SOURCE TRANSFORMATION OF NITROGEN COMPOUNDS IN HAYTON'S STREAM, A LOW LYING URBAN DRAINAGE SYSTEM IN CHRISTCHURCH

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ABSTRACT

Concentrations of nitrogen compounds in Haytons Stream, an urban waterway in Christchurch New Zealand, have been reported to be elevated. High levels of ammonia and/or related nitrogen compounds can be toxic to aquatic organisms and can have a significant effect on the stream's ecological health. Numerous environmental and physical factors such as organic matter content, hydrology/hydraulics, temperature, sediment characteristics and interactions with other contaminants can cause transformation or dilution of nitrogen compounds along the stream. The aim of this project was thus to assess the sources, types, and transformation of nitrogen compounds in Haytons stream through water quality monitoring at various locations along the stream, over time and in stormflow and baseflow conditions. Our initial results have confirmed previous reports. Levels of oxidized nitrogen were found to exceed the local guidelines in 90% of samples taken while ammoniacal nitrogen in some of the samples was up to 8 times higher than local guidelines. Our results also show that for both baseflow and stormflow conditions, there is an increase of total nitrogen downstream and that the predominant nitrogen form changes with flow conditions. During baseflow, nitrogen is mostly in its inorganic form at the upper and middle parts of the stream and in organic form at the lower part of the stream; during stormflow, the majority of the nitrogen is in its organic form. Nevertheless, the total nitrogen at each site is of about the same magnitude in both conditions, except at the lower part of the stream where the total nitrogen is considerably lower. A preliminary analysis suggests that both sediments in the stream bed and street runoff water are contributing to the nitrogen load of Haytons stream. Further research will be conducted to better understand the increase of nitrogen loads originating from stream bed sediments.

KEYWORDS

Nitrogen composition, urban runoff, urban waterways, water quality

PRESENTER PROFILE

Fabio Silveira (BE, Chemical Engineering) is a Masters student. His thesis is on the characterization of the nitrogen composition and possible sources of contamination of the Haytons Stream. He has previous experience in a wastewater treatment plant for 1 year as a volunteering student, 2 years in a pharmaceutical company in both Quality Control and Project departments and 2 years as Construction Engineer in Christchurch.

1 INTRODUCTION

Haytons Stream, a headwater tributary of the Heathcote River/Ōpāwaho, is located within a predominantly industrial catchment in south-west Christchurch. The Haytons Stream catchment (Figure 1) has an approximate area of 13 km^2, with around 5 km^2 of residential, 3 km^2 of industrial and 5 km^2 of rural land use. At its headwaters, stormwater is channeled through pipelines becoming an open stream at Waterloo Road and ending at the Wigram Retention Basin, which then discharges to the Heathcote River. The Paparua Stream subcatchment, on the northern side of the catchment, has rural and predominantly residential land use, covering a larger area of the catchment. According to previous water quality monitoring, the stream's water quality in this area is good (Moores et al., 2009). In the Haytons Stream sub catchment, which lies in the southeast part of the catchment, the predominant land use is industrial, which presents the potential for a wide range of contaminant sources.

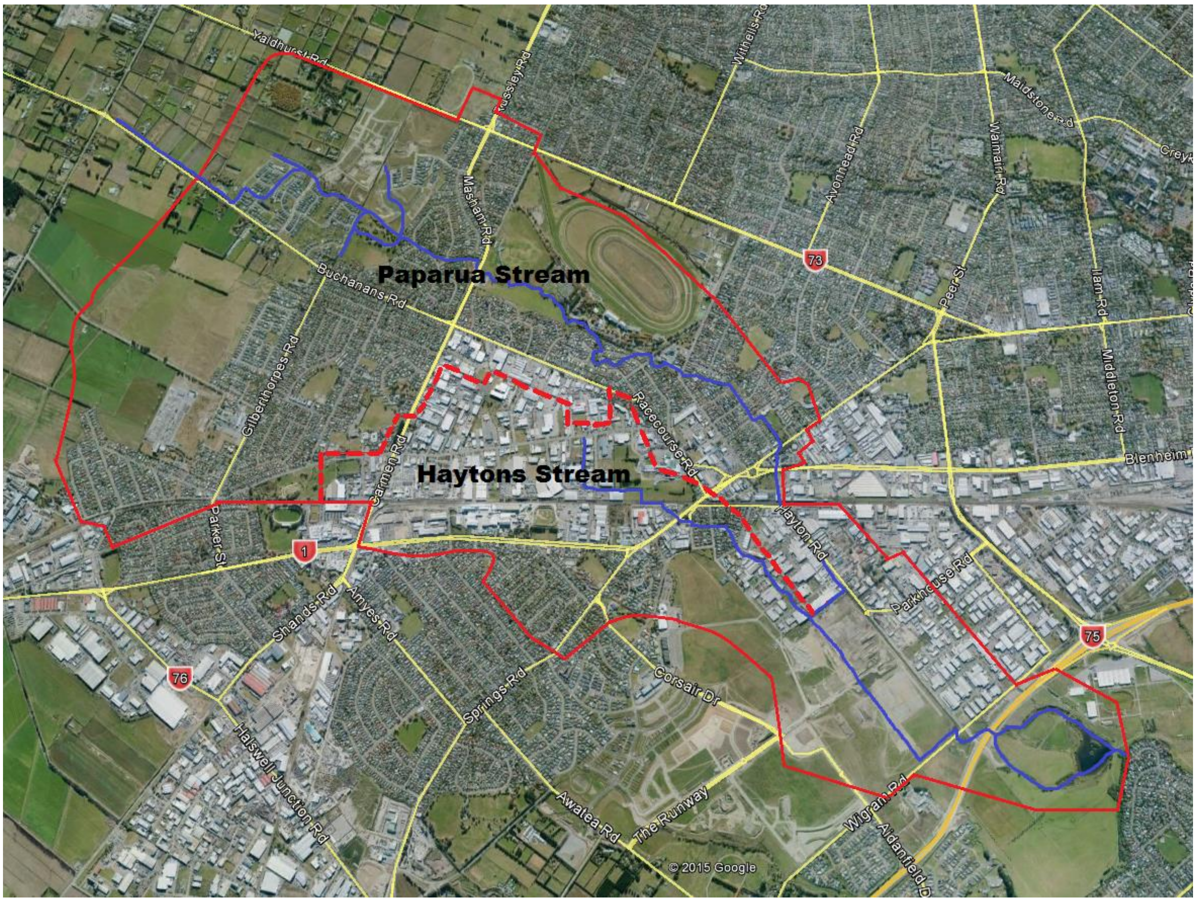

Figure 1: Aerial photograph of Haytons Stream catchment showing the catchment boundary (solid red line), the sub-catchment boundary between Paparua and Haytons Streams (dashed red line), Haytons and Paparua streams (dark blue) and the land use (industrial areas are occupied by larger white/grey roofed buildings; residential areas are occupied by small dark grey roofs; rural areas and parks are green color; developing areas are brown/sand color).

(www.maps.google.co.nz)

Given the industrial land use around Haytons Stream, a number of studies have been conducted over the past 20 year to determine contamination levels. An investigation of more than 10 years' worth of data showed that Haytons Stream had the highest concentration of ammoniacal nitrogen of all tributaries of the Avon/Otakaro and Heathcote/Opawaho rivers (ECan, 2007). Another investigation undertaken by Niwa for Environment Canterbury identified Haytons Stream as having the poorest water quality in the Heathcote/Opawaho tributary (Moores et al., 2009) with concentrations of nitrogen compounds being higher than local guidelines (ANZECC, 2000). Due to the poor water quality at Haytons Stream, an investigation was conducted in 2013 (O'Sullivan & Charters, 2014) at Gerald Connolly Place to determinate contaminant levels during baseflow and stormflow conditions. Results showed high concentrations of nitrogen compounds and differences in concentration between baseflow and stormflow conditions. However, this study investigated only the upper part of Haytons Stream and the source(s) of this contamination were not clearly determined. Understanding the dynamics of nitrogen compounds in Haytons Stream is necessary to identify likely sources of contamination.

The aim of this paper is to report on the ongoing characterization of nitrogen compounds along Haytons Stream in order to have a better understanding of their relation with the mainly industrial land use. Road runoff and sediments samples were also collected in an effort to identify the sources of the nitrogen in the Haytons Stream.

2 METHODOLOGY

To characterize the nitrogen compounds in Haytons Stream, water samples were collected at selected sites and at different times during baseflow and stormflow conditions (Table 1 and Figure 2). We report on samples taken from five different sites in three sampling campaigns per each weather condition, stormflow and baseflow. The sampling sites were carefully selected taking into account historical high level of nitrogen compounds, current changes on the stream's main course, points of runoff from different zones, and the presence of water flow during both the dry and wet season.

Water samples were manually collected and immediately transported to UC's Environmental Engineering Laboratory for analysis. Water temperature and dissolved oxygen were measured on site with field equipment. The pH of the samples was adjusted to below 2 with concentrated sulfuric acid and then the samples were stored in a refrigerator at 4°C. Before analysis, the samples pH was neutralized to have an accurate result.

Table 1: Sampling sites locations and descriptions

Site	Description	Location
Site 1	The first point where Haytons Stream becomes an open stream	Waterloo Road
Site 2	Previous monitoring station at that point	Gerald Connolly Place
Site 3	First big retention pool	Pilkington Way

Site 4	Wigram Retention Basin (WRB)	Upstream WRB
Site 5	Downstream Wigram Retention Basin	Downstream WRB

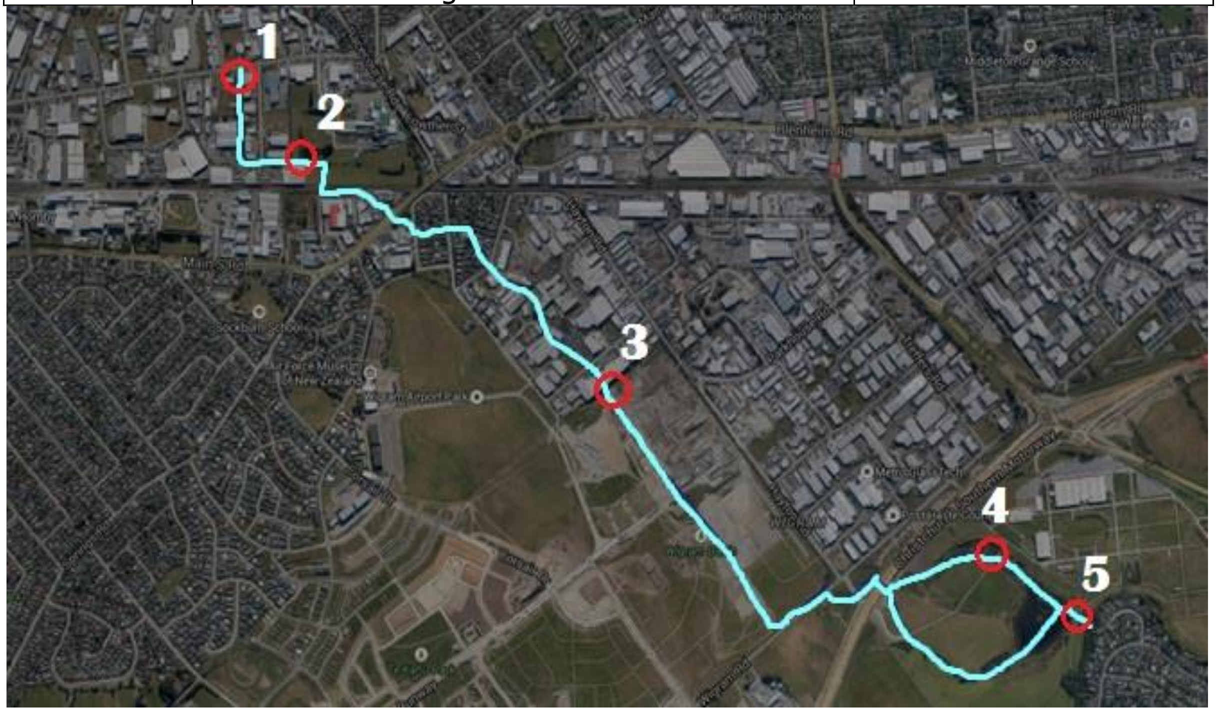

Figure 2: Sampling sites along Haytons Stream

Total Nitrogen (TN) was analyzed using HACH's 10071 Method (HACH, 2003). Total Dissolved Nitrogen (TDN) was analyzed by filtering the sample using a 0.45 µm membrane first and then following the same procedure as for TN analysis. Oxidized Nitrogen (NOx-N) was measured using HACH's Nitrate 8039 Method (HACH, 2003). Ammoniacal nitrogen (NH4-N) was obtained using the Phenate Standard Method (4500-NH_3 F) (APHA, 1999).

Nitrogen compounds are divided in ammoniacal nitrogen, oxidized nitrogen, particulate organic nitrogen (PON) and dissolved organic nitrogen (DON). PON concentration is estimated from the difference between TN and [(NOx-N) + (NH4-N)], whereas DON is the difference between TDN and [(NOx-N) + (NH4-N)].

Sediment samples were collected to verify the presence of nitrogen compounds. Samples were taken between the sites 1 and 3, where high concentrations of ammoniacal nitrogen and other nitrogen compounds have been observed, according to historical data (Moores et al., 2009; O'Sullivan & Charters, 2014) and the data collected in this study. Analyses were conducted at Hills Laboratory. Street runoff samples were collected at site 2 in two different storm events.

3 RESULTS AND DISCUSSION

3.1 COMPOSITION OF NITROGEN COMPOUNDS

The proportion of each nitrogen compound changed with the different sites along the Haytons Stream and the sampling condition (Figures 3 and 4).

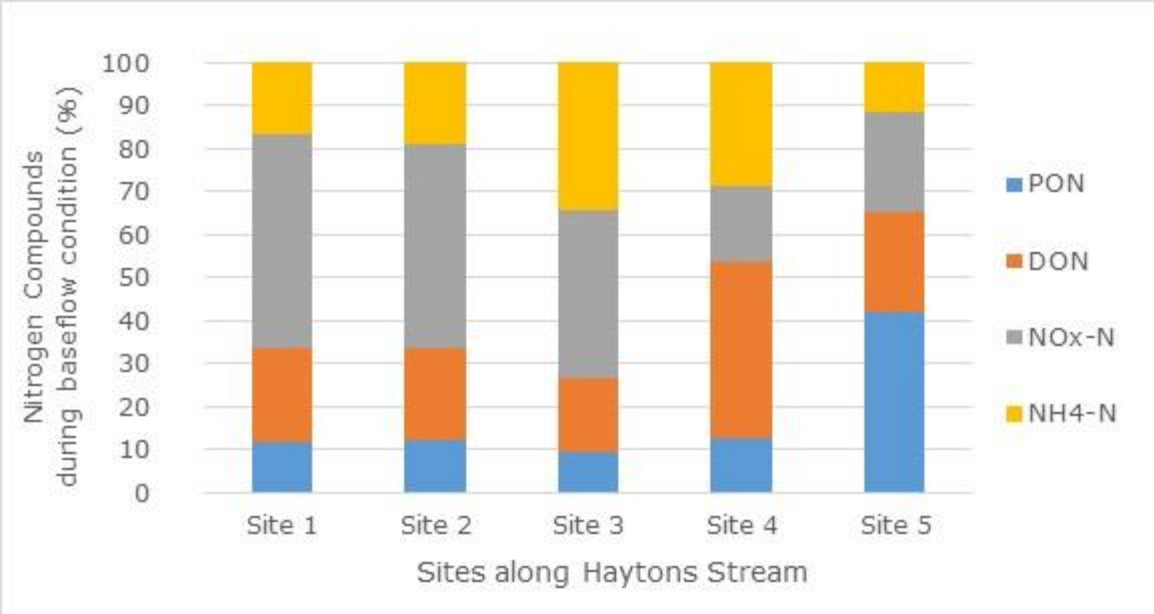

Figure 3: Composition of nitrogen compounds along Haytons Stream during baseflow conditions with PON (Particulate organic nitrogen), DON (Dissolved organic nitrogen), NOX-N (Oxidized nitrogen) and NH4-N (Ammoniacal nitrogen)

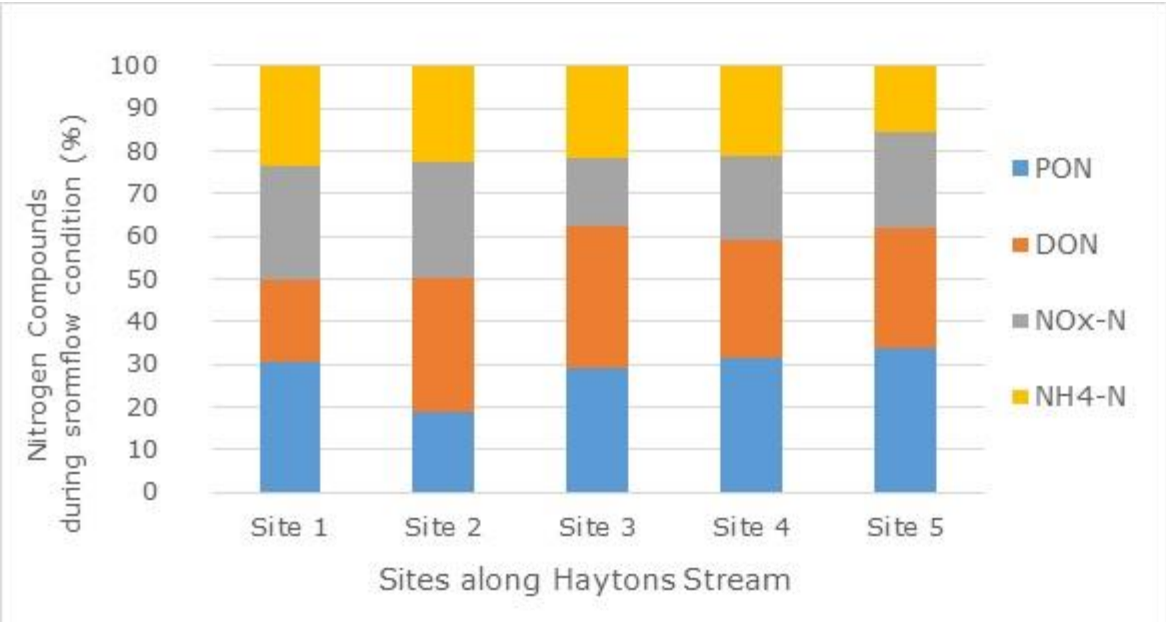

Figure 4: Composition of nitrogen compounds along Haytons Stream during stormflow conditions with PON (Particulate organic nitrogen), DON (Dissolved organic nitrogen), NOX-N (Oxidized nitrogen) and NH4-N (Ammoniacal nitrogen)

During baseflow conditions the majority of nitrogen was in its inorganic form; that is, as oxidized nitrogen and ammoniacal nitrogen which altogether represented up to 70% of the total nitrogen in the upper and middle parts of the stream (sites 1, 2 and 3). Oxidized nitrogen was the predominant form of nitrogen in most of the sites. Organic nitrogen represented a substantial proportion of the nitrogen compounds at sites 4 and 5; that is, in the lower end of Haytons Stream.

During stormflow conditions, the content of organic nitrogen increased in all sites as compared to levels under baseflow conditions. In the upper part of the stream, organic nitrogen represented 50% of the total nitrogen whereas in other sites the proportion was close to 60%. The organic nitrogen in particulate form increased from 10% during baseflow to 20-30% during stormflow. Even though the percentage of ammoniacal nitrogen remained similar in both baseflow and stormflow conditions (around 20-30%), it represents half of the inorganic form in most of the sites during stormflow compared to a lower proportion during baseflow condition.

3.2 TOTAL NITROGEN

The concentration of total nitrogen was different in each sampling campaign and site (Figure 5). The lowest registered concentration was 1.1 mg/L at site 3 during the second baseflow condition campaign with the majority of the nitrogen in its oxidized form. The highest concentration (12.7 mg/L) was observed at the same site during the third stormflow condition campaign, with most of the nitrogen in its organic form.

Variations in TN under stormflow conditions could be explained by changes in rainfall characteristics and by the effect of the first flush and steady-state runoff characteristics. The high TN concentration noted at site 3 did not occur at site 4 probably due to a sampling lag between sites; that is, when the sample was collected at site 4 the storm flush had not reached yet this sampling point, leading to a low nitrogen concentration. This can be explained by water infiltrating in the soil and by the presence of retention ponds along Haytons Stream.

A decrease on the total nitrogen concentrations was noted at site 5, which is an output of Wigram Retention Basin, a wetland. Wetlands are known to decrease total nitrogen due to the plant uptake and/or microbiological processes (Lee et al., 2009). Four out of five samples had lower concentrations at the output (site 5) than the input (site 4).

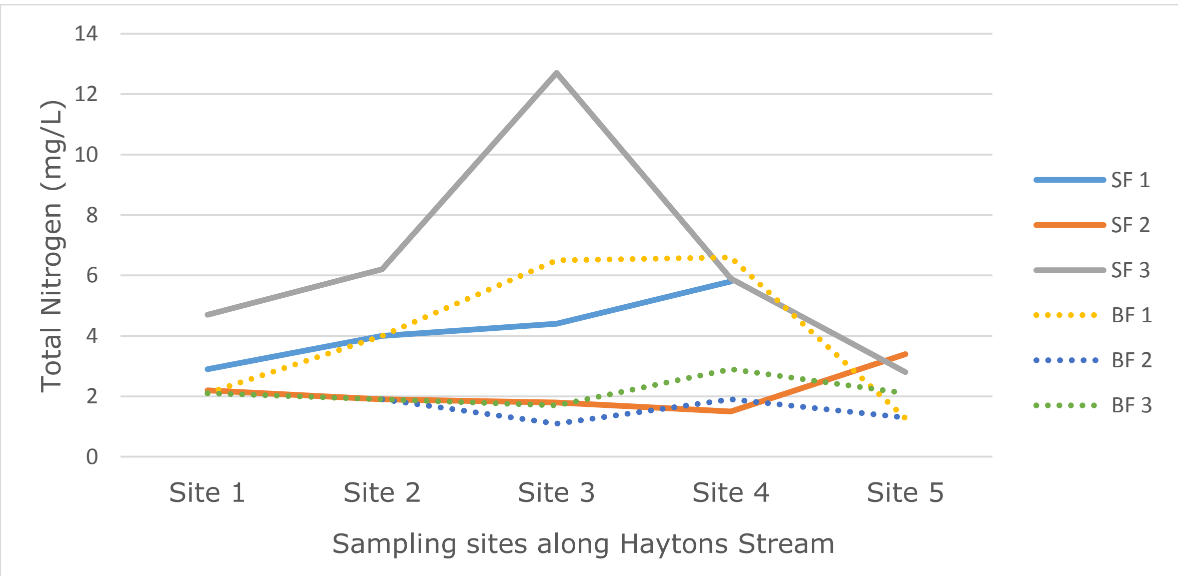

Figure 5: Total nitrogen concentrations at each site under stormflow conditions (SF) and under baseflow conditions (BF) for three sampling campaigns (1-3)

3.3 ORGANIC NITROGEN

The lowest concentration of organic nitrogen was observed at site 3 during baseflow conditions (Figure 3). However, the concentration of inorganic nitrogen in the same sample was high, which can be explained by the ammonification and nitrification process occurring on the organic matter at that site. Organic nitrogen includes the nitrogen in organic matter, such as microorganism, algae population, skin tissue, DNA, amino acids, etc. Organic nitrogen decomposes in nature releasing ammonia (ammonification), which due to the nitrification process is converted in oxidized nitrogen (Vesilind & Morgan, 2004). Previous studies at Haytons Stream did not measure organic nitrogen. It is evident that this form of nitrogen contributes to the loads of nitrogen in the stream due to its high concentration, especially during stormflow events (Figure 4).

It is worth noting that an algal bloom was observed at site 3 (see Figure 6), which results in the conversion of inorganic nitrogen into organic nitrogen. Algal blooms occur when there is availability of nutrients and light. One of the results of an algal bloom is the decrease of oxygen in the water, leading to a hypoxic condition, which leads to an inhospitable environment for fish and other living organisms, reducing the life diversity in the area (Johnson et al., 2010). This combination of light incidence and available nutrients might explain the higher proportion of organic nitrogen at the lower part of the stream.

Figure 6: An algal bloom happening at site 3 during a sediment sampling

3.4 AMMONIACAL NITROGEN

Ammoniacal nitrogen is the most toxic form of nitrogen in waterways particularly at high pH (at pH 7, toxic concentration is 2.2 mg/L whereas at pH 9 it is 0.2 mg/L). Out of 28 samples collected, 8 had ammoniacal nitrogen concentrations higher than toxic levels (Table 2). Considering the pH, the most toxicity concentration of NH_4-N was found in the stormflow sample collected at site 2 during the 3rd sampling campaign. In that sample (pH 9.5), ammoniacal nitrogen concentration was 1.8 mg/L, which is 9 times higher than the toxic concentration at that pH. The ammoniacal nitrogen concentrations found on this study are lower than those of previous reports (ECan, 2007; Moores et al., 2009; O'Sullivan & Charters, 2014).

High concentrations of ammoniacal nitrogen were found at sites 3 and 4 with three samples exceeding concentrations of 3.2 mg/L (Table 2). These high concentrations of nitrogen compounds might be the result of ammonification processes that occur on organic matter. Alternatively, they could also be linked to discharges to Haytons Stream (Moores et al., 2009), which are often associated with high turbidity, high/low pH, high conductivity, etc.

3.5 OXIDIZED NITROGEN

Oxidized nitrogen is the result of the nitrification of ammoniacal nitrogen. It is a high oxygen demanding process and hence it occurs in zones with high oxygen concentrations (Ahn, 2006). Most of the samples taken at Haytons Stream had oxygen concentrations higher than the guidelines. A high concentration of oxygen in water helps to promote the conversion of ammonia to nitrite and then nitrate, which is the potential source of oxidized nitrogen at Haytons Stream (Moores et al., 2009).

High concentrations of oxidized nitrogen (NOx-N) were detected at Haytons Stream during this study (Table 2). Nearly all of the collected samples (24 of the 28) had concentrations of NOx-N higher than the ANZECC (2000) trigger value of 0.444 mg/L. Furthermore, 12 of them had concentrations of NOx-N twice or higher than the guidelines, with the highest concentration of 1.7 mg/L (samples at sites 2 and 3) being approximately four times higher than the trigger value. Even though the oxidized nitrogen exceed guidelines in most of the samples, concentrations in this study are lower than those reported in previous studies (Moores et al., 2009; O'Sullivan & Charters, 2014).

3.6 INPUT OF NITROGEN FROM STREET RUNOFF

One of the potential sources of nitrogen compounds in urban streams is street runoff, particularly the first flushes since these wash away pollutants from the surfaces which are then discharged in high concentration into the urban streams. Data from stormwater first flush in a site near Haytons Stream showed high concentration of nitrogen compounds, which contributes to the loads of nitrogen in the steam.

Table 2: Concentration of nitrogen compounds at Haytons Stream.

Site	Condition	Sampling Campaign	TN (mg/L)	TDN (mg/L)	NO_x-N (mg/L)	NH_4-N (mg/L)	Maximum NH_4-N (mg/L)	pH
Site 1	Baseflow	1	2.1	2.0	**1.1**	0.6	0.2*	9.6
		2	Data not available					
		3	2.1	1.3	**1.0**	<0.1	2.0	7.2
	Stormflow	1	2.9	2.7	**0.5**	0.9	1.3	7.7
		2	2.2	1.4	**0.9**	**0.2**	0.2*	10.1
		3	4.7	2.4	**1.1**	**1.7**	0.4	8.5
Site 2	Baseflow	1	4.0	4.0	**1.7**	**1.6**	0.2*	9.1
		2	2.9	1.7	**1.3**	0.3	2.5	6.5
		3	1.9	1.4	**0.6**	<0.1	2.2	7.0
	Stormflow	1	4.0	3.7	**0.6**	1.3	2.0	7.2
		2	1.9	1.4	**0.9**	<0.1	0.2	9.0
		3	6.2	4.8	**1.2**	**1.8**	0.2*	9.5
Site 3	Baseflow	1	6.5	6.4	**1.7**	**3.2**	2.0	7.2
		2	1.1	1.0	**0.6**	0.5	2.4	6.7
		3	1.7	1.4	**0.6**	0.1	2.1	7.1
	Stormflow	1	4.4	4.5	**0.5**	1.4	1.6	7.5
		2	1.8	0.7	**0.5**	<0.1	0.4	8.5
		3	12.7	9.0	**1.2**	**3.2**	0.7	8.2
Site 4	Baseflow	1	6.6	6.5	**1.4**	**3.7**	1.5	7.6
		2	1.9	2.0	0.4	<0.1	2.4	6.7
		3	2.9	1.7	0.3	0.7	2.1	7.1
	Stormflow	1	5.8	5.0	**0.8**	1.8	2.2	7.0
		2	1.5	0.9	0.4	**0.2**	0.2	8.0
		3	5.9	3.5	**1.1**	1.1	1.8	7.4
Site 5	Baseflow	1	1.3	0.5	0.1	<0.1	1.5	7.6
		2	1.3	0.9	**0.6**	0.4	2.4	6.6
		3	2.1	1.4	**0.5**	<0.1	2.3	6.9
	Stormflow	1	Data not available					
		2	3.4	2.2	**0.8**	1.0	1.2	7.8
		3	2.8	1.9	**0.6**	<0.1	2.1	7.1

Values in bold are equal or higher than the local Guidelines.
The guideline value for NO_x-N is 0.444 mg/L (ANZECC, 2000).
Maximum ammonia concentration for 95% species protection is a pH dependent value (ECan, 2011).
*Assuming pH > 9.0 the maximum concentration is 0.2mg/L.
TN: Total nitrogen; TDN: Total dissolved nitrogen; NOx-N: Oxidized nitrogen and NH4-N: Ammoniacal nitrogen.

Two street runoff samples were collected from Gerald Connolly Place (Site 2). The first runoff sample was collected during the first campaign and had a total nitrogen concentration of 1.3 mg/L (Figure 7). The second runoff sample, collected during the third campaign, had a total nitrogen concentration of 2.1 mg/L and an oxidized nitrogen concentration of 0.5 mg/L (Figure 7), which is higher than the ANZECC trigger value of 0.444 mg/L (ANZECC, 2000).

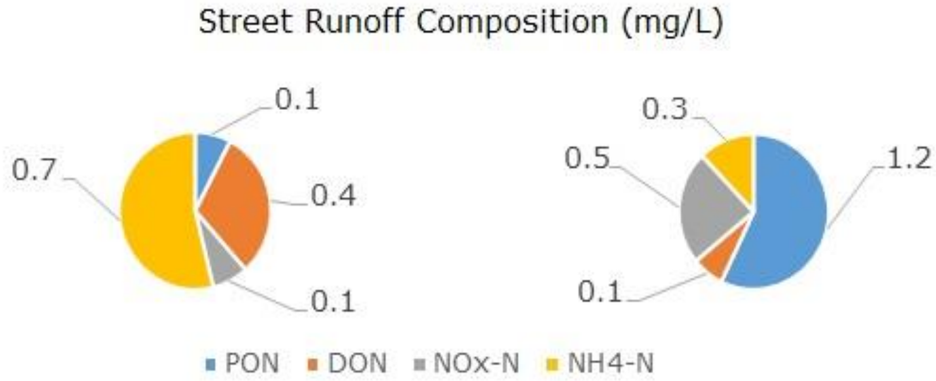

Figure 7: Nitrogen composition in two street runoff samples collected at site 2 during the first stormflow campaign (left) and during the third stormflow campaign (right)

3.7 NITROGEM FROM SEDIMENT AND STORM DRAINAGE SYSTEM

Another possible source of nitrogen in the stream is the sediments. Part of Haytons Stream is underground and studies suggest that dry ponds along streams are sources of nitrogen compounds (Collins et al., 2010). The drainage system may also be contributing to the levels of nitrogen in the stream. For example, organic matter in the city drainage system was observed to be composed of leafs, sediments and rubbish, which could contribute nitrogen to the system. Gully pots, or sinks, can accumulate sediments and organic matter and the decomposition of the latter releases ammoniacal nitrogen which can then be converted to nitrate (Memon & Butler, 2002).

Initial results of sediments analysis showed low concentrations of nitrogen and total carbon. However, during a routine re-test of the sediment samples, an increase of ammoniacal nitrogen was noticed in a sample collected in site 3 (Figure 8). This sample was collected on 26/11/2016, analyzed on 8/12/2015 and retested on 23/12/2015. Analyses on 31/12/2015 and 8/01/2016 were performed in duplicate. It is important to note that the sample was wet (around 38% of dry mass) and it was kept in a 4°C chiller until drying. Taking that into account, the observed increase in concentration is quite high. Normal temperatures in the stream water are around 14°C, which can accelerate the reaction and increase the release of ammoniacal nitrogen from the sediment.

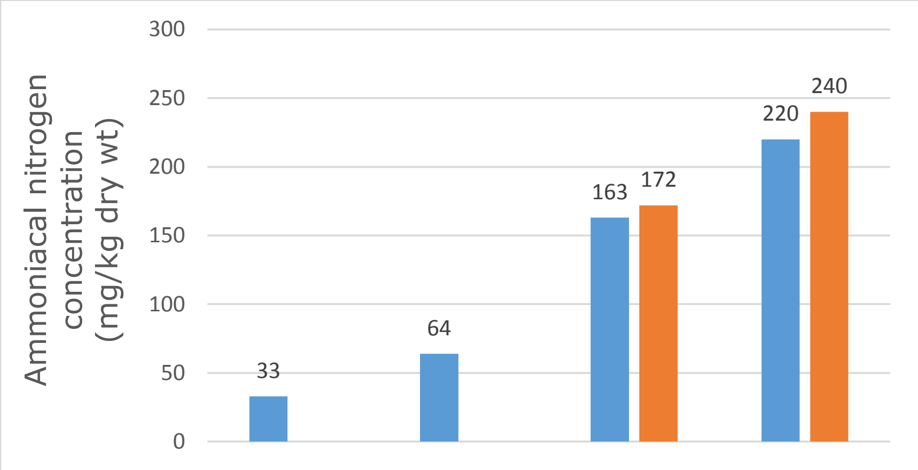

Figure 8: Ammoniacal nitrogen concentration in the sediment sample reported by Hills Lab

3.8 POINT DISCHARGES AT HAYTONS STREAM

Point discharges of pollutants to Haytons Stream were noticed during this study and in previous studies (Bolton-Ritchie et al., 2016). A white color was noticed in Haytons Stream during the second stormflow sampling campaign at site 1 (Figure 9). Analyses showed high turbidity, pH, temperature, and conductivity and total nitrogen, compared to downstream levels.

In order to reduce discharges and rubbish getting into the stream, it is necessary to increase the awareness of the community in relation to discharge prevention and the importance of preserving and revitalizing Haytons Stream. The protection and improvement of the riparian zone would also help to decrease the impact of street runoff as well as reduce the incidence of sunlight thus reducing algal blooms.

Figure 9: Discharge at Haytons Stream, indicated by a white water color, high turbidity, high conductivity and pH

4 CONCLUSIONS

This study shows that the composition of nitrogen compounds changes along the Haytons Stream. It demonstrates the importance of measuring the concentration of all nitrogen compounds since they all are related to each other. This information is also important to identify and to understand the sources of the contamination, the contribution of each nitrogen compound to the total nitrogen loads, and the influence of baseflow and stormflow conditions on nitrogen levels.

Further research is needed to verify the contribution of street runoff, sediments and the drainage system on the nitrogen loads and to locate point discharges in Haytons Stream. More samples and sampling sites are necessary to draw conclusions on trends in composition and concentration and to understand the dynamics of nitrogen compounds at Haytons Stream. The outcomes of this study can provide a basis for better stream management.

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