DIESEL EXHAUST FLUID - UNDERSTANDING A FUTURE STORMWATER CONTAMINANT

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ABSTRACT

Over the past two years, field and desktop assessments have been carried out by Pattle Delamore Partners (PDP), Z Energy Limited (Z) and BP Oil (New Zealand) Limited (BP) to ascertain the potential water quality effects associated with diesel exhaust fluid (DEF) products.

DEF is currently used by newer heavy diesel vehicles to reduce the oxide of nitrogen (NO_x) concentration in exhaust emissions. The product is comprised of purified urea (~32% or 320,000 ppm) and mineral water.

Whilst the Material Safety Data Sheet (MSDS) for DEF specifies that a large spill event will have significant effects on the environment, no concern is identified for the accumulation of minor spills or drips during a truck stop's 'normal' operation. Faced with a lack of information on the potential environmental effects of this substance, both Z and BP carried out field experiments to determine the products potential environmental effects.

Using real and simulated rainfall events, water quality monitoring investigations were carried out at two truck stops to identify if environmental effects could occur whilst the truck stops were operated under 'normal' conditions. This paper presents the sampling methodology carried out, results obtained, and discusses the various chemical transformations that can occur as the product migrates through a stormwater network.

The paper also discusses how Z and BP selected truck stops for DEF installation, and also the limited stormwater management options available in the current market to deal with the potential stormwater effects of this product.

KEYWORDS

ZDEC, ADBLUE, Euro5 Emission Standards, Ammoniacal Nitrogen, Nitrite-Nitrogen.

PRESENTER PROFILE

Hayden is an Environmental Services Leader with Pattle Delamore Partners Ltd. With approximately 13 years of experience, he has extensive knowledge in the following fields: Stormwater quantity and quality management, flood assessment and management, Integrated Catchment Management Planning, Water Sensitive Design, and environmental monitoring.

1 INTRODUCTION

As a result of the Land Transport Rule: Vehicle Exhaust Emissions Amendment 2012, heavy diesel vehicles imported into New Zealand from November 2013 were required to meet Euro Emission 5 standards. Similarly, new light diesel vehicles were required to meet these standards from January 2014.

The fundamental objective of the Euro Emission 5 standards is to achieve improvements to air quality by reducing levels of harmful emissions from motor vehicles. Specifically, air pollutants such as oxides of nitrogen, which are a leading cause of ozone depletion and respiratory illnesses, are a key contaminant which this legislation seeks to reduce. For diesel vehicles to meet this new standard, a new technology called a 'selective catalytic reactor' (SCR) has to be used.

An SCR converts up to 85% of oxides of nitrogen discharges into nitrogen gas, carbon dioxide, and water. To facilitate this conversion, a Diesel Exhaust Fluid (DEF) is used. Z Energy Limited (Z) and BP Oil (New Zealand) Limited (BP) market their DEF product as ZDEC and AdBlue, respectively.

DEF is comprised of ~32% high purity urea, and mineral water. Given the high concentrations of urea, both Z and BP have raised concerns regarding the potential environmental effects that could be caused should DEF spills occur. Material Safety Data Sheet (MSDS) for DEF specify that a large spill event will have significant effects to the environment, however, no concern is identified for accumulation of minor spills or drips during 'normal' operation. Whilst all DEF dispensers are fitted with spill prevention mechanisms, minor spills and drips still can occur. This is commonly as a result of: 'topping up' i.e. adding additional fluid once the magnetic shutoff valve has been activated, by slighting withdrawing the nozzle from the tank inlet; and splash back, due to the nozzle being incorrectly inserted into the tank inlet.

Not convinced with the conclusion that only significant spill events could cause and environmental effect, and faced with a lack of information on the potential environmental effects of this substance, both Z and BP carried out field experiments to determine DEF's potential environmental effects.

2 FIELD INVESTIGATIONS

Both Z and BP independently engaged Pattle Delamore Partners Limited (PDP) in 2013 and 2014 respectively, to carry out field investigations to determine the likelihood and significance of any environmental effects as a result of accidental DEF spills during normal operating conditions at a truck stop.

Field investigations entailed the collection of stormwater discharges throughout the site's drainage network.

At the time of PDP's engagement, Z Sanson and BP Bulls were the only Z and BP sites that dispensed DEF. Both sites are located in rural dominant communities, where stormwater discharges from the sites are to ephemeral streams.

Field investigations at Z Sanson were carried out during a single rainfall event (17 May 2013), whilst three simulated rainfall event investigations were assessed at BP Bulls (28 Feb 2014, 13 March 2014, and 2 April 2014).

At Z Sanson, stormwater discharges are treated via an API oil-water separator, whilst at BP Bulls a Spel Purceptor (coalescing plate oil-water separator) provides treatment to stormwater discharges.

2.1 WATER QUALITY PARAMETERS

Based on MSDS information for DEF, PDP considered that potential environmental effects from accidental spill events, would likely be as a result of the various nitrogen species, dissolved oxygen depletion, and pH effects. As such, a stormwater monitoring programme was designed to target these as primary contaminants of concern.

Parameters assessed in all field assessments conducted were:

- Total Nitrogen.
- Total Ammoniacal Nitrogen.
- Total Kjeldahl Nitrogen.
- Nitrate.
- Nitrite.
- Dissolved Chemical Oxygen Demand.
- Total Suspended Solids.
- Total Alkalinity.
- Apparent Hazen Colour.
- pH.
- Electrical Conductivity.

In addition to the above suite of sample parameters, the following field measurements were also obtained:

- Water Temperature.
- Dissolved Oxygen.
- Oxygen Reduction Potential.
- Turbidity.

All water samples were collected using manual grab sampling methods and were analysed by Hills Laboratories, Hamilton.

2.2 RAINFALL CONDITIONS

The single field assessment at Z Sanson was triggered by a 'real' rainfall event. PDP were onsite at the commencement of the storm event. The peak rainfall intensity was 3.6 mm/hour whilst sampling was carried out.

At BP Bulls, all assessments were carried out using simulated rainfall assessments. PDP have developed a methodology and equipment that enables variable rainfall intensities to be assessed across a given drainage catchment.

For each of the three assessments, equivalent rainfall intensities of 19 mm/hour were applied across the forecourt. This rainfall intensity was selected as it was equivalent to the water quality design storm event for Bulls. Manawatu (Horizons) Regional Council does not have a guideline to quantify water quantity effects. As such, the Auckland Regional Council TP 10 guideline (ARC, 2003) was applied to provide the required flow rate that should be applied to the site.

Antecedent rainfall conditions prior to each field investigation are presented in Table 1 below.

Location	Date of sampling	Days of dry antecedent weather prior to sampling
Z Sanson	17/5/2013	12
BP Bulls	28/2/2014	13
BP Bulls	13/3/2014	6
BP Bulls	2/4/2014	15

Table 1: Weather Characteristics Prior to Sampling

2.3 SAMPLE LOCATIONS AND SAMPLE COLLECTION

Sample locations chosen by PDP were selected to allow stormwater discharges to be assessed throughout a site’s stormwater network. By doing so, it not only assessed where contaminants/effects were being introduced into the stormwater, but also allowed PDP to identify if any chemical transformations were occurring within the stormwater network.

Monitoring locations assessed included:

- Forecourt effluent: where stormwater discharges from the active forecourt hardstand and into the stormwater reticulation network.
- Oil-water separator effluent: discharges once onsite stormwater treatment has been provided.
- Receiving environment: at the discharge outfall from the site to the receiving environment.

- Irrigation water: water used to create the simulated rainfall.

Samples were collected at each of the above monitoring locations at the following times:

- As discharge first occurs at each sampling location. This sample obtained was considered as the first flush from the site.
- Approximately 5-10 minutes after the first flush sample was collected.
- Approximately 30 minutes after the first flush was collected.

2.4 ENVIRONMENTAL PROTECTION GUIDELINES

To determine if potential environmental effects could be realised, a range of environmental protection guidelines were reviewed.

The following guidelines were used to assess if environmental effects specific to total ammoniacal nitrogen, nitrite and nitrate were present. Also provided below are the relevant environmental protection trigger value, and the context to which the trigger value should be applied:

- USEPA (2013): Total Ammoniacal Nitrogen, 17 mg/L acute toxicity for freshwater environments.
- USEPA (1989): Total Ammoniacal Nitrogen, 11 mg/L acute toxicity for saline environments.
- Ministry of Health (2008): Nitrite, 3 mg/L short-term exposure trigger (maximum acceptable) to maintain and improve the quality of drinking water.
- Ministry of Health (2008): Nitrate, 50 mg/L short-term exposure trigger (maximum acceptable) to maintain and improve the quality of drinking water.

ANZECC (2000) water quality guidelines were considered inappropriate for assessing environmental effects resulting from a DEF discharge. This is due to ANZECC (2000), only providing chronic toxicity guidelines, which are suitable for long-term discharges (discharges that are greater than 96 hours) only. The occurrence of DEF discharges (during 'normal' operations) are from rainfall events that are typically short in duration, and therefore acute toxicity guidelines were considered appropriate.

2.5 RESULTS

Table 2 below, presents the minimum and maximum data that were obtained from the investigations carried out at Z Sanson and BP Bulls.

In addition, Figures 1 to 3 present plots of concentrations of total nitrogen, total ammoniacal nitrogen and dissolved oxygen, respectively.

Sample Parameter	**Sample Location**			
	Forecourt area Effluent	**Oil-water separator Effluent**	**Receiving Environment[1]**	**Irrigation Water**
Total Nitrogen (mg/L)	7.1 to 3,300	42 to 137	7.8 to 137	<0.11 to 0.12
Total Ammoniacal Nitrogen (mg/L)	0.08 to 0.4	38 to 132	4.1 to 132	<0.01
Total Kjeldahl Nitrogen (mg/L)	7.0 to 3,300	42 to 132	6.9 to 132	<0.1
Nitrite (mg/L)	0.004 to 0.055	0.009 to 0.067	0.116 to 2.1	<0.002
Nitrate (mg/L)	0.024 to 0.22	0.004 to 0.024	0.044 to 0.79	0.011 to 0.068
Chemical Oxygen Demand (mg O_2 /L)	11 to 192	37 to 270	35 to 80	<6 to <6
Total Alkalinity (mg/L as $CaCO_3$)	51 to 102	114 to 650	136 to 330	48 to 94
Apparent Hazen Colour (Hazen Units)	<5 to 102	30 to 85	40 to 150	<5 to 5
pH (pH Units)	6.2 to 8.1	8.6 to 8.9	7.7 to 8.7	7.5 to 8.0
Total Suspended Solids (mg/L)	<10 to 470	<10 to 28	9 to 79	<8 to <10
Electrical Conductivity (m S/m)	17.3 to 33.9	39.8 to 101.9	38.3 to 75.6	15.1 to 25.7
Water Temperature (°C)	16.2 to 26.3	8.74 to 20.8	19.2 to 21	18.2 to 20.0
Dissolved Oxygen (% sat)	59.3 to 94	8.7 to 87	59.4 to 107	74 to 124
Oxygen Reduction Potential (mV)	-6.1 to 207	-214 to 174	-135.5 to 115	119 to 292
Turbidity (NTU)	15.3 to 45.9	1.7 to 33.1	2.1 to 6.5	0.0 to 5.7
Notes 1. Results are prior to reasonable mixing within the receiving environment.				

Table 2: Field investigation results, minimum and maximum are provided.

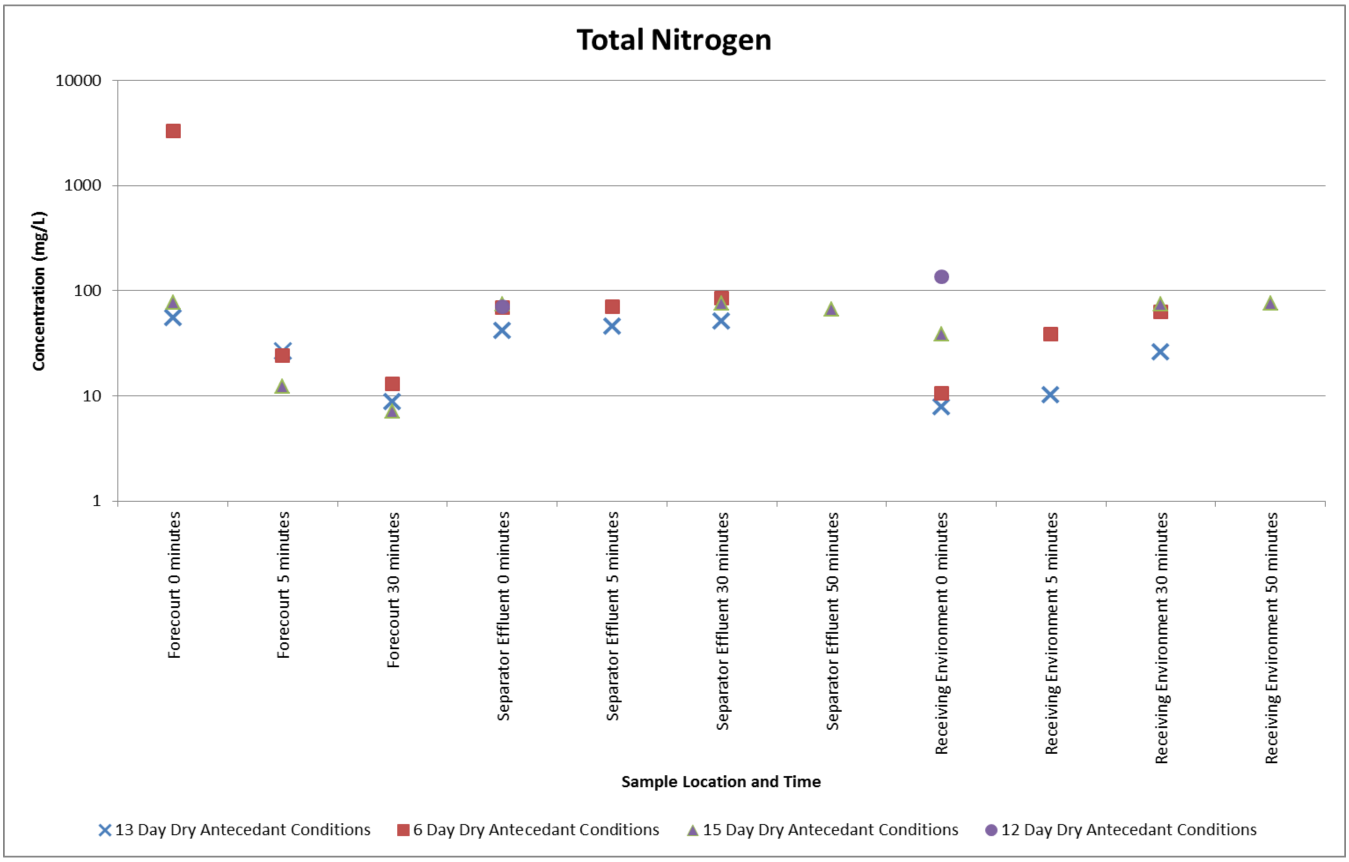

Figure 1. Total Nitrogen (note y-axis is log scale).

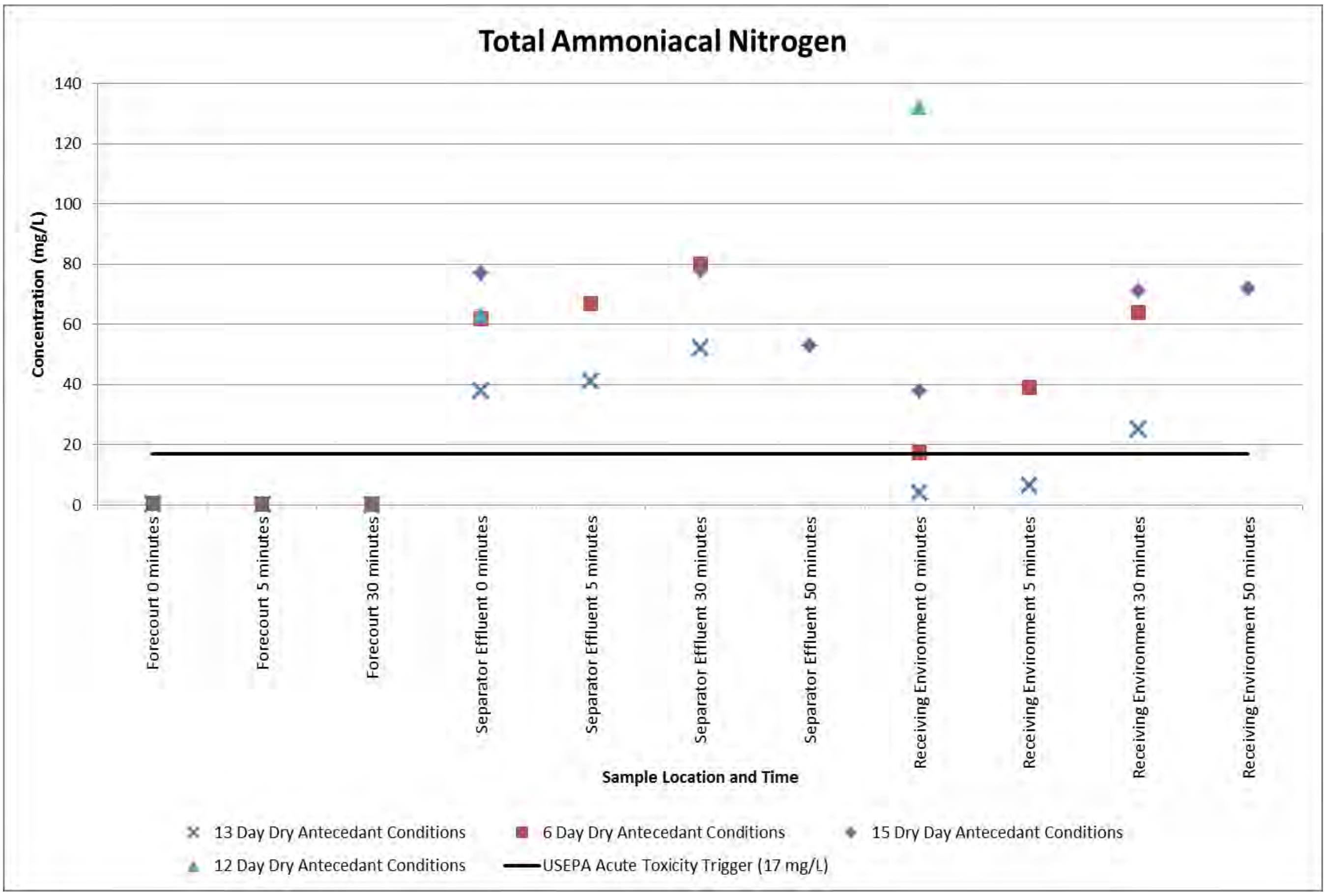

Figure 2. Total Ammoniacal Nitrogen.

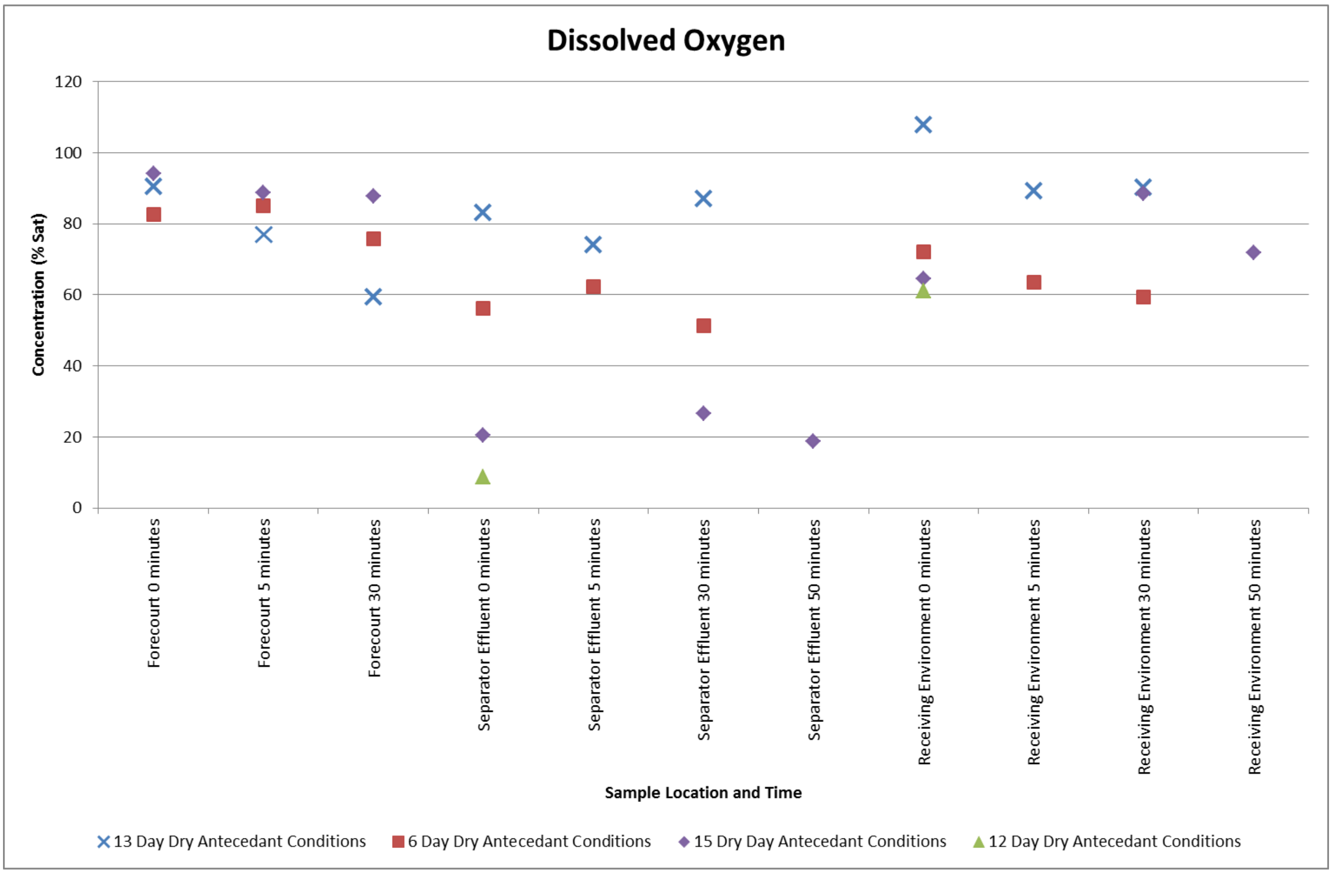

Figure 3. Dissolved Oxygen.

2.6 DISCUSSION

From results obtained, the only contaminant of concern that consistently exceeded identified environmental triggers was total ammoniacal nitrogen. Nitrite concentrations were also consistently elevated at the BP Bulls site; however these concentrations did not exceed Ministry of Health (2008) environmental triggers.

Dissolved oxygen concentrations monitored within the stormwater networks did exhibit significant suppressions. These suppressions were however, in majority, alleviated by the turbulent nature of the site's drainage network, thereby allowing aeration of the stormwater prior to the discharge entering into the receiving environment.

2.6.1 TOTAL AMMONIACAL NITROGEN AND NITRITE

The highest concentration of total ammoniacal nitrogen in the results obtained was 132 mg/L. This obtained value is just under 8 fold greater than acute toxicity guidelines (USEPA, 2013). To compare this concentration with other wastewater discharges, this obtained concentration is equivalent to approximately 2.5 times greater than treated municipal wastewater (D. Irvine *pers* comm. 2014). The median total ammoniacal nitrogen concentration from all receiving environment effluent results obtained was 39 mg/L (2.3 fold greater than acute toxicity guidelines (USEPA, 2013)).

Interestingly, there was a significant difference in obtained nitrite concentrations between the Z Sanson site and the BP Bulls site. The highest concentration of nitrite at BP Bulls was 2.1 mg/L, whilst the highest concentration at Z Sanson, was only 0.015 mg/L. The difference between these two sites has been identified as the observed presence of biofilms within the stormwater network at BP Bulls. It is considered that these biofilms may have been providing a nitrification process within the BP Bulls stormwater network.

2.6.2 CHEMICAL TRANSFORMATIONS

The presence of total ammoniacal nitrogen and nitrite (and a minor presence of nitrate) indicates that chemical transformations are occurring throughout both site′s stormwater networks.

Key chemical transformations that are considered likely to be occurring are:

- Hydrolysis: The conversion of total nitrogen (derived from urea within the DEF product) to total ammoniacal nitrogen.
- Nitrification: The conversion of total ammoniacal nitrogen into nitrites and nitrates.

The following chemical formula describe these chemical transformation processes.

$$H_2NCO - NH_2 + 3H_2O \xrightarrow{Urease\ Enzyme} CO_2 + 2NH_4^+ + 2OH^- \qquad \text{] Hydrolysis}$$

$$\left.\begin{array}{l} 2NH_4^+ + 3O_2 \xrightarrow{Nitrisomonas\ Bacteria} 2NO_2^- + 2H_2O + 4H^+ \\ 2NO_2^- + O_2 \xrightarrow{Nitrobactor\ Bacteria} 2NO_3^- \end{array}\right] \text{Nitrification}$$

Where:

$H_2N\text{-}CO\text{-}NH_2$ = Urea (derived from the DEF product)

NH_4^+ = Ammonium

NO_{2-} = Nitrite

NO_{3-} = Nitrate

Urease Enzyme = Naturally occurring enzyme found in numerous bacteria, fungi, algae, plants and some invertebrates, as well as in soils. Urease catalyzes the hydrolysis of urea to produce ammonium.

Nitrisomonas bacteria = Bacteria that oxidises ammonia to nitrites

Nitrobactor bacteria = Bacteria that oxidise nitrites to nitrates.

The two critical features that enable the above chemical transformations to occur are the presence of the urease enzyme and nitrifiers (nitrosomonas and nitrobactor bacteria).

Urease Enzyme

The urease enzyme is a naturally occurring protein that occurs within organisms and soil. At the monitored sites, the most likely source would be soil from the surrounding landscaped areas and grassed areas. Soil (including the urease enzyme) is likely to be transported into the stormwater network during stormwater events, where it deposits within settling areas, such as within the sites ACO drains and the oil-water separator.

The chemical reaction of urea to ammonia (in stormwater) by the urease enzyme is very rapid. This rate of reaction is very apparent when comparing results from the hardstand discharge into the stormwater network and the effluent discharge from the oil-water separator. Commonly results at both sites indicated that the ratio between total nitrogen and total ammoniacal nitrogen results were close to 1:1 at the oil-water separator monitoring location. This implies that nearly all of the available nitrogen in the system (i.e. the total nitrogen) has been rapidly converted into the total ammoniacal nitrogen form by the urease enzyme.

Nitrifiers

As earlier discussed, it was observed that nitrifiers (biofilms) were present within the BP Bulls stormwater network. These biofilms only occur in specific conditions. These conditions are:

- A preferable pH within the range of 8-9 pH units.
- Having an adequate source of carbon within the stormwater discharge.
- Having a significant source of oxygen within the stormwater.

It is important to note that if the above specific conditions are not present, nitrification would not occur. This is likely to be the situation at Z Sanson. As a consequence, total ammoniacal nitrogen concentrations (within the receiving environment) would likely be more elevated at a site that does not have nitrification processes.

2.7 FIELD INVESTIGATION SUMMARY

Based upon the datasets obtained at Z Sanson and BP Bulls, it is considered that environmental effects, particularly from total ammoniacal nitrogen, can be realised by DEF products within receiving environments. As such it is considered that site specific assessment of these potential effects should be made before DEF is installed.

3 INSTALLATION OF DEF

As a result of the findings achieved from field investigations, both Z and BP further engaged PDP to carry out desktop technical assessments to identify where future DEF installations could occur across their truck stop networks. From these assessments, identification of potential sites that could facilitate DEF installation without having a potential adverse effect were identified. Furthermore, using these assessments both Z and BP, prepared and lodged relevant resource consent applications prior to the installation of their DEF products.

To identify potential DEF sites, a mass balance model was developed to determine mixing processes within the various discharge waters that DEF interacts with (e.g. surrounding impervious areas, upstream drainage networks, groundwater and/or surface water receiving environments) to determine total ammoniacal nitrogen concentrations within the stormwater network and the receiving environment. Total ammoniacal nitrogen was the only contaminant assessed, due to the findings achieved from the earlier field investigations.

As later discussed in Section 4, there are at present limited stormwater treatment options to manage DEF contaminants from an active truck stop. As such, the primary means for determining if a site can facilitate DEF installation, was if sufficient dilution of the DEF contaminants occurs.

The objective of the technical assessments were to if identify environmental effects would be present as a result of 'normal' operating conditions only, i.e. what potential environmental effects would be caused by accumulation of DEF accidental spills - not large spill events. It was considered that if a large spill event were to occur, spill response procedures would be initiated to contain the spill onsite, for instance, using the emergency shut-off valves located on Z and BP sites.

The equation (Eqn 1) used to develop the mass balance model was:

$$Contaminant\ Concentration = \frac{C_1 \times V_1 + C_2 \times V_2}{V_1 + V_2} \qquad \text{Eqn.1}$$

Where:

C_1 = Concentration containing DEF contaminants.

V_1 = Flow rate containing DEF contaminants.

C_2 = Concentration from 'upstream' water.

V_2 = Flow rate from 'upstream' water.

Where stormwater discharges were disposed to groundwater and there was a short residence time for the DEF discharge to remain in groundwater, a derivative of Darcy's Law (Eqn 2) was applied to determine groundwater flow through rates.

$$Q = K \times A \times I \qquad \text{Eqn. 2}$$

Where:

Q = Groundwater through flow.

K = Hydraulic conductivity.

A = Mixing zone cross sectional area.

I = Groundwater hydraulic gradient.

If the distance between the groundwater aquifer and the surface water body (where the DEF discharge ultimately discharges to) was large, i.e. the potential residence time of the DEF discharge within the groundwater was for a long period of time, a mass flux approach was applied. We note however, for the majority of the technical assessments carried out, equations 1 and 2 were utilised, as such only this methodology is discussed below.

The most elevated measurements obtained during field investigations (i.e. a total ammoniacal nitrogen concentration of 132 mg/L) were applied to the mass balance model to determine potential environmental effects. Findings obtained were then compared against relevant environmental protection guidelines for acute toxicity. For freshwater environments this was USEPA (2013), whilst for saline environments USEPA (1989) was used.

In addition to determining resultant concentrations of total ammoniacal nitrogen within the receiving environment, Equation 1 was rearranged to determine what DEF spill volume that would cause an exceedance to the relevant environmental protection guideline.

If the calculated spill volume (to cause an exceedance of the environmental protection guideline) was less than 100 L, discussion was had between PDP and either Z or BP to determine forward options for the site. Typically options considered were to either undertake further fieldwork at the subject site to ground truth data, or alternatively, reduce the quantity of dispensers that can deliver the DEF product on site. By reducing the quantity of dispensers it reduces the potential contaminant yield area and consequently the DEF contaminant concentrations that would be discharged from the site.

Discussions regarding potential environmental guideline exceedance were had for multiple sites assessed at both Z and BP sites.

To date, all applications that have sought resource consent have been approved by relevant Regional Council authorities.

4 FUTURE MANAGEMENT OF DEF

Photograph 1 below, illustrates a small spill (~5-10 litres) of DEF that has then dried on the forecourt. As the figure illustrates, the high concentration of urea has led to a significant quantity of white crystals (urea) to form once the DEF has dried. These crystals bind well to concrete aggregate and are very difficult to scrap away (J. Court *pers comm.*, 2013). The only way that this spill was removed was by applying water to the crystals, thereby allowing the crystals to dissolve, and then absorbing the water again using absorbing pads.

Photograph 1. Dried DEF on a forecourt.

DEF is a water soluble product. Once mixed with stormwater, it becomes a very difficult to treat the associated contaminants. As demonstrated by the results obtained, and as expected, an oil-water separator provides no treatment of DEF contaminants.

At the present time, limited management options are available for the treatment of DEF discharges from a truck stop.

Based on information available to date, the most effective treatment for DEF is the urease enzyme. With direct application of the enzyme to the DEF (without water), the ammonium is rapidly converted into ammonia gas. This gas can then easily be dispersed within an open truck stop environment. Whilst this chemical reaction is a straight forward process, the drawback to its use is the current market cost of urease enzyme. Current market prices of the enzyme are just under $1,000 USD per 50 mg (as of January 2015). Whilst no analysis has been carried out to determine how much enzyme would be required to cause the reaction to occur, the raw cost of the material is considered too significant as a management option.

Another alternative considered to allow for the treatment of DEF discharges was the use of perlite/zeolite filters. Effectively, these products would allow the DEF contaminant to be adsorbed. The difficulty however with truck stop applications, is the additional hydrocarbon contaminants that are also associated within the stormwater discharge. It is anticipated that the hydrocarbons would cover the perlite/zeolite surface area and therefore reduce the absorbance surface area of the material. By doing so, it is anticipated that a reduced treatment performance would occur over a short period of time.

The use of zeolite/perlite however is still considered to have its merits. At present BP are considering having it available within spill response kits to manage small (<20 L) spill events.

As earlier stated, through the Land Transport Rule: Vehicle Exhaust Emissions Amendment 2012, we can expect a growing number of diesel vehicles to need DEF. The authors concern therefore, is the potential future need for DEF to be installed into drainage catchments which may have sensitive receiving environments. There is therefore a need for new technologies to be sought now to manage the potential environmental effects of DEF discharges.

5 CONCLUSIONS

The need for DEFs within New Zealand has been initiated as a result of diesel vehicles having to be designed to meet recent new Land Transport legislation amendments to reduce adverse air quality effects. By doing so, a new stormwater contaminant that has the potential to cause adverse environmental effects within aquatic environments has been introduced.

Recognising the potential for the DEF to cause adverse environmental effects, both Z and BP instigated field investigations to determine the possibility of such effects being realised.

Monitoring data obtained to date has identified a series of chemical transformations that can occur within the stormwater network as a result of the DEF product. At both Z Sanson and BP Bulls, hydrolysis was found to be occurring, whilst at BP Bulls, minor nitrification processes were also observed.

Results obtained identified that total ammoniacal nitrogen concentrations discharged from a truck stop that dispenses DEF, can achieve concentrations that are up to 2.5 times the concentration of an average municipal wastewater discharge.

Measured dissolved oxygen concentrations exhibited a significant suppression in water discharged from oil-water separators located on site. These concentrations were, in majority however, alleviated prior to their discharge to the receiving environment due to turbulent nature of the downstream stormwater network.

Whilst the discharges from the monitored sites were elevated, based upon modelling of these discharges within the receiving environment, these elevated concentrations were able to be reduced to below guideline values. What was clearly apparent from the field investigations carried out however, was the need for site specific assessment of DEF discharges before it is installed. The purpose of these assessments would be to determine if potential concentrations of the DEF contaminants could remain elevated within a given receiving environment, and consequently, cause an adverse environmental adverse effect.

Using the field data obtained, both Z and BP carried out such technical investigations to identify where installation of DEF should be carried out.

At present, there are limited options available to the market that can effectively treat stormwater flows containing DEF contaminants. Therefore, for the majority of technical assessments undertaken, the only method to mitigate potential environmental effects was via the dilution of contaminants within surrounding stormwater flows. It is considered that as the demand for future DEF increases, the potential for installations of this product into more sensitive locations could also increase. As a result new technologies must be sought now to manage the potential effects of DEF.

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