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Nitrogen composition in urban runoff—implications for stormwater management

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Abstract

A study was conducted to characterise the composition of nitrogen in urban stormwater in Melbourne, Australia, during baseflows and storm events, and to compare the results with international data. Nitrogen in Melbourne stormwater was predominantly dissolved (~80%), with ammonia the least-abundant form (~11%). *Concentrations* of nitrogen species did not vary significantly between baseflow and storms, although the *proportion* of nitrogen in particulate form was higher during storm events ($p = 0.04$).

Whilst the composition of nitrogen in Melbourne was broadly consistent with international data, the level of dissolved inorganic nitrogen was higher in Melbourne ($\mu = 48\%$ during baseflows and 49% during storms) than in the international literature ($\mu = 29\%$). Limitations in the international dataset precluded comparison of total dissolved nitrogen.

The results have implications for stormwater management. Whilst nitrogen species concentrations are variable, they are not strongly related to flow conditions, so treatment systems must be designed to cope with stochastic inflow concentrations at all times. To optimise their performance, stormwater treatments should be designed to improve dissolved nitrogen removal. Further research is needed to improve the ability of treatment systems to achieve this aim.
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1. Introduction

Urban runoff contributes to the eutrophication of receiving waters around the world, and while phosphorus is normally the limiting nutrient in fresh water, nitrogen may also be of concern (Field et al., 1998; Heaney et al., 1999; Lee and Bang, 2000; Novotny and Witte, 1997). Whilst considerable data exist on the concentration of nitrogen in urban runoff (Duncan, 1999), there are less on its composition.

Particulate nitrogen in urban runoff enters receiving waters predominantly in organic form (Harris et al., 1996). However, it cannot be assumed that all organic nitrogen (Org-N) is particulate. Unfortunately, the

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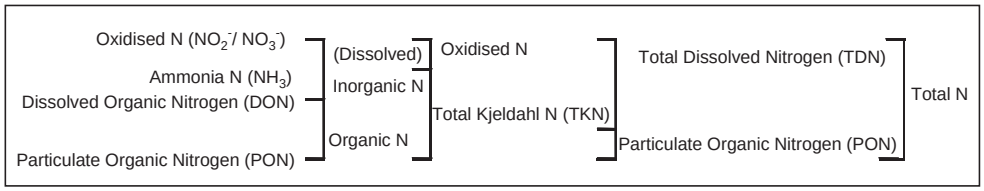

Fig. 1. Individual constituents of total nitrogen, and their named combinations.

proportions of Org-N in dissolved or particulate form are rarely quantified in the literature (Seitzinger et al., 2002).

Dissolved inorganic nitrogen (DIN) includes ammonia (NH_3), nitrite (NO_2^-), and nitrate (NO_3^-) (Fig. 1). These constituents have the greatest impact on water bodies because they are readily available for uptake by simple organisms (Seitzinger et al., 2002), and may lead to eutrophication, hypoxia, and loss of biodiversity and habitat (Galloway et al., 2003). Nitrate is often the most common soluble species in aquatic systems and urban runoff (Feth, 1966; Galloway et al., 2003; Oms et al., 2000), and is not well retained by soil particles. High nitrate concentrations in receiving waters can indicate general urban impacts, whilst high ammonia concentrations may indicate anaerobic conditions, or organic pollution from sewers (Gibb, 2000). While many data exist for DIN, less are available for dissolved organic nitrogen (DON); yet it may contribute up to half the total nitrogen (TN) load (Cerda et al., 2000).

Many studies have demonstrated the impacts of excessive nitrogen loads on receiving waters. For example, the Chesapeake Bay study showed that increases in reactive nitrogen contributed to increased anoxic and hypoxic waters within the bay (Galloway et al., 2003). Similarly, a study of Melbourne's Port Phillip Bay identified the need to reduce annual nitrogen loads by 1000 tonnes, to reduce the risk of eutrophication (Harris et al., 1996). In Moreton Bay in Queensland, Australia, nitrogen was identified as a key pollutant influencing ecological sustainability (Abal et al., 2001). Given its bioavailability, appropriate management strategies are therefore required to reduce the loads of dissolved nitrogen entering receiving waters.

Current approaches to stormwater management aim to treat stormwater to remove pollutants, often using a "treatment train" approach, whereby coarse material is removed first, followed by finer particulates and finally dissolved components (Kadlec, 1999; Mitsch and Gosselink, 2000; Wong et al., 1999). For example, a stormwater wetland's inlet zone promotes coarse-particulate sedimentation (Urbonas and Stahre, 1990), whilst downstream shallower macrophyte zones facilitate biofilm growth, which remove fine particulates and dissolved pollutants (Brix, 1994; Brock et al., 1994; Hart and Grace, 2000). Similarly, stormwater biofiltration systems typically use a vegetated buffer strip to remove coarse particulates, whilst the filter medium (gravel, sand or soil) promotes biochemical and fine particulate removal (Fletcher et al., 2003).

In designing stormwater treatment systems, however, it is necessary to understand the composition of nitrogen in urban runoff, to maximise the removal of nitrogen forms which are dominant or of most concern to receiving environments. Understanding nitrogen composition in urban runoff will assist in proportioning and prioritising the processes to be facilitated by treatment systems.

2. Study overview

This study seeks to characterise the composition of nitrogen in urban baseflow and stormflow, with the ultimate aim of improving treatment strategies for nitrogen reduction. The study was undertaken in Melbourne, Australia. To place the results in context, the Melbourne data were compared to a review of international data.

3. Materials and methods

3.1. Nitrogen composition

Water samples were collected from 14 monitoring sites in urban catchments (Table 1) ranging in area from 0.8 to 122 ha, and from 35% to 80% impervious cover. Flow-weighted composites were collected during storm events ($n = 32$ events) using Sigma 900 autosamplers, with 24 1 L polyethylene bottles, to derive an event mean concentration. Baseflow samples ($n = 23$) were collected manually with a 10 L polyethylene bucket.

Samples were stored and analysed according to Standard Methods (Greenberg et al., 1999) (Fig. 2). TN samples were stored in 1 L polyethylene bottles and refrigerated at $<4\,^{\circ}C$. Dissolved nitrogen forms were filtered into two 12 mL polyethylene sample vials using 25 mm diameter 0.45 μm pore size nylon membrane and glass pre-filters in a polypropylene housing, and stored frozen. Samples were analysed for TN, total dissolved nitrogen (TDN), oxidised nitrogen (NO_x) and ammonia

Table 1
Melbourne monitoring sites

Site	Catchment area (ha)	Imperv. area (%)	Land use	*N* (base)	*N* (storm)
Bonview	105.6	51	85% residential, 13% commercial, 2% parkland	4	4
Lynbrook	4.65	35	90% medium density residential, 10% parkland		9
Keilor	57	44	86% residential, 14% school		6
Kings Park	35	51	98% residential, 2% parkland		4
Wantirna	26	42	90% residential, 10% parkland		6
Shandford Avenue	0.8	40	100% residential	2	
Green Point	25	45	90% residential, 9% parkland, 1% commercial	3	
Global Drive	25	75	100% industrial	5	
Pascoe Vale	122	46	80% residential, 20% commercial	2	
St. Kilda	94.5	80	50% commercial, 40% residential, 10% parkland	3	
Albion Street	108.8	65	65% residential, 35% commercial		1
Westmeadows	4.4	60	60% Commercial, 40% Residential		1
Mordialloc	29.4	70	60% residential, 40% commercial		1
Bay Street, Brighton	8.3	60	92% residential, 8% parkland	4	

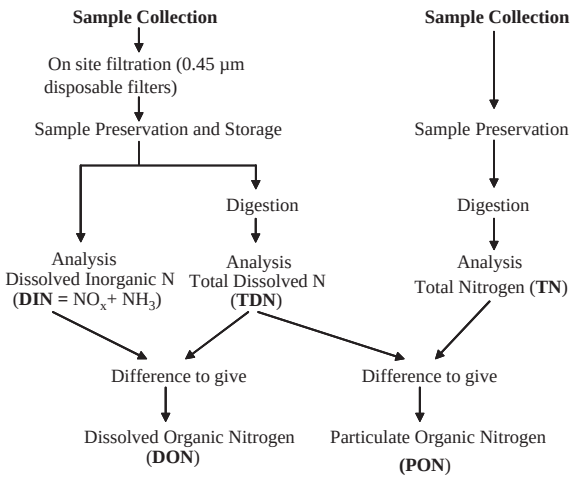

Fig. 2. Laboratory analysis and reporting of nitrogen composition.

(NH_3). All nitrogen forms analysed were reported as mg/L N, to allow the proportion of TN to be calculated. Other forms—total Kjeldahl nitrogen (TKN), Org-N, particulate Org-N (PON), DON and DIN—were determined from these constituents (Fig. 2).

3.2. Sample storage: stability of nitrogen composition over time in storage

Dissolved nitrogen forms (e.g. NO_x, DON and NH_3) are known to be bio-available, and have the potential for change over time (Kadlec, 1999; Kotlash and Chessman, 1998). An assessment of changes in the nitrogen composition in stored samples was undertaken, to assess the reliability of samples which remained in situ prior to preservation. A 10 L polyethylene bucket was used to collect samples from the end of stormwater pipes. Six 1 L polyethylene bottles were filled from the 10 L bucket, and stored for 30 h in conditions comparable to typical field conditions (i.e. without refrigeration or filtration). Progressive sampling every 6 h, from the six replicates, showed that no significant changes in most nitrogen forms occurred over the 30 h (Fig. 3). Only the proportion made up by NH_3 changed significantly (repeated measures ANOVA; $p = 0.02$), when the initial NH_3 concentration was unusually high, leading to a change ($p = 0.03$) in TKN. Based on these results, our protocol permitted samples to be preserved up to 24 h after collection.

3.3. Comparison of Melbourne data with international literature

International data were obtained from an extensive review conducted by Duncan (1999). Land use in these catchments included proportions of residential (11–100%), commercial (2–30%), industrial (52% for one site) and parkland (10–41%), with an imperviousness range of 4–68%. Data were limited to cities with separate stormwater systems (as is the case in Melbourne). A total of 40 data sets were collected from 22 catchments. The number of storm events sampled at most sites ranged from 1 to 47, except for one site, where

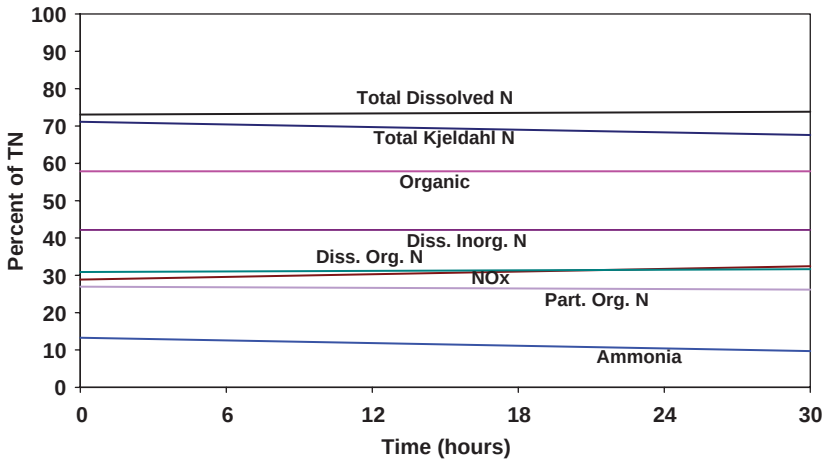

Fig. 3. Changes in nitrogen form over time in storage (where 0 is time of sampling).

247 events were sampled. Nitrogen concentrations for each site were variously reported as the geometric mean (57%), median (10%) or arithmetic mean (5%), with the remaining 28% composed of grab samples and event mean concentrations. Data included TN, along with NO_x and NH_3, from which DIN and TKN concentrations could be calculated. However, TDN could not be determined because no data on DON were available.

3.4. Data analysis

For the Melbourne data, nitrogen species were expressed both in concentration (mg/L), and composition (% of TN). Prior to statistical testing, concentrations of the nitrogen forms were log-transformed (Eq. (1)) to achieve normality (Kolmogorov–Smirnov $p > 0.10$). Distributions of composition data already satisfied assumptions of normality ($p > 0.10$). Independent sample t-tests were used to compare baseflow and storm event mean nitrogen concentration (mg/L) and composition (%); significance was accepted at $p < 0.05$. Differences between sites were examined by one-way ANOVA:

$$X' = \log_{10}(X + 1). \quad (1)$$

4. Results

4.1. Comparisons between Melbourne baseflow and storm events, and international data

In Melbourne, TDN made up the largest proportion of TN ($\mu = 84\%$ during baseflows, 77% during storms), PON thus accounting for 16% and 23% in baseflows and storms, respectively (Fig. 4). Ammonia was consistently the least-abundant constituent. Variability (shown by coefficient of variation, CV; Table 2) was high during both dry and wet weather. There were no significant differences in the *concentration* of any of the nitrogen species between baseflow and storm event conditions (Table 2). However, the *composition* (percentage of TN made up by each species) did vary, with lower PON during baseflow ($p = 0.04$), but higher DON ($p = 0.04$) and thus higher TDN ($p = 0.01$).

Nitrogen composition did not vary between sites. Concentrations were also consistent, with a few exceptions. During storms, DON and NH_3 concentrations varied between sites (ANOVA $p = 0.01, 0.04$, respectively), leading to variation in TDN ($p = 0.03$).

While a visual comparison could be made between Melbourne and international storm datasets (Fig. 4), statistical comparison was precluded by the varied nature of sampling and reporting of the international data. The international literature provided information only on the amount of NO_x and NH_3, which were both lower than either the Melbourne baseflow or storm event composition, suggesting that the proportion of Org-N is higher in the international data. Org-N makes up the largest component of nitrogen in the international data, but the proportion of Org-N that is particulate or dissolved cannot be determined, as TDN was not reported. Consistent with the Melbourne baseflow and storm event data, ammonia was the least-common species in the international literature (Fig. 4).

5. Discussion

5.1. Nitrogen behaviour

Concentrations of most nitrogen species were highly variable, supporting other studies such as Duncan, 2003

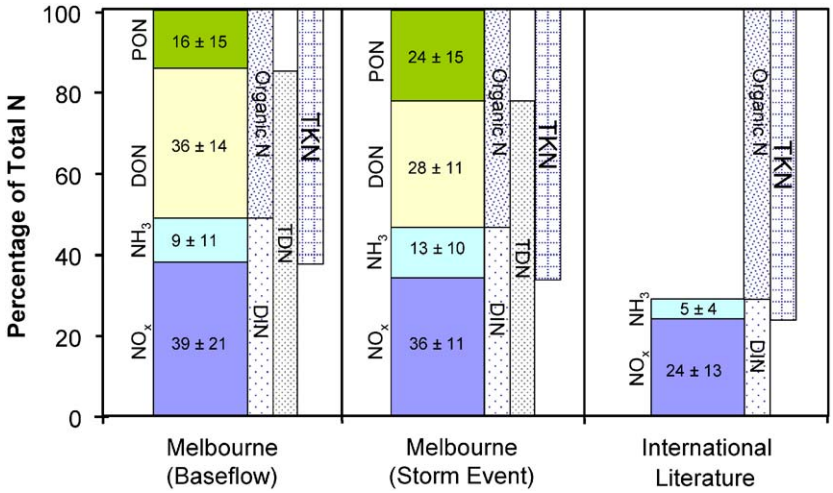

Fig. 4. Nitrogen composition for baseflows and storm flows in Melbourne, and the review of international literature. Numbers in each box show the mean ± 1 standard deviation.

Table 2
Summary statistics for Melbourne data

	Baseflow concentration (mg/L)			Stormflow concentration (mg/L)			Independent *t*-test *p*-values	
	Mean	Median	C.V.	Mean	Median	C.V.	Concentration	Composition
TN	2.17	2.10	0.56	2.13	1.80	0.79	0.99	—
TKN	1.30	1.13	0.67	1.39	1.00	0.86	0.81	0.43
Org N	1.09	0.98	0.64	1.10	0.81	0.90	0.87	0.89
TDN	1.84	2.00	0.61	1.63	1.15	0.82	0.68	**0.04**
PON	0.33	0.20	1.25	0.50	0.34	1.11	0.21	**0.04**
DIN	1.08	1.02	0.71	1.03	0.80	0.80	0.81	0.88
NO_x	0.87	0.59	0.81	0.74	0.54	0.76	0.96	0.38
DON	0.76	0.70	0.65	0.60	0.42	0.93	0.25	**0.01**
NH_3	0.20	0.05	1.55	0.29	0.17	1.37	0.29	0.09

Independent *t*-test *p*-values (significant differences at $p = 0.05$ shown in bold) show comparisons between baseflow and stormflow concentrations in mg/L and composition in % (df = 52).

and Terstriep et al., 1986. High variability during storm events is a well-known phenomenon caused by variations in aerial deposition and rainfall quality (Duncan, 1995; Zhang et al., 1999), catchment soils (Feth, 1966) and past and present catchment activities (e.g. Mayer et al., 2002).

The observed variability during baseflows has a number of possible causes, including impacts from groundwater (Linderfelt and Turner, 2001), or from improperly functioning sewers (Hatt et al., 2004). Urbanised catchments also have a range of possible point-source inputs which will vary through space and time, and importantly, since their drainage systems bypass riparian zones, they preclude the buffering and denitrification that would normally occur (Groffman et al., 2002). Another important contributor to high variability during baseflow may be the presence of interflow. A recent study of two catchments in Melbourne has shown this effect (Duncan, 2004; Fletcher et al., 2004); PON concentrations peak very early during a storm event (due to washoff), lowest concentrations occur during the event (dilution by rainfall) and high TDN (and NO_x) persist for several days after the event (i.e. interflow).

The lack of major differences in *concentration* between baseflows and storm events observed in this study contrasts with some previous studies (e.g. Lee and Bang, 2000). However, clear relationships between runoff and nitrogen species concentrations are also not well-established (Lee and Bang, 2000). Whilst higher PON

concentrations during storms may be expected, due to washoff by high flows, they were not observed in this study. In part, this is a statistical consequence of the high variability discussed above. In particular, the coefficient of variation for PON was very high during both baseflows (1.25) and storm events (1.11). When the *compositions* are considered, there was a significant variation between dry and wet weather (Fig. 4), with a higher proportion of dissolved forms in baseflow (baseflow mean = 84.6%, storm mean = 75.9%), and PON during storms (baseflow mean = 15.4%, storm mean = 24.1%), although the differences are small. The general lack of difference could also be explained by the previously described interflow behaviour; in the Melbourne studies described (Duncan, 2004; Fletcher et al., 2004), the results were similar mean and variance during both baseflow and storm events—a function of their interflow-induced merging.

The consistency between baseflow and storm events in the concentration of nitrogen compounds may also be a reflection of the equilibrium of nitrogen composition in the highly turbulent and thus oxygen-rich conditions, present in urban stormwater drainage systems. As nitrogen species are transported in aqueous conditions, they are subject to a range of transformation processes. In urbanised catchments, the bypassing of riparian zones by constructed drainage systems (Groffman et al., 2002), and the channelisation of streams result in decreased detention times, reducing nutrient cycling, and thus high levels of TDN (Galloway et al., 2003). Whilst detention times will be shortest during high flows (i.e. storm events), the high degree of turbulence (thus oxygen availability) will, to some extent, compensate for the short detention times, resulting in a rapid breakdown of Org-N, and production of NO_x by nitrification. Since NO_3 is persistent (Singh, 1987), this equilibrium will be quite stable in either condition, thus leading to relative consistency in composition.

5.2. Comparison of Melbourne and international data

A recent world database compilation (Fuchs et al., 2004) reports overall median TN concentrations of 2.36 mg/L (for separate stormwater outlets), slightly higher than the Melbourne data (median = 2.10 mg/L during baseflow and 1.80 mg/L in storm flows).

Whilst the proportion of Org-N is higher in the international dataset than in the Melbourne data (and thus NO_x and NH_3—and hence DIN—are lower in the international data), it is not possible from these data to determine whether the overall proportion of dissolved nitrogen (TDN) is higher in Melbourne than in the international data. From the available data, the causes of such differences cannot be hypothesised with great confidence. The relatively low proportion of deciduous trees in Melbourne (Allison et al., 1998) may explain the smaller proportion of organic N. The sclerophyllous leaves which are typical of the dominant Australian genera (*Eucalyptus* and *Acacia*) fall relatively uniformly throughout the year (albeit with a typical summer peak) and are slower to break down than those of deciduous leaves (Keith, 1997).

Of all nitrogen compounds, PON is the most difficult to quantify, however, given that a proportion of its load will pass as bedload, and thus not be measured by standard autosampler or dry-weather sampling techniques using Standard Methods (Greenberg et al., 1999). This makes comparisons between studies difficult, since studies often do not make clear how samples were collected, and thus whether bedload would be sampled (e.g. Cowen et al., 1976).

5.3. Implications for stormwater management

Whilst catchment management activities can be implemented to reduce nitrogen inputs, these will obviously have no effect on the significant loads contributed by atmospheric deposition (Duncan, 1995). Therefore, systems are required which either remove the nitrogen by 'removing' the water (by infiltration, or stormwater harvesting and re-use systems), or intercept and treat the stormwater to reduce the dominant or biologically important nitrogen compounds.

This study has shown that dissolved nitrogen forms dominate urban runoff, during both dry and wet weather (Fig. 4). In addition, given the biological availability of dissolved nitrogen, its concentrations must be reduced to achieve any positive ecological response (Hart and Grace, 2000). Systems that remove NO_x and DON through a combination of nitrification and subsequent denitrification will fulfill this requirement. Long detention times and low flow rates are needed (Bavor et al., 1995; Sakadevan and Bavor, 1999) to allow both nitrification and denitrification to occur. Systems that rely primarily on physical processes such as short-detention sedimentation (e.g. sediment traps) or aerobic filtering (e.g. vegetated swales) are unlikely to be satisfactory.

Specifically, treatment systems must provide both aerobic conditions to drive nitrification (conversion of ammonia and Org-N to NO_x), but also allow enough detention time in an anaerobic state to promote denitrification (the conversion of NO_x to N_2O and N_2 gas). Given the relatively high proportion of TN which is made up of NO_x (Fig. 4), promotion of denitrification would appear to be the critical element to achieve effective nitrogen removal. Systems such as stormwater wetlands and biofiltration (also called bioretention) systems (which filter stormwater through a vegetated filter media, discharging it via a perforated collection pipe) can fulfill this role, provided that they have a distinct anaerobic zone. For example, Kim et al. (2003)

demonstrated little NO_x removal from 'conventional' biofiltration systems, but were able to consistently remove 70–80% of NO_x once an anaerobic sump was added. Similarly, in wetlands, denitrification occurs largely within the sediment–water interface, where the aerobic water containing NO_x comes into contact with anaerobic sediment (Galloway et al., 2003; Yousef et al., 1986). Effective treatment of dissolved nitrogen is therefore likely to increase the relatively limited (30–40%) removal of TN that is typical of current wetland design (Duncan, 1998; Hammer and Knight, 1994).

Management of particulate organic matter into stormwater treatment measures must also be given careful attention. If systems become overloaded by organic matter, the depletion of oxygen may prevent nitrification. However, a lack of labile organic matter will reduce denitrification potential (Galloway et al., 2003).

The observed variability in nitrogen concentrations and composition (Table 2) suggest that stormwater treatment systems should be designed to operate under stochastic conditions (Wong and Geiger, 1997). The results also suggest that for many urban areas (those studied in Melbourne had a diversity of land uses, size and impervious area (Table 1)), the variation in the concentration of nitrogen species *within* dry or wet weather may be as important as the variation *between* wet and dry weather. Systems therefore need to provide enough detention time and buffering capacity to cope with this variation.

In addition, the variation between the Melbourne and international data suggests that caution should be used in transferring stormwater treatment designs from one part of the world to another.

5.4. Future research

There is a clear need to better understand the dynamics of nitrogen compounds in urban runoff. In particular, the relative lack of published data on TDN is of concern (Seitzinger et al., 2002). Establishing typical nitrogen-budgets for a range of land uses and catchment characteristics would help stormwater managers to better target treatment systems. Influences of two processes in urban environments are of specific interest: interflow, and instream transformation processes.

Perhaps the most important area of future research is to focus on enhancing stormwater treatment, by promoting denitrification (Kim et al., 2003) and plant-uptake (Brock et al., 1994; Roberts, 2000) to enhance dissolved nitrogen treatment.

6. Conclusion

The composition of TN in both baseflow and storm events was dominated by TDN (typically around 80% of TN). Examination of international data showed a lower proportion of DIN, with a subsequently higher proportion of Org-N.

The composition of nitrogen prior to entering treatment systems such as constructed wetlands is an important consideration for enhancing current wetland treatment capabilities. Nitrogen concentrations appeared to be highly stochastic, but did not vary significantly between baseflow and storm event conditions, thus facilitating the design of wetlands which are effective in treating both dry and wet weather flows. However, changes in the percentage of TN made up by each species may impact on treatment efficiency.

We propose that the performance of stormwater management systems could be improved, by refining their design to better match the inflow nitrogen composition, with a focus on dissolved nitrogen.

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