DIESEL EXHAUST FLUID – INNOVATIVE STORMWATER TREATMENT TRIALS FOR HIGH AMMONIACAL NITROGEN CONCENTRATIONS

***Dr. John Cheah*[1], *Troy Brockbank*[1], *Michael Hannah*[1]**
[1]Stormwater360 NZ

ABSTRACT

Stormwater360 have been working on a treatment solution for high ammoniacal nitrogen concentrations (38 to 132 mg/L) that have been measured in stormwater effluent discharges downstream of existing oil/water separators at refueling truck stops. The high concentrations were identified to originate from urea deposited on the pavement during the Diesel Exhaust Fluid refueling process.

Aquatic organisms are sensitive to ammoniacal nitrogen concentrations and the concentrations entering waterways from truck refueling sites well exceed safe levels for both freshwater and saline environments. ANZECC guidelines list ambient water trigger values at 0.01 and 0.021 mg/L of ammoniacal nitrogen for upland and lowland rivers respectively. The United States Environmental Protection Agency specify acute (1-hour averaged) trigger values for Total Ammoniacal Nitrogen in freshwater and saline environments at 17 mg/L and 11 mg/L respectively.

The paper presents three stages of testing: -

Stage 1 focused on identifying the amount of zeolite media that was required to observably reduce the concentration of ammoniacal nitrogen in solution. At a ratio of 1g of zeolite to 11mg of ammoniacal nitrogen, ammoniacal nitrogen concentrations were observed to decrease from 132 mg/L to 3 mg/L (98% reduction) over 24 hours.

Stage 2 determined the adsorption rate of two different zeolite media blends followed an exponential decay curve relationship with 50% of the total adsorption occurring within the first 4% of the test duration.

Stage 3 established that ammoniacal nitrogen could be removed in a continuous flow arrangement. The testing was conducted using a horizontal flow column (HFC). Influent with 42 mg/L of ammoniacal nitrogen was gravity fed into the HFC at three different flow rates; 1.1, 0.57 and 0.23 l/min.

The research has shown that it is viable to reduce ammoniacal nitrogen concentrations in stormwater effluent flows from truck refueling stops to below the USEPA acute trigger values for freshwater using a proprietary flow-based zeolite media StormFilter cartridge treatment device.

KEYWORDS

Diesel exhaust fluid (DEF), AdBlue, ammoniacal nitrogen, urea, refueling, truck stop, zeolite, StormFilter

PRESENTER PROFILE

Dr. John Cheah graduated with his doctorate from the University of Auckland in Civil and Environmental Engineering in 2015. In 2016, he was selected as a finalist for the IPENZ Young Engineer of the Year award. Over the past three years John has been working as a R&D engineer for Stormwater360 to develop engineered bioretention media and conduct laboratory and field tests on stormwater treatment technologies.

1 INTRODUCTION

Diesel Exhaust Fluid (DEF) is a fuel additive that is added into the combustion process of diesel engines to reduce the concentration of NO_x in vehicle gas emissions. DEF consists of Urea (67.5%) and distilled water (32.5%). During the refueling process, DEF is deposited onto the pavement via drips and leaks. The urea converts into nitrates, nitrites and ammoniacal nitrogen as it is washed through the stormwater system.

The concentration of ammoniacal nitrogen is of concern as it is toxic to aquatic environments, even in small concentrations. The United States Environmental Protection Agency (USEPA, 2013) recommends ammoniacal nitrogen concentration limits to be below 17 mg/L for acute exposure (1-hour average concentration) and 1.9 mg/L for chronic exposure (30-day average concentration) to prevent unacceptable harm to aquatic life in freshwater. The Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC) (ANZECC, 2000) guidelines list ambient water trigger values at 0.01 and 0.021 mg/L of ammoniacal nitrogen for upland and lowland rivers respectively.

In a study done quantifying pollutants in stormwater runoff from two truck stops, ammoniacal nitrogen concentrations between 38 and 132 mg/L were measured in oil/water separator effluent (Easton, Robertson, & Court, 2015). The average ammoniacal nitrogen concentration was 42 mg/L.

Stormwater360 have conducted laboratory research with the goal of developing a Zeolite StormFilter™ that can reduce ammoniacal nitrogen concentrations from the range observed in stormwater influents at truck stops, to below the USEPA acute exposure concentration of 17 mg/L. The results of this research can be used in the design of a StormFilter™ to target ammoniacal nitrogen. The research has measured: -

- Ammoniacal nitrogen adsorption capacity of two grades of zeolite
- Ammoniacal nitrogen adsorption rate of two grades of zeolite
- Removal of ammoniacal nitrogen through a horizontal flow column filled with zeolite

The research has shown that ammoniacal nitrogen concentrations in stormwater can be targeted and reduced considerably. Aquatic environments are sensitive to ammoniacal nitrogen concentrations and certain activities and locations release harmful levels into receiving water bodies via stormwater. To protect organisms in receiving aquatic environments there is a need for stormwater discharge regulations to address ammoniacal nitrogen as a pollutant of concern. Operators of activities and sites that are known to introduce ammoniacal nitrogen into stormwater need to be guided to prevent the introduction of ammoniacal nitrogen into stormwater, and to provide stormwater treatment where isolation of polluting sources is not possible.

2 TEST PROGRAM

A three-stage research plan was devised to determine the viability of using zeolite to reduce the concentrations of ammoniacal nitrogen observed in the field to acceptable levels.

Stage 1 determined the maximum adsorption capacity of zeolite.

Stage 2 determined the rate of adsorption

Stage 3 measured adsorption rates in a continuous flow arrangement.

Two grades of zeolite were used during the tests: -

- zeolite between the particle sizes of 2.5-5.0 mm (Z1)
- zeolite between the particle sizes of 2.0-4.0 mm (Z2)

It should be noted that the performance of zeolite from different sources can vary and that the zeolite used is a specific proprietary blend used by Stormwater360.

3 ZEOLITE ADSORPTION CAPACITY OF AMMONIACAL NITROGEN (STAGE 1)

The purpose of stage 1 was to get an indication of the quantity of zeolite that would be required to reduce a solution with an ammoniacal nitrogen concentration of 132 mg/L to acceptable levels (<17 mg/L) and to measure the adsorption capacity per gram of zeolite with a contact time of 24 hours.

3.1 METHOD

Varying weights of zeolite (10g, 1g, 0.1g, 0.05g, and 0.01g) were put in 5 sterile plastic jars with 80 mL of 132 mg/L ammoniacal nitrogen solution for 24 hours. Jars were lightly shaken by hand 2-3 times during the test. A control was included in the test.

Figure 1: Six jars with varying amounts of zeolite (Z1) in 132 mg/L ammoniacal nitrogen solution

A 132 mg/L ammoniacal nitrogen solution was made by dissolving fine ammonium chloride crystals in water. The ammoniacal nitrogen concentration was the highest value measured in a study monitoring stormwater composition at two diesel exhaust fluid refueling sites in New Zealand (Easton et al., 2015).

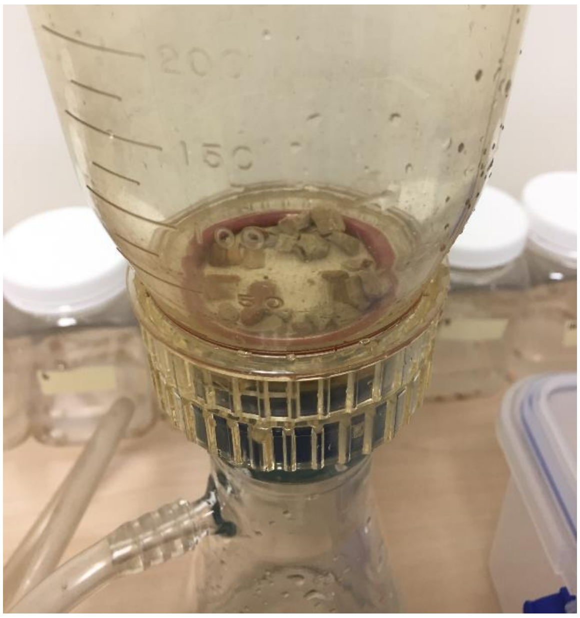

Figure 2: Zeolite separated from solution using a 0.45 µm filter paper

After 24 hours, the contents of each jar were filtered through a 0.45 um filter paper. The filtered solution was transferred into sterile plastic containers and sent to a third party IANZ accredited laboratory to evaluate ammoniacal nitrogen concentrations.

3.2 RESULTS - ZEOLITE ADSORPTION CAPACITY

Table 1: Ammoniacal nitrogen concentration after 24 hours (Stage 1)

	Control	Weight of zeolite				
	0g	0.01g	0.05g	0.1g	1g	10g
Ammoniacal Nitrogen (mg/L)	118	123	126	119	70.3	3.0

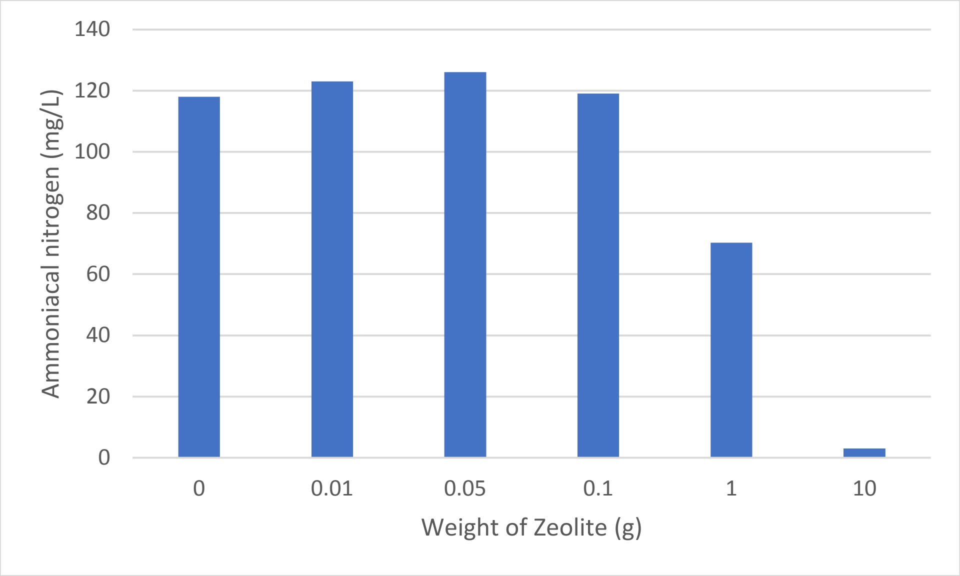

Figure 2: Ammoniacal nitrogen concentration in solution after 24 hours (Stage 1)

The results showed that a mass greater than 1g of Z1 (per 80 mL of 132 mg/L ammoniacal nitrogen solution) would be needed to noticeably reduce ammoniacal nitrogen concentrations. On a gram to gram basis, at least 95g of zeolite would be needed to react with 1g of ammoniacal nitrogen.

Over 24 hours, 10g of Z1 reduced ammoniacal nitrogen concentrations from 132 mg/L to 3 mg/L which was below the acute toxicity level listed for freshwater (17 mg/L) (USEPA, 2013). The next step was to determine the rate of adsorption.

4 ZEOLITE ADSORPTION RATE OF AMMONIACAL NITROGEN (STAGE 2)

The purpose of stage 2 was to measure the adsorption rate of zeolite (Z1 and Z2) for ammoniacal nitrogen over time (Stage 2A), and the initial rate of adsorption during the first 15 minutes of contact (Stage 2B).

4.1 METHOD FOR STAGE 2A – ADSORPTION RATE OVER 30 HOURS

11 sterile containers were filled with 1 gram of Z1. 80 mL of 132 mg/L ammoniacal nitrogen solution was added to each jar. The zeolite was separated from solution by passing the mixture through a 0.45 µm filter paper after durations of 0.5, 1, 3, 5, 7, 22, 24, 26, 28 and 30 hours. The filtered solution was sent to a third-party laboratory for testing.

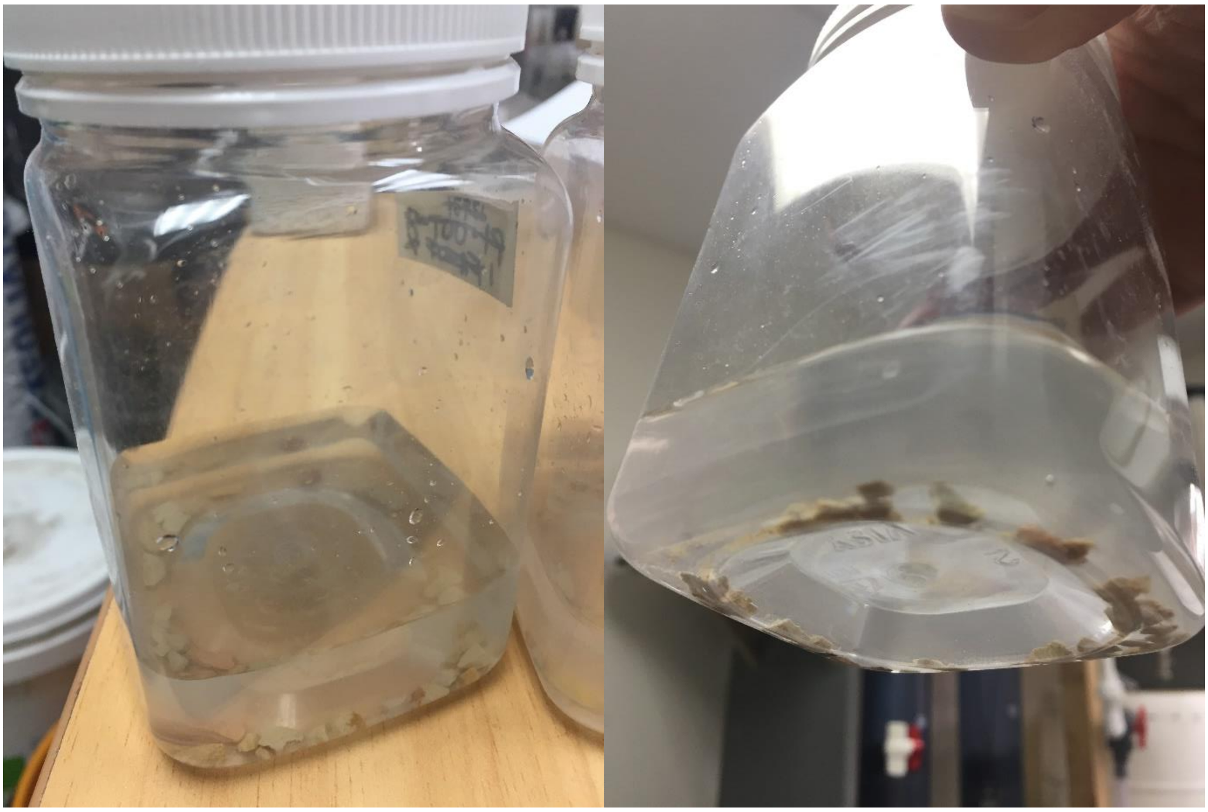

Figure 3: Top view - One gram of Zeolite in 80 mL of 132 mg/L ammoniacal nitrogen solution (left)

Figure 4: Bottom view - One gram of Zeolite in 80 mL of 132 mg/L ammoniacal nitrogen solution (right)

4.1.1 RESULTS

The total amount of ammoniacal nitrogen adsorped was divided by the contact time to calculate the average adsorption rate. The spot adsorption rate was calculated from the previous measurement point (as opposed to the beginning of the test) and provides a more accurate indication of the adsorption rate over time.

Table 2: Adsorption rate of 1g of Z1 in 132 mg/L ammoniacal nitrogen solution over 30 hours (Stage 2A)

Duration (hours)	0.5	1	3	5	7	22	24	26	28	30
Ammoniacal nitrogen (mg/L)	112	107	96.6	93.9	86.1	67.2	63.9	62.4	59.7	59.6
Spot adsorption rate per 1g of Z1 (mg/hr)	1.600	0.800	0.416	0.108	0.312	0.101	0.132	0.060	0.108	0.004
Avg adsorption rate per 1g of Z1 (mg/hr)	1.600	1.200	0.677	0.450	0.410	0.199	0.194	0.183	0.178	0.166

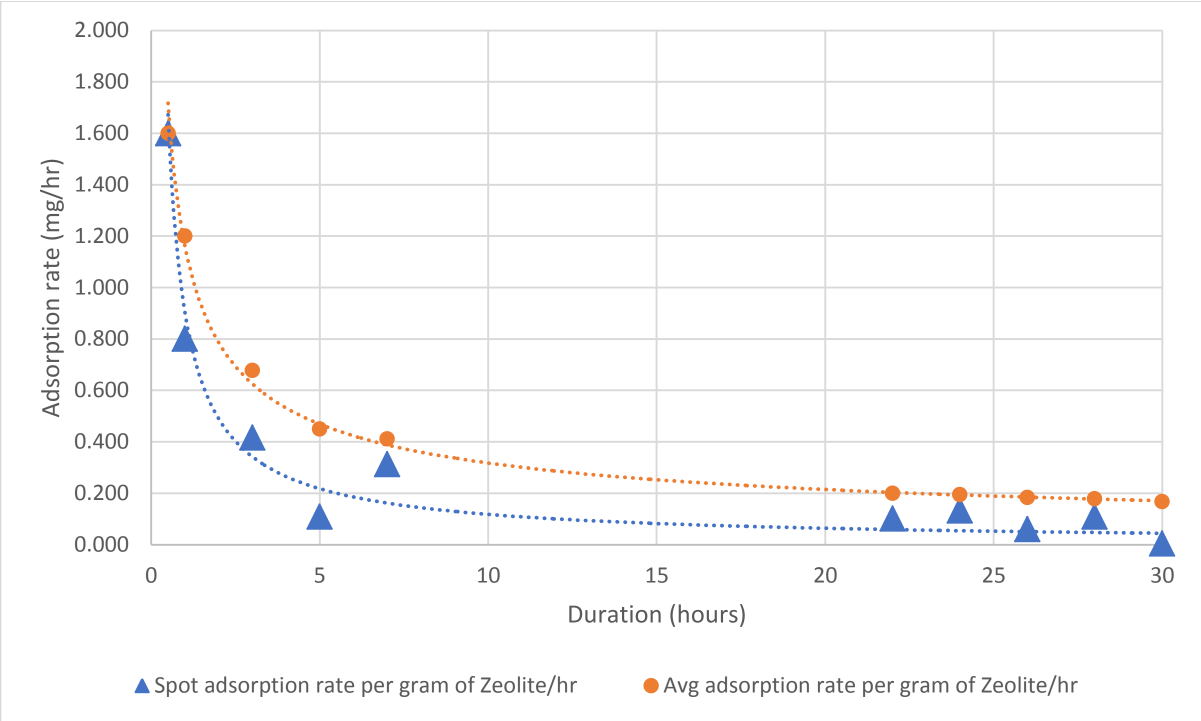

Figure 5: Adsorption rate of 1g of Z1 in 132 mg/L ammoniacal nitrogen solution over 30 hours (Stage 2A)

The adsorption rate decreased exponentially over time. While ammoniacal nitrogen continued to be adsorped after 30 hours, 50% of the total amount adsorped in 30 hours was adsorped within the first 68 minutes, and 80% after 9 hours 20 minutes.

The adsorption rate test was repeated to examine the adsorption rate within the first 15 minutes of contact.

4.2 METHOD FOR STAGE 2B – ADSORPTION RATE OVER 15 MINUTES

Four sterile containers were filled with 10 grams of Z2. 80 mL of 42 mg/L ammoniacal nitrogen solution was added to each jar. The zeolite was separated from solution by passing the mixture through a 0.45 µm filter paper after durations of 5, 10, 15 minutes. The filtered solution was sent to a third-party laboratory for testing.

The amount of zeolite was increased to 10g and the influent ammoniacal nitrogen concentration decreased to 42 mg/L to test whether the average ammoniacal nitrogen concentration observed at truck stop sites could be reduced to below the USEPA acute trigger value for freshwater receiving environments within a 15-minute contact period.

4.2.1 RESULTS

The ammoniacal nitrogen concentrations decreased over 75% despite the short contact time. After 5 minutes, the ammoniacal nitrogen concentration had decreased from 41.3 mg/L to 6.9 mg/L (83% removal). The 15-minute measurement seemed to be an outlying result as the ammoniacal nitrogen concentration measured was higher than both results obtained for the specimens with less contact time (5 and 10 minutes). Despite the outlying result, the 15-minute specimen still showed a 75% removal.

Table 3: Adsorption rate of 10g of Z2 in 42 mg/L ammoniacal nitrogen solution over 15 minutes (Stage 2B)

Duration (min)	0	5	10	15
Ammoniacal nitrogen (mg/L)	41.3	6.9	6.8	10.3
Spot adsorption rate per 1g of Z2 (mg/hr)		3.30	1.66	0.99

Avg adsorption rate per 1g of Z2 (mg/hr)	3.30	0.005	-0.11

4.3 DISCUSSION AND ANALYSIS

4.3.1 INITIAL AMMONIACAL NITROGEN ADSORPTION RATE

While the 30-hour adsorption rate tests indicated the absorption rate over the first 30 minutes to be 1.6 mg/hr (per gram of Z1), the tests focusing on the first 15 minutes showed the adsorption rate over the first 5 minutes to be higher at 3.3 mg/hr (per gram of Z2).

A higher initial adsorption rate was expected to be recorded due to the adsorption rate following an exponential decay curve and the smaller time step between measurements. The adsorption rate would have been further increased using Z2 which is a finer zeolite grade than Z1.

4.3.2 POTENTIAL FOR A FLOW-BASED TREATMENT DEVICE

The vigorous adsorption of ammoniacal nitrogen within the first 5 minutes of contact and the demonstrated ability of Z2 media to reduce average ammoniacal nitrogen levels measured at a truck stop to concentrations below the acute trigger value show that there is the potential to develop an ammoniacal nitrogen stormwater treatment solution using a flow-based approach.

5 STAGE 3 – CONTINUOUS AMMONIACAL NITROGEN REMOVAL THROUGH A HORIZONTAL FLOW COLUMN

The purpose of stage 3 was to measure the adsorption rate of Z2 for ammoniacal nitrogen when subjected with a continuous flow of influent.

5.1 METHOD FOR STAGE 3

A horizontal flow column (HFC), modelled off a 1/24 wedge of a proprietary StormFilter™ cartridge, was built. The HFC was filled with Z2 media and compacted on a vibrating table. As shown in Figure 6, the influent flowed in from the wide part of the wedge (right-side of Figure 6) toward the thin end of the wedge (left).

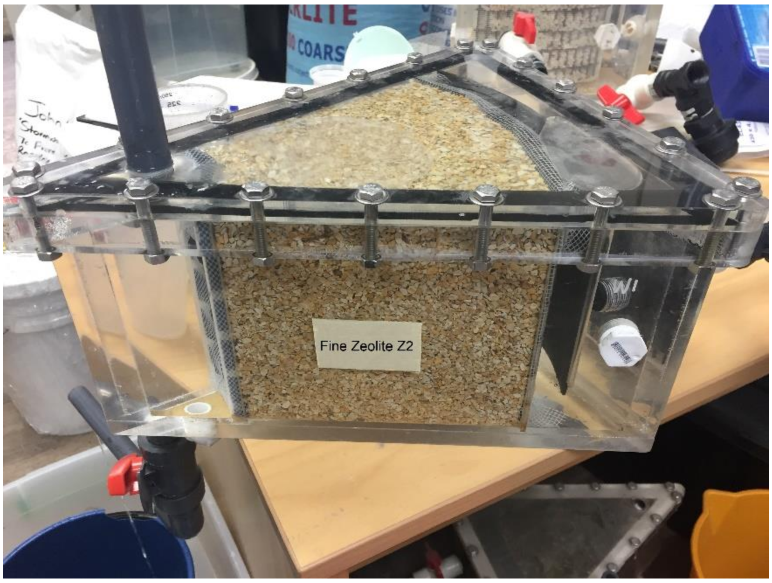

Figure 6: Horizontal flow column filled with Z2 media

A 15L Churn splitter was connected to the HFC column and was positioned a metre above the HFC to provide the driving head to achieve the target flow rates. An ammoniacal nitrogen influent of 42 mg/L was mixed in this container. An external flow control connected to the outgoing pipe of the HFC was used to reduce the flow through the device to the targeted rates. HFC tests at three different flow rates were conducted

- 1.10 L/min - 50% StormFilter flux rate
- 0.57 L/min - 25% StormFilter flux rate
- 0.23 L/min - 10% StormFilter flux rate

Paired influent and effluent samples were taken at 5, 10 and 15 minutes for each flow rate.

5.2 RESULTS

The paired influent and effluent results were averaged for each flow rate and are summarized below in Table 4.

Table 4: Ammoniacal nitrogen removal rates from HFC tests

	50% flux	25% flux	10% flux
Flow rate (L/min)	1.1	0.57	0.23
Average influent (mg/L)	41.1	46.4	46.9
Average effluent (mg/L)	20.3	19.2	12.7
Average removal	51%	59%	73%

The results show a clear relationship between decreasing flow rate and improved removal percentages. At a 10% flux, the ammoniacal nitrogen concentrations were reduced to below the USEPA acute trigger value for freshwater.

6 DISCUSSION

6.1 ADSORPTION LIMIT (BREAKTHROUGH POINT) OF MEDIA

The adsorption rate is dependent on the availability of adsorption sites on the zeolite media. As the zeolite adsorps more ammoniacal nitrogen, the rate of adsorption will decrease and eventually cease to adsorp. Stage 1 test results indicate that 95g of Z1 can adsorp 1g of ammoniacal nitrogen.

The HFC tests were done using a continuous flow of water for over an hour with the 50% flux rate tested first followed by the tests at 25% and 10% flux rates. The increasing performance of the latter 25% flux rate test and then a further performance increase during the 10% flux rate tests shows that the zeolite performance was more dependent on flux rate than the availability of adsorption sites remaining in the media.

6.2 AN ACCEPTABLE TARGET FOR AMMONIACAL NITROGEN IN STORMWATER EFFLUENT

In this research, the acute trigger level for freshwater of 17 mg/L of ammoniacal nitrogen was selected as the target to reduce effluent concentrations below. The USEPA states that freshwater organisms should not be unacceptably affected if the 1-hour average does not exceed 17 mg/L more than once every 3 years (acute) or if the 30-day average does not exceed 1.9 mg/L more than once every 3 years (chronic) (USEPA, 2013).

While the goal of 17 mg/L is a challenging goal and a good initial treatment level to aim for, present science indicates that keeping ammoniacal nitrogen concentrations in freshwater bodies below an ambient level of 0.01 mg/L is the target required if we are to not unacceptably affect aquatic organisms.

7 CONCLUSIONS

The laboratory tests conducted in this research have shown that Z1 and Z2 zeolite grades in a StormFilter™ media cartridge can reduce the average concentrations of ammoniacal nitrogen measured in New Zealand truck stops (42 mg/L) to below the USEPA acute trigger value of 17 mg/L. Treatment of ammoniacal nitrogen removing up to 73% has been demonstrated in a continuous flow arrangement.

8 REFERENCES

ANZECC, 2000. Australian and New Zealand Guidelines for Fresh and Marine Water Quality. Australian and New Zealand Environmental and Conservation Council (ANZECC), October 2000.

Easton, H., Robertson, M., & Court, J. (2015). Diesel exhaust fluid - Understanding a future stormwater contaminant. 2015 Asia Pacific Stormwater Conference, (p. 14). Auckland.

USEPA. (2013). Aquatic Life Ambient Water Quality Criteria for Ammonia - Freshwater 2013. EPA-822-R-13-001. Washington, DC: United States Environmental Protection Agency, Office of Water, Office of Science and Technology.