Overall, the stormwater quality exceeding nutrient trigger values indicates adverse consequences on aquatic biota in the receiving environment. In particular, the stormwater drainage channels investigated in this study terminate at ICOLLS, and regular exceedances may lead to an imbalance in the nutrient dynamics of the ICOLLS.

Table 2. Comparison of mean nutrient and physicochemical concentrations with ANZECC/ARMCANZ (2000) trigger values for aquatic species health. Trigger value exceedances are in bold underlined text.

		TP (0.025 mg/L)*	FRP (0.02 mg/L)*	TN (0.35 mg/L)*	NOx (0.04 mg/L)*	ODO (85- 110%Sat)*	pH (6.5- 8.0)*	Turbidity (6-50 NTU)*	TSS (No trigger value)*
Above baseflow	Forested	0.006	0.001	<u>0.47</u>	0.01	93.93	7.05	3.54	3.19
	Industrial	<u>0.120</u>	<u>0.062</u>	<u>1.01</u>	<u>0.52</u>	95.93	7.57	46.56	19.03
	Mixed	<u>0.071</u>	0.020	<u>0.69</u>	<u>0.22</u>	77.83	7.50	16.74	57.70
	Residential	<u>0.067</u>	0.033	<u>0.92</u>	<u>0.51</u>	90.34	7.23	11.34	40.17
Baseflow	Forested	0.004	0.002	0.17	0.01	87.74	6.77	1.19	2.09
	Industrial	<u>0.045</u>	0.019	<u>0.98</u>	<u>0.60</u>	93.74	7.38	19.80	8.01
	Mixed	<u>0.069</u>	0.020	<u>0.85</u>	<u>0.20</u>	61.54	7.10	12.88	21.34
	Residential	<u>0.046</u>	0.009	<u>0.95</u>	<u>0.53</u>	80.75	7.00	4.96	5.60

*ANZECC/ARMCANZ (2000) trigger values.

4. Discussion

4.1 Hydrological patterns

The discharge curves (**Figure 3**) show a high R^2 suggesting consistent stage-discharge relationships. The quadratic regression fits the observations well (a separate test using a logarithmic regression provided a similar, but slightly lower fit). The discharge time series shows that the same rain events influence all sites. However, the relationship between rainfall and discharge is non-linear due to spatial rainfall coverage, routing and surface absorption. Apart from NRB3 and NRB5, other sites show a reasonable level of predictability.

The current study found separating a hydrograph into event flow from baseflow conditions and defining a clear 'event' to be challenging. In the study, the water levels at all sites were influenced by multiple small-scale fluctuations during dry weather and before, during and after rainfall events creating multiple peaks of varying magnitudes. The salinity variation was also minimal between and within sites. It is hypothesised that fluctuations in the baseflow are

due to groundwater seepage and discharges of anthropogenic origin. The approach adopted in this study for hydrograph separation was based on the estimated discharge using empirical measurements at different stages of a hydrograph and determining the baseflow cut-off level through the assessment of the discharge values relative to total rainfall in the catchment within 24 to 48 hrs before undertaking the sampling surveys, observations at the time of the sampling and shape of the discharge curve. In the absence of time series rainfall and flow data at the scale of stage measurements, this approach can help to separate flow conditions and is more suitable for urban stormwater studies compared to other methods such as the straight-line method, constant-k method (Blume et al., 2007) and electrical conductivity-based methods (Nakamura, 1971) proposed for this purpose. However, the limitations of this method are also acknowledged, such as its inability to capture the first flush effects when pollutant loads may differ between the rising or falling limbs of a flow event.

Flow velocity plays a key role in DON, DOP, FRP and TP mobilisation at baseflow conditions. Velocity became more associated with TSS and turbidity at above-baseflow conditions and mobilised FRP and TP. As flow conditions improved, more TSS and TP entered the drainage channel (**Figure 6B**). These results highlight the need for a suite of specific interventions targeting baseflow and above-baseflow conditions for mitigating stormwater impacts in receiving waters.

4.2 Total and dissolved nutrients

The quality of the stormwater is governed by several anthropogenic and natural factors such as the catchment surface characteristics, precipitation patterns, soil compaction and channelisation (Goonetilleke et al., 2005, Van der Sterren et al., 2012, Egodawatta et al., 2007, Booth and Jackson, 1997, Ballo et al., 2009, Vaze and Chiew, 2004). Urban runoff is associated with a range of pollutants, including organic and inorganic compounds (Gilbert and Clausen, 2006, Yu et al., 2014; Ma et al., 2018) and plant nutrients (Lin et al., 2014; Wijesiri et al. 2022) originating from anthropogenic activities, vehicular traffic, sewage contamination and lawn fertilisers (Ferreira et al., 2016, Le Pape et al., 2013, Carey et al., 2013). The sources of nitrogen and phosphorus can also be partially attributed to the geology of the catchment. A clear pattern in elevated nutrient loads which were statistically significant was observed. Dissolved nitrogen (DON and NO_x) and phosphorus (DOP and FRP) concentrations in stormwater originating from industrial, mixed-use and residential catchment types were higher than in the forested land use. These elevated dissolved nutrient fractions are a concern for ICOLLs as these can rapidly alter the nutrient dynamics in the receiving waters.

In Australian forested catchments, Harris (2001) reported little nitrogen and phosphorus export and the predominant form of nitrogen is DON. As catchments are cleared, increased DON and DIN in the receiving waters were observed. Based on tropical and subtropical catchments in Queensland, Eyre et al. (1999) noted an increase in phosphorus exports from catchments with little forest cover. Similar to these past studies, the current study observed some dominance of DON in the forested catchment and significantly different elevated DON in stormwater originating from the cleared catchments, industrial, mixed-use and residential land use. TN and TP values observed in this study are a few orders of magnitude lower than what has been reported in European stormwater studies (Fuchs et al., 2004, Pitt et al., 2004, Boogaard et al., 2014).

The dissolved and organic forms of nitrogen are readily mobilised by stormwater and show a positive correlation with rainfall intensity, total rainfall and antecedent dry period (Jani et al., 2020, Miguntanna et al., 2013). Noting the high levels of dissolved nitrogen, in both flow conditions in the present study, treatment considerations should be more focused on capturing these nutrients to mitigate any adverse impacts on the receiving waters.

Generally, up to 80% of the pollution load is carried by the first 20-40% of the first flush during an event (Stenstrom and Kayhanian, 2005). To capture the first flush in urbanised areas, sampling should be undertaken at the right time and standardised by defining an 'event' which is complex with stochastic flow levels. Francey et al. (2010) reported the non-significance of the first flush phenomena when assessing stormwater quality across multiple sites in Melbourne. The present study did not aim to capture the magnitude of the first flush. Nevertheless, high nutrients and TSS loads at above-baseflow conditions were noted, indicating nutrient inputs into the stormwater even after the first flush.

From the study outcomes, it was noted that TP and FRP are mobilised in all catchment types at above base-flow levels and follow a similar pattern with flow velocity, turbidity and TSS, indicating that phosphorus movement in the stormwater is directly through particulate matter at the above-baseflow levels. Francey et al. (2010) also reported a high correlation between TSS and TP and TP and TN in stormwater originating from residential catchments. Similar to the findings of Taylor et al. (2005), a strong association between nitrogen species and flow velocity at both flow conditions was not evident. DOP and velocity correlated well, meaning that in the absence of rain, DOP is associated with the baseflow. This means that under land use intensification scenarios, increased flow volumes will likely result in sediment and phosphorous export, suggesting stormwater treatment always requires strategies to mitigate receiving environments sensitive to sedimentation, such as seagrass beds that are likely to be impacted following land use change.

All stormwater drainage channels included in this study terminated at an ICOLL, meaning the aquatic biota living in the waterways and receiving lagoons are affected by the quality and quantity of the stormwater. At both flow conditions, the stormwater flowing over industrial, mixed-use and residential land uses exceeded TP, TN, FRP and NO_x ANZECC/ARMCANZ (2000) trigger values for aquatic species health. In particular, stormwater from the industrial area (DY4) exceeded all nutrient trigger values during initial and high flow conditions. The ammonium concentration exceedances at baseflow are of particular concern as flows rich in ammonium can increase ammonia toxicity in the receiving waters. Non-compliance with ecosystem health guidelines for stormwater quality is typical in most parts of the world. For example, Boogaard et al. (2014) reported that based on the largest stormwater database in Europe, which has data over 15 years, pollution in many cities in the Netherlands did not meet the requirements of the European Water Framework Directive and Dutch Water quality standards. Similarly, Ferreira et al. (2016) found exceedances in nitrogen species in Portuguese water quality. In Australia, ammonia, NO_x and chlorophyll-a levels increased when the mouth is closed for flow to the ocean in the Smith Lakes ICOLL system (Everett, 2007). Exceedances in the stormwater need to be managed through ongoing monitoring to ensure that the measures implemented are effective and do not lead to the proliferation of algal blooms harmful to the health of the receiving aquatic environment.

4.3 TN:TP ratio

Developed based on the elemental composition of marine water, the Redfield ratio has gained worldwide acceptance as a stoichiometric reference indicator of phytoplankton growth and nutrient cycling. The ratio plays a key role especially when bioavailable nutrients are low in concentrations. The original TN:TP ratio of 16:1, assumes that phytoplankton is nitrogen-limited at a ratio <16, and that it is P-limited at a ratio >16 (Redfield, 1934). Although the N:P composition is closely approximated to the Redfield ratio, local conditions could vary between 5 and 34 (Geider and La Roche, 2002). In freshwater systems, phosphorus is reported as the primary nutrient-limiting factor for phytoplankton biomass (Smith et al., 2002). However, some studies point to the co-limiting role of N and P (Elser et al., 1990, Kagami et al., 2013). Dzialowski et al. (2005) produced threshold ratios for freshwater systems to interpret water quality results using TN:TP ratios <18 (molar) indicating limited

nitrogen, 20-46 indicating the water column is co-limited by both nitrogen and phosphorus and >65 indicating phosphorus limitation. Similarly, Guildford and Hecky (2000) proposed TN:TP of 20 (molar) where nitrogen deficiency in growth would become apparent, 20-50 where either nitrogen or phosphorus becomes deficient and > 50 where phosphorus becomes deficient. The results for the current study varied between 8 to 47, with an average of 37 at baseflow and 22 at above-baseflow originating from all land use types, indicating the stormwater is co-limited by both nutrients. Also except for the forested site, these ratios vary considerably during base flow and above baseflow conditions. Nutrient co-limited systems are delicate as the addition of either nutrient will increase the activity of primary producers in the receiving waters (Harpole et al., 2011, Bracken et al., 2015). Scanes et al. (2014) confirmed this phenomenon using ICOLLS in New South Wales and showed how the addition of either nutrient contribute to eutrophication and excessive algal growth. As such, the variable nutrient loadings entering the ICOLLS and other receiving waters have an increased potential to alter the nutrient dynamics and result in important management implications.

4.4 Water clarity

Total suspended solids concentration is an important characteristic of stormwater, influenced by the level of urbanisation, rainfall characteristics and antecedent flow conditions. Suspended solids can smother aquatic habitats and inhibit light availability for primary producers in the receiving environment (Ferguson, 1998, Chui, 1997). Suspended materials in stormwater are generally fine (25-44 μm), have a high settling velocity (4-11m/h) and resuspension of sediments during events is a major concern in managing TSS (Yu et al., 2001, Chebbo and Bachoc, 1992). The study found elevated turbidity levels and corresponding high annual TSS loadings in stormwater from mixed-use areas compared to the forested area during both flow conditions. In particular, TSS and turbidity are significantly correlated with industrial and residential areas showing a strong association ($r = 0.92$ and $r = 0.78$, $p < 0.05$, respectively) (**Supplementary material 1**). This means that suspended particulate matter (not coloured dissolved organics) is responsible for turbidity in stormwater for all land use types. Particulate matter also acts as a vector for particulate-bound nutrients and heavy metals (Sansalone et al., 2005) and can pose a risk to the receiving environments over time (Liebens, 2001). Nutrients agree with this pattern and as noted, a significant association between velocity and TP and FRP indicates the mobilisation of nutrients as the increase in flow leads to scouring of the land surface.

The mean TSS reported in this study is similar to the mean values reported for Dutch cities (Fuchs et al., 2004). However, the median values are lower than the reported values elsewhere (Boogaard et al., 2014, Brombach et al., 2005). TP and TN values are a few orders of magnitude lower than the reported values for European cities (Brombach et al., 2005). Although some of the patterns in the current study are aligned with past studies, there is considerable heterogeneity in the water quality patterns influenced by the land use characteristics. For example, a considerable variation can be noted in the TN, TP and TSS values obtained in the current study with those reported from Europe (Pitt et al., 2004, Boogaard et al., 2014).

The study outcomes confirmed that stormwater from less vegetated catchments is high in nutrients and TSS (Figure 8A). In line with other studies, riparian and catchment tree cover helps to minimise soil erosion, slow down the overland flows and capture nutrients (Mohammad and Adam, 2010, O'Toole et al., 2013). However, many urbanised catchments lack space to retrofit stormwater treatment devices or increase tree cover. Post-development ambient monitoring programs such as the present study pose an interesting question as to whether a paradigm shift to current stormwater quality and quantity management approaches is required to protect the aquatic health of receiving water bodies and the marine environment.

Conclusions

This study provides evidence of stormwater quality patterns originating from different land use types, which has considerable management implications for similar catchments in other parts of the world. Identifying flow events in urban stormwater studies is challenging. The baseflow and above-baseflow conditions are influenced by small-scale fluctuations during dry weather and before and during rainfall, creating multiple peaks of varying magnitudes due to groundwater seepage and industrial discharges.

The physicochemical and hydrological variables showed different patterns across the four land use types at baseflow and above-baseflow conditions highlighting the complex nature of stormwater quality influenced by catchment and rainfall characteristics. For example, elevated baseflow nutrients and high annual loads of dissolved nutrients originating from catchments other than the forested catchment were noted. On average, residential, mixed-use and industrial catchments transported over 50 times more NO_x and FRP loads to the receiving waters when compared to the forested catchment. In line with past studies, it is hypothesised that the modifications to a forested catchment, such as removing vegetation, introducing artificial surfaces, and changing land use, are invariably linked to these results. The amount of vegetation cover in the catchment and the riparian vegetation cover can help to mitigate the adverse impacts to receiving waters from stormwater. This study also found high turbidity and TSS concentrations at the industrial site and low turbidity at the forested site during both flow conditions due to suspended particulate matter. This means that management strategies need to focus on solutions that minimise suspended solids transported to the ICOLLs. The study revealed that TSS is not only driven by increased rain events but also strongly influenced by the range of catchment surface characteristics. To minimise TSS inputs to stormwater drainage channels, a range of land use-specific measures are required.

Managing water in tomorrow's cities requires a new way of thinking from the users' and managers' perspectives, well supported by institutional capacity and new technological innovations to capture, minimise and retain water in urban environments. This study further highlights that a one-size-fits-all approach to stormwater management will not be particularly effective. The management of the urban water cycle is a complex task that requires in-depth considerations of the drainage and supply system and the impacting weather patterns. A suite of tailor-made approaches at the source (catchment) and the receiving waters, aiming at baseflow, above-baseflow and catchment surface types are needed.

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Supplementary material 1

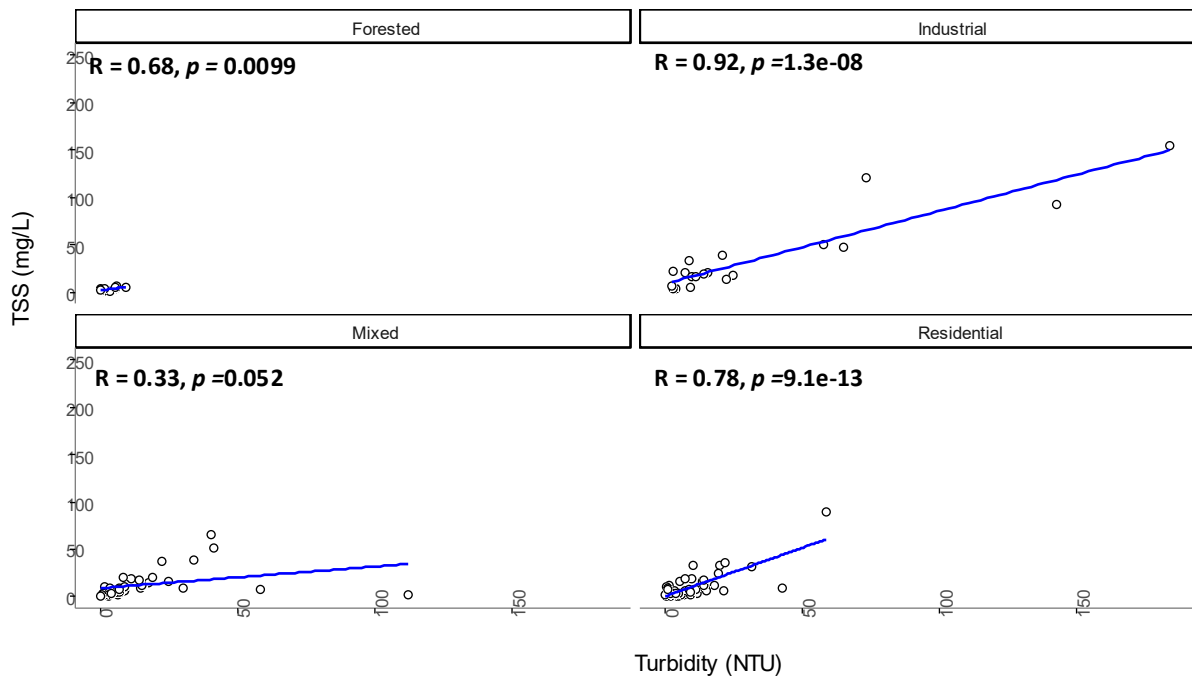


Figure S1. Correlation between turbidity (NTU) vs TSS (mg/L) at different land use types.