Nitrogen Removal in a Foam Media Biofilter for On-site Wastewater Treatment Systems

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Abstract

Discharges of nitrogen can contaminate groundwater, and cause algal blooms or eutrophication in surface waters. On-site wastewater treatment systems (OWTS) have been identified as significant sources of nitrogen. Homeowners and manufacturers are under increasing pressure to install OWTS capable of effective nitrogen removal.

Biological nitrogen removal in OWTS usually takes place in a fixed growth biofilter, following primary treatment in a septic tank arrangement. Three configurations of OWTS using foam media biofilters were assessed in the field. Foam media has advantages over sand, as high porosity and large air gaps allow the simultaneous flow of wastewater and air, thus reducing clogging and allowing higher loading rates.

Septic tank effluent had lower concentrations of TSS, COD and TN in configurations with larger tank volume. Biofilters provided additional removal of TSS and COD to give effluent concentrations as low as 9 mg/L and 36 mg/L respectively. TN concentration in the effluent varied from 41-53 mg/L depending on configuration. The least nitrogen removal occurred in the configuration with the highest loading rate (in terms of $L/m^2/d$).

A bench-scale biofilter constructed using a single foam block (200 x 160 x 60 mm) achieved TN removal up to 10.7 mg/L (0.024 g-N/d at a dosing rate of 2.2 L/d). It was observed that nitrification and denitrification can both occur in a single foam block. Assimilation was also a significant nitrogen removal mechanism, accounting for up to 49 % of total removal.

DO concentrations at microenvironments within the bench-scale biofilter were determined using a miniature membrane electrode. A syringe needle and custom-made plunger with the electrode fitted inside allowed DO concentration to be determined in sample volumes as small as 1 mL. The empirical equation derived to calculate DO concentration was accurate to within ± 2.9 %.

The extent of nitrification was greatest after an overnight rest period. At microenvironments within the bench-scale biofilter, nitrification increased at longer hydraulic residence time. Nitrification increased at high feed concentrations of carbon, which was not expected, and did not decrease at DO concentrations as low as 0.88 mg/L.

Denitrification was greatest when feed was high in carbon and low in DO, but was not affected by DO concentrations as high as 2.70 mg/L.

The effects of loading rate, biofilter depth, recirculation ratio and flooding need to be investigated further to optimise the design of biofilters in the field.

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Abbreviations

Amm-N	ammonia-nitrogen (NH_3/NH_4^+)
AOB	ammonia-oxidising bacteria
AS	activated sludge
AUF	anaerobic upflow filter
BNR	biological nitrogen removal
BOD	biological oxygen demand
BOD_5	biological oxygen demand (5 day)
COD	chemical oxygen demand
FISH	fluorescence i*n situ* hybridisation
FSS	fixed suspended solids
HLR	hydraulic loading rate
HRT	hydraulic residence time
ISF	intermittent sand filter
LGA	local government authority
MABR	membrane aerated biofilm reactor
MBR	membrane biofilm reactor
N	nitrogen
Nit-N	nitrified nitrogen (NO_2^-/NO_3^-)
NOB	nitrite-oxidising bacteria
NTF	nitrifying trickling filter
OLR	organic loading rate
Org-N	organic nitrogen
OWTS	on-site wastewater treatment system
PPD	per person per day
PPY	per person per year
RSF	recirculating sand filter
SAF	soil absorption field
SND	simultaneous nitrification and denitrification
SS	suspended solids
STE	septic tank effluent
TKN	total Kjeldahl nitrogen (sum of Org-N and Amm-N)
TN	total nitrogen
TOC	total organic carbon
TSS	total suspended solids
VSS	volatile suspended solids
WWTP	wastewater treatment plant

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1 Introduction

The harmful effects of nitrogen on the environment and human health are now well recognised. Algal blooms or eutrophication in areas such as Rotorua, Taupo and Horowhenua have highlighted the need to reduce nitrogen inputs to sensitive receiving waters. Protection of groundwater from nitrate leaching is also a concern, especially in areas such as Hawkes Bay which have shallow aquifers.

Where sewer connections are not available, such as rural areas or in some cases new subdivisions, on-site wastewater treatment is the only option. On-site wastewater treatment systems (OWTS) are significant sources of nitrogen, and several local authorities now require resource consents for OWTS in sensitive areas. This places pressure on homeowners and OWTS manufacturers to ensure that systems meet the requirements for effluent nitrogen concentration.

This research project was conducted in order to assess and improve three configurations of OWTS using foam media biofilters. Overall goals of the project were to identify the factors affecting performance, and recommend design changes to reduce effluent concentration of TN, while maintaining low effluent concentrations of TSS and BOD/COD. Requirements were for a passive system, with minimal inputs and operating costs. This meant that solutions such as forced aeration or addition of carbon from an external source could not be considered.

A review of the literature currently available in this area was conducted. This covered the problems associated with nitrogen pollution, domestic wastewater composition and flow rates, on-site wastewater treatment, and current practices in on-site nitrogen removal. Mechanisms of nitrogen removal were identified. A broad review of factors affecting biological nitrogen removal was conducted, with particular emphasis on the importance of DO concentration. Extensive information was available on biological nitrogen removal in suspended growth systems and municipal wastewater treatment plants. The literature review therefore attempts to bring together knowledge from

several distinct, but related fields, and apply this to nitrogen removal in foam media biofilters for on-site wastewater treatment.

Throughout the course of the project, the performance of three configurations of OWTS was assessed by sampling systems in the field. Data were analysed to determine the extent of nitrogen removal achieved, and the effects of system configuration on overall performance. Changes made to the initial configuration were based partly on data from this testing programme and advice from Massey University.

Based on initial assessment of the foam media biofilter, and the literature review, it was hypothesised that within each foam block, aerobic and anoxic microenvironments existed. This would allow both stages of biological nitrogen removal, nitrification and denitrification, to occur in a single foam block, and would also mean that a single stage biofilter could achieve overall nitrogen removal. To test this hypothesis, a bench-scale biofilter was constructed, and methods were developed to allow the sampling and measurement of DO concentration at nodes within a foam block. The bench-scale biofilter allowed the nitrogen removal ability of foam media to be tested in a controlled environment. The effects of factors such as feed composition, hydraulic residence time and DO concentration on nitrification and denitrification were also examined.

2 Literature Review

2.1 Introduction

This chapter presents a summary of the information currently available on nitrogen removal and on-site wastewater treatment systems.

The effects of nitrogen on the environment are discussed, and information given regarding on-site wastewater treatment. An investigation of various nitrogen removal mechanisms is presented, and an in-depth discussion of biological nitrogen removal follows. The systems that have been used to achieve biological nitrogen removal in on-site wastewater treatment systems are reviewed, and an attempt is made to present information critical for the design of such systems. An emphasis is placed on foam media biofilters.

Information on biological nitrogen removal is often based on large-scale municipal trickling filters, or even suspended growth processes. This review attempts to bring together some of this knowledge and apply it more specifically to nitrogen removal in on-site wastewater treatment systems.

2.2 Nitrogen in Domestic Wastewater

Nitrogen is one of the major elements essential to life. Figure 2.2.1 shows that nitrogen is present in the environment in many forms, and can undergo a wide range of conversions:

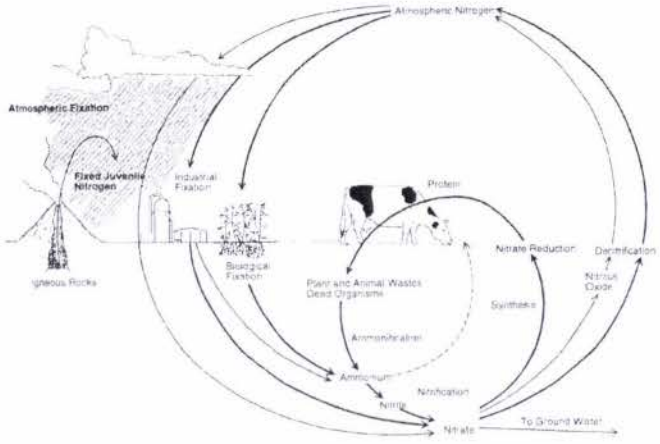

Figure 2.2.1: The nitrogen cycle (USEPA, 1993).

In recent years, anthropogenic inputs of nitrogen to land and water have come under increasing scrutiny. Significant changes to the nitrogen balance are made by farming through nitrogen fixation by legumes, the application of nitrogen fertiliser, and by runoff contaminated with animal manure. Domestic wastewater contains high concentrations of nitrogen, and as our population continues to grow, so does the strain on our water resources.

The discharge of nitrogen to groundwater or water bodies (such as lakes or streams) can have significant adverse impacts on the environment and human health. The harmful effects of nitrogen pollution on water bodies have led to increasingly strict discharge limits. Weatherley & Miladinovic (2004) after Nguyen & Tanner (1998) report that limits in Aotearoa/New Zealand range from 0.22 to 0.77 mg-N/L when discharging directly to a water body.

The health effects and environmental impact resulting from nitrogen pollution can be summarised as follows (Burks & Minnis, 1994):

- methaemoglobinemia in infants caused by NO_3^-
- formation of carcinogenic nitrosamines from NO_2^-/NO_3^-
- oxygen depletion of surface waters
- algal blooms and eutrophication due to nutrient enrichment
- toxicity of NH_3 and NO_2^- to aquatic organisms

Health Concerns

High nitrate concentrations in drinking water have led to some previous outbreaks of methaemoglobinemia in infants in the United States (Burks & Minnis, 1994). Bacteria in the gut of infants under 6 months reduce nitrate to nitrite. Nitrite then reacts with haemoglobin to produce methaemoglobin, which is not capable of carrying oxygen in the bloodstream. A bluish tinge to the skin develops as the body is starved of oxygen; the condition can be fatal.

When water used for food preparation contains nitrite, this can combine with organic nitrogen compounds (formed from breakdown of proteins) to form carcinogenic nitrosamines (Winkler, 1981).

The USEPA and World Health Organisation (WHO) have set drinking water guidelines for NO_2^-/NO_3^- of 10 mg-N/L.

Toxicity

Winkler (1981) stated that aquatic life exposed to free ammonia (NH_3) levels of 1 mg/L may suffocate, as the oxygen-combining capacity of blood is significantly impaired. The proportion of ammonia present as NH_3 depends on the NH_3/NH_4^+ equilibrium, and is affected by temperature and pH. Concentrations of NH_3 dissolved in wastewater increase at high pH and low temperature (Winkler, 1981). De Beer *et al* (1997) reported that NO_2^- is also toxic to aquatic life.

Oxygen Depletion

The oxidation of ammonia consumes oxygen (Section 2.4.6). The discharge of significant amounts of ammonia nitrogen can deplete oxygen in a water body, leading to the suffocation of fish species and other forms of aquatic life.

Algal Blooms

Also, nutrient enrichment of rivers, lakes and marine environments can result in algal blooms. Under normal conditions, low concentrations of nitrogen and phosphorus in these environments limit the growth of algae and cyanobacteria. The discharge of nitrogen or phosphorus to these environments can cause blooms (rapidly increasing growth) in the population of these species. As well as the considerable visual impact,

algal blooms can produce toxins that affect marine life, contaminate shellfish and make fish unsafe for consumption (e.g. Northland Age, 2004).

Eutrophication

In extreme cases, nutrient enrichment of a water body can lead to eutrophication. During warm weather, the availability of nutrients produces dense growth of species such as algae, cyanobacteria, rooted aquatic vegetation or duckweed. As large masses of these nuisance species die off, they are consumed by aerobic bacteria, and oxygen in the water body is depleted. The oxygen depletion may cause reduction in the populations of fish and other aquatic species. Extreme cases of eutrophication can lead to decomposition of organic material by anaerobic bacteria, resulting in foul odours coming from the water body.

2.2.1 Nitrogen Loading and Concentration

The main sources of nitrogen in domestic wastewater are human excreta (organic nitrogen) and urine (urea). Kitchen waste can also be a significant contributor to the nitrogen load of a household, since some foods are high in nitrogen. Wastewater from the laundry contributes the least significant amount of nitrogen to domestic wastewater (Patterson, 2003).

Wastewater flow rates vary widely between households. Shaw & Turyk (1994) found that water use varied from 97-327 L/c.d between 6 households studied. Charles *et al* (2004) measured flows of 132 L/c.d, significantly different to the recommended guideline of 180 L/c/d. The average top-loading washing machine uses over 1000 L of water per load (Patterson, 1999). Laundry habits can have a large effect on wastewater flow rates.

At an individual household, wastewater flow rate and composition varies widely with time and day. Figure 2.2.2 shows the variation in average hourly flow rates, with the error bar representing one standard deviation:

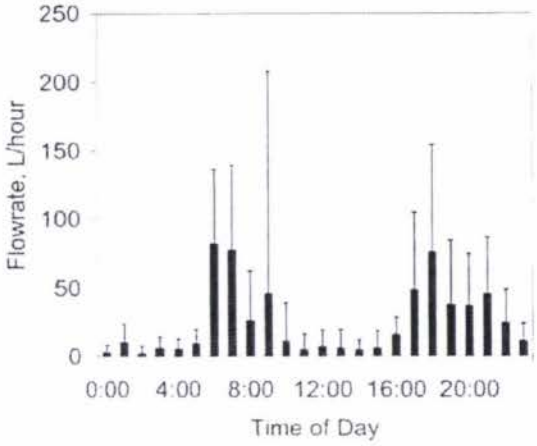

Figure 2.2.2: Average hourly flow to an OWTS (Edvardsson & Spears, 2000).

Values reported for the load of total nitrogen (TN) in domestic wastewater vary widely (Table 2.2.1):

Table 2.2.1: Total nitrogen (TN) loading (per capita per day).

Source	TN Load (g/c.d)
Burks & Minnis (1994)	16.0
Shaw & Turyk (1994)	15.3
Vant (1999) after Huser (1989)	8.6

Patterson (2003) after Wahlquist (1986) reported TN loading as 0.16 g per kg body weight (12.8 g/c.d for an 80 kg person). Gunn (2004) reported several values from literature, and suggested an average of 12.0 g/c.d.

The concentration of TN in domestic wastewater varies widely depending on water usage. The use of water-saving devices in a household can lower the volume of water used, and increase the TN concentration of wastewater. TN concentrations observed in domestic wastewater by several researchers are shown in Table 2.2.2:

Table 2.2.2: Average influent concentrations of TN to OWTS.

Source	TN Conc (mg/L)
Burks & Minnis (2003)	86.0
Canter & Knox (1985)	50.0
Tchobanoglous *et al* (2003)	70.0

Edvardsson & Spears (2000) observed that even when influent characteristics to an OWTS were highly variable, effluent quality was not significantly affected.

2.3 On-site Wastewater Treatment Systems (OWTS)

On-site wastewater treatment involves the treatment and disposal of wastewater at the point of origin, for example at a single household. On-site treatment is also referred to as a decentralised or unsewered system. This is an alternative to the collection and transport of wastewater to a centralised treatment plant. OWTS are common in rural areas, or in semi-rural areas outside the limits of a municipal sewerage system.

In the United States, 25 % of the 100 million homes use OWTS (Bruen & Piluk, 1994). Similarly, 27 % of the population of Japan rely on OWTS, although this includes systems serving up to 500 population equivalents (Kondo *et al*, 1992). Between 1980 and 1990, 3.4 million unsewered housing units were constructed in the United States (Bruen & Piluk, 1994). In some cases the cost of providing centralised treatment to a community is prohibitively expensive and involves time-consuming construction (Geary, 1994). The demand for OWTS can be expected to increase in the future.

In Aotearoa/New Zealand, local authorities are responsible for the management of discharges to land, such as those from OWTS. The Local Government Act (1989) and the Resource Management Act (1991) provide the legal framework for regional councils to place limits on the concentration of pollutants discharged from OWTS. Usually, an OWTS serving a single household is only required to have a resource consent (discharge permit) if the receiving environment is sensitive (close proximity to surface waters or groundwater).

However, variations in wastewater characteristics and OWTS performance can make monitoring and compliance difficult. Edvardsson & Spears (2000) believed that testing methodology must rely on composite, flow-averaged sampling of removal efficiency.

2.3.1 Basic OWTS (Septic Tanks)

The most basic form of on-site wastewater treatment is a septic tank. Septic tanks have been in use for over 100 years, and serve two major functions: (1) clarification by physical means, and (2) biological treatment by anaerobic digestion (Burks & Minnis, 1994).

Septic tanks act as clarifiers in two ways: large particles are removed by settling, and flotation removes substances such as insoluble fats and oils. Anaerobic digestion in a septic tank converts organic molecules into more soluble forms (Osesek *et al*, 1994; Patterson, 2003). It is common for septic tanks to have either one or two chambers.

After treatment, septic tank effluent (STE) is discharged to a soil absorption field (SAF). In some cases, effluent is filtered before disposal. Providing only primary treatment in an OWTS places a high demand on the soil. In many cases, the soil category is not suitable for wastewater receiving such a low level of treatment. In addition, many areas are considered sensitive due to high water table or proximity to surface water. This means that the level of treatment expected from an OWTS is frequently greater than that provided by a septic tank.

Historically, septic tanks have been effective at decreasing concentrations of total suspended solids (TSS) and biological oxygen demand (BOD) in wastewater. Ammonification, the conversion of organic nitrogen to ammonia, occurs in a septic tank (Section 2.4.1). However, the extent to which a septic tank can remove nitrogen is debatable. Concentrations of TN, TSS and BOD_5 in septic tank effluent (STE) as reported by various sources are given in Table 2.3.1:

Table 2.3.1: Concentration of TN, TSS and BOD_5 in septic tank effluent.

Source	Concentration (mg/L)		
	TN	BOD_5	TSS
Boyle *et al* (1994)	47.0	193	50
Charles *et al* (2004)	160.0	-	-
Gold *et al* (1992)	52.0	92	-
Patterson (2003) after Patterson (2001)	69.9	-	-
Piluk & Hao (1989)	69.4	435	94
Piluk & Peters (1994)	57.0	235	75

Patterson (2003) after Patterson *et al* (2001) observed high variability of TN concentration in STE. The least variable system studied had concentrations of 39-83 mg/L; the most variable was 55-182 mg/L.

Osesek *et al* (1994) after Laak *et al* (1981) stated that a septic tank should remove 10 % of influent organic nitrogen, which is stored in the sludge. However, Gunn (2004) pointed out that although bound organic nitrogen settles in the septic tank, eventually this will be converted to ammonia and leave in the effluent. Gunn stated that a conservative design approach would assume no overall reduction of TN takes place in the septic tank; a nominal reduction of 3.5 % TN was suggested (Gunn, 2004 after Crites & Tchobanoglous, 1998).

STE is discharged to the soil absorption field (SAF) for aerobic treatment; however, the level of treatment depends on soil conditions, which may be unsuitable (Jowett & McMaster, 1994). The soil texture must be such that it can retain wastewater for an adequate treatment time, but be permeable enough to allow for drainage of wastewater, and diffusion of air into the soil (Jowett & McMaster, 1995). Winkler & Veneman (1991) confirmed that virtually no removal of NO_2^-/NO_3^- occurs in the unsaturated soil zone below the clogging layer, since the anoxic conditions required for denitrification do not exist.

The general consensus is that treatment of wastewater using a septic tank and soil absorption field is not sufficient. Technologies must be developed that remove nitrogen in an OWTS before disposal to land (Jowett & McMaster, 1994; Winkler & Veneman, 1991; Lamb *et al*, 1990).

2.4 Nitrogen Removal Mechanisms

2.4.1 Ammonification

Anaerobic digestion results in the conversion of large, organic molecules to smaller, soluble compounds. Nitrogenous compounds such as ammonia and amines are formed from larger nitrogenous substances (Burks & Minnis, 1994). The formation of ammonia from organic nitrogen compounds is referred to as ammonification, and is conducted by heterotrophic microorganisms (Anthonisen *et al*, 1976).

In an OWTS, an anaerobic environment exists in the septic tank (Osesek *et al*, 1994), which promotes ammonification. While this does not directly result in nitrogen removal, it is an important step in the overall treatment process. The soluble compounds produced can be removed in later treatment stages.

2.4.2 Biological Assimilation

Bacterial cells are composed of 12 % nitrogen on a dry weight basis (Tchobanoglous *et al*, 2003 after Madigan *et al*, 1997). Nitrogen removed from wastewater for bacterial growth is said to have been removed by biological assimilation. Heterotrophic bacteria, which also use wastewater as a carbon source, have higher growth rates than autotrophic bacteria, which rely on inorganic sources of carbon such as atmospheric CO_2 (Tchobanoglous *et al*, 2003).

De Renzo (1978) stated that removal by assimilation could be increased to significant levels by the addition of an organic carbon source such as ethanol or glucose. The disadvantages are that large quantities of sludge are produced, and difficulties can occur in regulating the addition of the carbon source.

2.4.3 Mineralisation and Uptake/Release

Effluent concentrations of nitrogen higher than influent concentrations (negative removal) have been observed. Two mechanisms proposed by researchers that account for this are mineralisation, or uptake followed by release.

Loomis *et al* (2001a) observed that TN concentrations across two foam biofilters increased on several occasions. It was suggested that this may have been the result of mineralisation, which is the breakdown of large organic molecules such as proteins into inorganic (mineral) compounds such as ammonia. However, it was noted that the conversion of organic nitrogen to ammonia nitrogen would not change the TN concentration.

Boyle *et al* (1994) observed significant nitrogen release from a peat filter over a period of 2 months. Okabe *et al* (1999) reported production of NO_2^-/NO_3^- exceeding consumption of NH_3/NH_4^+. The release of bound nitrogen from biofilms or biomass decay was believed to be the cause. Ball (1994) found that an ISF initially removed 50 % of influent nitrogen; after 1 month of operation, the effluent concentration of nitrogen exceeded the influent concentration.

Wik (1999) reported that ammonia adsorption to and desorption from the biofilm occurs in a nitrifying trickling filter; adsorption of NH_4^+ is possible because of the net negative surface charge on many organic compounds.

Winkler & Veneman (1991) also reported increases in TN concentration, in 3 out of 4 OWTS studied.

2.4.4 Ammonia Stripping

Ammonia in wastewater is present as either dissolved ammonia gas (NH_3) or aqueous ammonium ions (NH_4^+), according to the equilibrium shown by Equation 2.4.1:

$$NH_4^+ + OH^- \Leftrightarrow NH_3 + H_2O \qquad (2.4.1)$$

NH_3 dissolved in wastewater is also in equilibrium with NH_3 in the gas phase, with the concentration of dissolved NH_3 determined by its partial pressure in the gas phase. Reducing the partial pressure will draw NH_3 out of the liquid phase and into the gaseous phase, thereby 'stripping' it from the wastewater. This process is also referred to as desorption, or volatilisation of ammonia (De Renzo, 1978).

Wastewater pH has a large effect on the viability of ammonia stripping for nitrogen removal. The value of K_a for Equation 2.1 is 1 x $10^{-9.3}$, which means that the concentration of NH_3 is only significant at high pH. Table 2.4.1 shows how the NH_3 concentration changes with pH, and with the overall ammonia concentration:

Table 2.4.1: Concentration of NH_3 at varying pH and NH_3/NH_4^+ concentration.

pH	Concentration (mg-N/L)	
	NH_3/NH_4^+	NH_3
7	50.0	0.3
	70.0	0.4
9	50.0	16.7
	70.0	23.4

Wastewater pH is usually too low for substantial removal by volatilisation. This is confirmed by Lamb *et al* (1990), who observed no significant removal due to volatilisation from wastewater with a pH of 7.0 to 7.5.

2.4.5 Ion Exchange

In ion exchange, wastewater is put in contact with an ion exchange resin, which can be a natural or synthetic material. Ions in the wastewater are preferentially adsorbed onto the exchange resin, displacing existing surface ions. Either cations or anions can be removed from wastewater using this method, depending on the exchange resin chosen. The most common ion exchange resin is clinoptilolite, a type of zeolite, which is a cationic exchange resin.

Weatherley & Miladinovic (2004) showed that clinoptilolite is effective for removal of NH_4^+. 84 % removal was achieved from an influent concentration of 70 mg-N/L, and 99 % removal from a concentration of 10 mg-N/L. However, this was achieved under laboratory conditions, using a contact time of 3-5 days. Removal at shorter HRT was not reported. Although it was reported that Ca^{2+}, Mg^{2+} and K^+ ions did not significantly affect removal rates, the effect of suspended solids or organic matter was outside the scope of the study.

USEPA (1993) reported that ion exchange has been used for nitrogen removal in some OWTS. The major problem with ion exchange is that resins require off-site

regeneration. This increases the time and cost involved in maintaining an OWTS. Also, wastewater must be filtered effectively before ion exchange, to prevent fouling of the resin.

2.4.6 Biological Nitrogen Removal (BNR)

Biological nitrogen removal occurs through two reactions: the conversion of ammonia to nitrate (nitrification), and the subsequent conversion of nitrate to N_2 gas (denitrification). These reactions are carried out by two groups of microorganisms (nitrifiers and denitrifiers respectively). The end result is a non-reactive gas, which escapes to the atmosphere. This makes BNR an attractive option for nitrogen removal, and this has become the most common method of removing nitrogen from wastewater.

Nitrification

Nitrification is a two step process in which ammonia is oxidised to nitrite (NO_2^-), which is subsequently oxidised to nitrate (NO_3^-). The first reaction (nitritation) is carried out mainly by *Nitrosomonas* bacteria, and the second reaction (nitratation) by *Nitrobacter*. Although these two groups of bacteria are the most common, seven genera of nitrifiers have been identified (Jang *et al*, 2002).

The overall stoichiometry of the nitrification process is shown in Equation 2.4.2 (USEPA, 1993):

$$NH_4^+ + 2\,O_2 + 2\,HCO_3^- \rightarrow NO_3^- + 2\,H_2CO_3 + H_2O \qquad (2.4.2)$$

An aerobic environment is essential for nitrification. It can be seen that nitrification requires 2 mol of oxygen for every 1 mol of ammonia. Nitrifiers also require a constant supply of ammonia, otherwise nitrification is inhibited (Wik, 2000; Parker *et al*, 1997). Alkalinity is consumed by nitrification, resulting in a decrease in pH; this is discussed further in Section 2.6.3. According to the above stoichiometry, nitrification removes 4.57 g of oxygen for every 1 g-N oxidised.

Nitrifiers are autotrophic, and use carbon dioxide, carbonates or bicarbonates as sources of carbon for cell synthesis (Osesek *et al*, 1994 after Delwiche, 1981). These

substrates are poor sources of energy for nitrifiers, which as a result have small cell yields and low specific growth rates (Jang *et al*, 2002). De Renzo (1978) gives the yield of *Nitrosomonas* and *Nitrobacter* as 0.15 g per g NH_4^+-N, and 0.02 g per g NO_2^--N respectively. Overall, this implies that the nitrification of 10 mg/L of ammonia would produce only 1.8 mg/L of nitrifiers.

Denitrification

Denitrification is the reduction of NO_3^- (or NO_2^-) to inert N_2 gas, which is then released to the atmosphere. This is the final step in BNR, and represents an overall loss of nitrogen from the treatment system.

The overall reaction for denitrification is shown by Equation 2.4.3 (USEPA, 1993). Although methanol is given as the carbon source in the equation, denitrification can occur via a range of carbon compounds.

$$NO_3^- + 5/6\ CH_3OH + 1/6\ H_2CO_3 \rightarrow 1/2\ N_2 + 4/3\ H_2O + HCO_3^- \qquad (2.4.3)$$

The reaction is carried out by a group of facultative heterotrophs known as 'denitrifiers'. Denitrifiers include species from the *Psuedomonas*, *Micrococcus*, *Archromobacter* and *Bacillus* genera (Osesek *et al*, 1994 after USEPA, 1975).

It is critical that anoxic conditions exist for denitrification; under oxic conditions, denitrifiers will preferentially consume molecular oxygen (Burks & Minnis, 1994). It was also stated by Burks & Minnis (1994) that denitrifiers cannot survive in an anaerobic environment.

Equation 2.4.3 shows that denitrification consumes carbonic acid and produces bicarbonate ions, raising the pH (partially reversing the effect of nitrification on pH). Denitrification also requires a heterotrophic carbon source, which can either be present in the wastewater to be treated, or an additive such as methanol or acetate.

Patterson (2003) after Tisdale *et al* (1985) state that anaerobic soil conditions could lead to denitrification and removal of nitrogen. However, it has been reported elsewhere that significant denitrification does not occur in a well-aerated sandy

subsoil or in carbon-deficient groundwater (Osesek *et al*, 1994 after Walker *et al*, 1973). Therefore, it cannot be assumed that denitrification will occur in the soil; nitrogen must be removed from wastewater before disposal.

Simultaneous Nitrification and Denitrification (SND)

As described above, nitrification is an aerobic process, while denitrification requires an anoxic environment. In practice, this means that separate treatment stages are usually required for nitrification and denitrification.

However, at certain bulk DO concentrations, both aerobic and anoxic zones can exist within the same reactor. Simultaneous nitrification and denitrification (SND) can therefore occur. The existence of SND in large activated sludge (AS) flocs has been confirmed by many researchers (Schramm *et al*, 1999; Satoh *et al*, 2003; Terada *et al*, 2003). Where SND is used for nitrogen removal, savings in capital cost and land use are achieved; in addition, a neutral pH is maintained in the reactor (Yoo *et al*, 1999).

Bulk DO concentration affects oxygen penetration and the creation of anoxic microenvironments. Satoh *et al* (2003) detected anoxic zones at bulk oxygen concentrations less than 1.44 mg/L (45 μM) in AS flocs larger than 3 mm. Nitrification was restricted to the aerobic zone; denitrification occurred mainly in the anoxic zone. Nitrification rate increased with bulk oxygen concentration, but was constant above 1.28 mg/L (40 μM). SND was observed at bulk oxygen concentrations between 0.32 and 1.12 mg/L (10-35 μM), but nitrification was incomplete in these cases.

Significant denitrification rates were observed by Schramm *et al* (1999) in AS when anoxic zones existed in flocs during aeration, and very low denitrification rates in AS with no anoxic zones. Schramm *et al* (1999) found that the oxygen concentration within a sludge floc was significantly less than the concentration in the bulk liquid. Denitrification occurred in the anoxic zone within the floc, and so NO_3^- concentration was also significantly lower in the floc than in the bulk liquid (Figure 2.4.1):

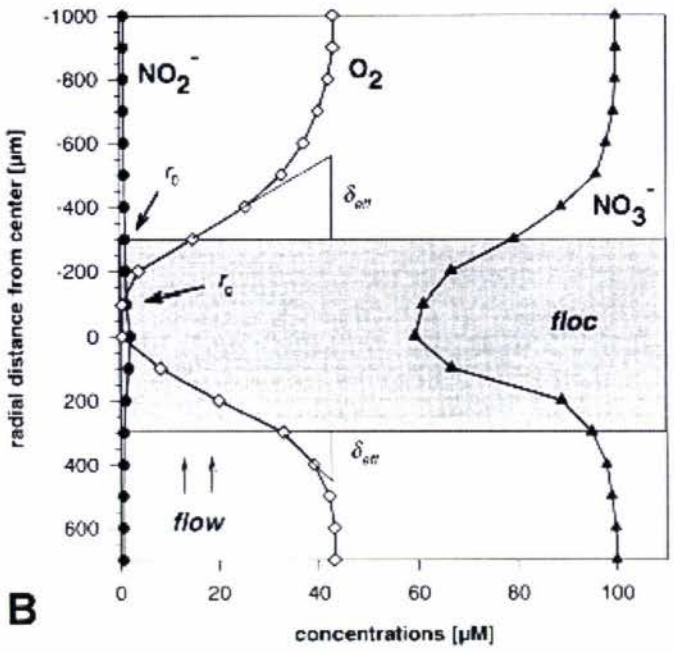

Figure 2.4.1: Concentration profiles of O_2, NO_2^- and NO_3^- in AS flocs (Schramm *et al*,1999).

These results show that denitrification can occur within activated sludge flocs even when the bulk O_2 concentration seems relatively high (40 µM O_2 is equal to 1.28 mg/L).

Piluk & Hao (1989) stated that the coupling of the nitrification and denitrification processes is the most practical means of reducing nitrogen concentrations in OWTS effluent.

2.5 Biological Nitrogen Removal in OWTS

2.5.1 Trickling Filters

A trickling filter is an attached-growth wastewater treatment system, consisting of a column packed with inert media (e.g. sand, rock, plastic or foam). Wastewater flows (upwards or downwards) through the column, and a layer of microorganisms develops on the media. This biologically active layer provides treatment of the wastewater.

Sand Filters

Although designed mainly for removal of TSS and BOD, sand filters have also shown significant nitrogen removal. As the name states, the support media is sand; a gravel subsurface is usually provided to retain the media in position.

An aerobic zone exists at the top of a sand filter; as wastewater penetrates deeper into the filter, and airflow is reduced, anoxic conditions exist, where denitrification can occur (Gold *et al*, 1992 after Rittman & Langeland, 1985).

The nitrogen removal performance of two sand filters was reported by Hoover *et al* (1991); see Table 2.5.1:

Table 2.5.1: Nitrogen removal performance of sand filters (Hoover *et al*, 1991).

Site	Nitrogen Removal	Nitrification		
		Minimum	Average	Maximum
1	42%	71%	90%	99%
2	30%	5%	72%	94%

A high extent of nitrification was reported in the two sand filters studied (81 % average). Nitrification varied widely at site 2; it was believed that during initial sampling, an excessively high pressure head resulted in rapid delivery of wastewater and poor nitrification. After the pressure head was reduced, nitrification was a minimum of 70 %. It was concluded that the dosing regime had a significant effect upon the performance of the sand filters, and that it should be regularly monitored.

Contrary to these findings, Winkler & Veneman (1991) studied two sand filters and found that although nitrification did occur, there was an overall gain in TN across the filters (negative removal).

Problems associated with sand filters have included infiltration by rainwater during major rainfall events. Researchers such as Hoover *et al* (1991) and Piluk & Peters (1994) have stressed the importance of keeping filters and septic tanks watertight.

Sand filters are prone to clogging (Jowett & McMaster, 1994b; Piluk & Peters, 1994). For this reason, loading rates of wastewater to single-pass sand filters must be kept low.

Recirculating Sand Filters (RSFs)

In a recirculating sand filter, effluent is returned and distributed over the filter media again. Treated effluent is usually returned to a recirculation tank, where it is mixed with STE. The recirculation tank provides an environment for denitrification, with STE providing the carbon source necessary (Piluk & Peters, 1994).

Higher hydraulic loading rates are possible with RSFs. Jowett & McMasters (1995) after several researchers reported low HLRs for single-pass filters: 4.7 cm/d for sand filters, 4.1 cm/d for peat filters and 1-7 cm/d for soil treatment only. It was stated that RSFs can be loaded at 10-20 cm/d, or up to 41 cm/d using a coarse gravel and frequent dosings.

Osesek *et al* (1994) achieved 97 % denitrification of RSF effluent by recirculating directly into the septic tank. Osesek *et al* (1994) constructed an RSF with a limestone underdrain, through which STE passed to ensure adequate alkalinity for nitrification.

The quality of RSF effluent reported by various researchers is shown in Table 2.5.2 below. During the study performed by Sack *et al* (1991), the system treated effluent from 5 households; approx 1.25 hours of maintenance was performed on the system each week.

Table 2.5.2: Effluent concentrations of TSS, BOD_5, TN and NH_3/NH_4^+ from RSF systems.

Source	Effluent Conc (mg/L)			
	TSS	BOD_5	TN	NH_3/NH_4^+
Lamb *et al* (1990)			11.2	
Piluk & Peters (1994)	8	5	20.0	
Sack *et al* (1991)	7	7		5.0

The effluent concentration taken from Lamb *et al* (1990) was achieved using methanol as a carbon source. When STE was the carbon source, the effluent TN

concentration was 39.2 mg/L. Loomis *et al* (2001a) reported that an RSF achieved greater nitrogen removal than a single-pass sand filter (Table 2.5.3):

Table 2.5.3: Nitrogen removal in RSF vs single-pass sand filter (Loomis *et al*, 2001a).

System	TN Removal (%)	Effluent Conc (mg/L)
Sand Filter	16%	38.0
At-Grade RSF	73%	13.5

Piluk & Peters (1994) suggested that an RSF should have improved aeration and less clogging compared with a single-pass sand filter. However, several researchers have experienced clogging and weed growth in RSFs (Miller *et al*, 1994; Osesek *et al*, 1994; Boyle *et al*, 1994). Routine weed removal and raking of the media has been recommended; in one case raking every 2 months was suggested (Boyle *et al*, 1994). Miller *et al* (1994) reported that clogging occurs because most TSS is removed (through interception and straining) in the top layers of the filter; clogging was also reported as dependent on wastewater pre-treatment, media characteristics and loading rates. Gold *et al* (1992) observed that over a 3-year trial, RSFs required raking and weeding during each growing season, and periodic maintenance; single-pass buried filters (RUCK arrangement) required no maintenance.

Plastic Media Biofilters

Biofilters have been constructed using various types of plastic, foam and fabric media. The advantage of these synthetic media over alternatives such as peat, is consistency. For example, the properties of peat vary considerably with geography, age and decomposition (Jowett & McMaster, 1995).

Trickling filter media must maximise the surface area available for growth of microorganisms, and also provide a large void space for aeration (Särner, 1980). In accordance with this, Särner (1980) listed the following advantages that plastic media has over rock media:

- high specific surface (m2/m3)
- high void fraction

- lightweight (reducing construction cost)
- high stability at shock loads

Although it was stated that media with higher specific surface should give better treatment, Särner (1980) stated that several investigations showed this was not always the case. Treatment efficiency depends not only on specific surface, but on the geometry of the media (largely due to the effect of geometry on hydraulic flow and retention time).

Ball (1994) achieved an effluent TN concentration of 14.8 mg/L (78 % TN removal) from a plastic-media biofilter with recirculation into a septic tank.

Foam Media Biofilters

Jowett & McMaster (1994b) stated that the use of an absorbent media such as foam provides a high specific surface area, but without the problem of clogging experienced with sand filters. This was confirmed over a 20-month period of operation at several field sites (Jowett & McMaster, 1995). Significant air gaps exist between blocks in a foam media biofilter, as shown in Figure 2.5.1 and Figure 2.5.2. This allows for the movement of air and the growth of biofilm (Jowett & McMaster, 1995).

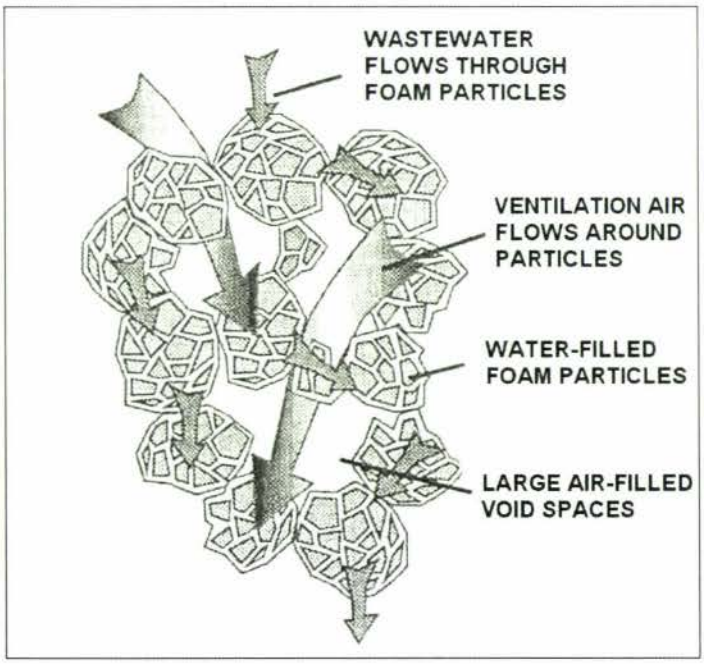

Figure 2.5.1: Air gaps between blocks in a foam media biofilter.

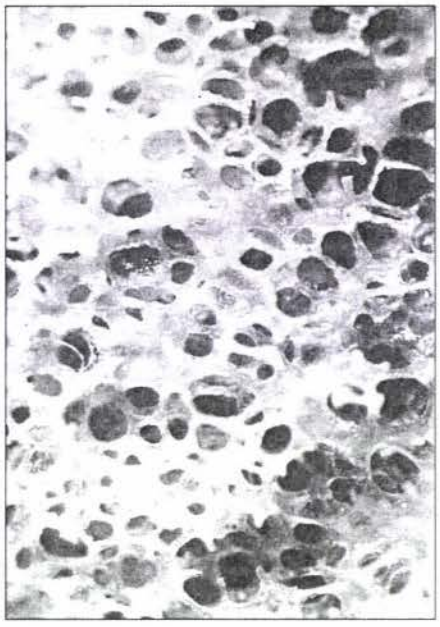

Figure 2.5.2: Foam media, showing large pores and thin walls (Jowett & McMaster, 1995).

The use of foam media in a biofilter allows for higher HLR. In a sand filter, wastewater must drain from the interstices before aeration is possible. Foam media allows simultaneous flow of wastewater and air, improving aeration. Jowett & McMaster (1994b) report that a loading rate of 50 cm/d was possible in a foam media biofilter. In comparison, a typical loading rate for a sand filter is 4.7 cm/d, one order of magnitude lower (Jowett & McMaster, 1994b after Ball, 1991). Peat and coarse sand filters are subject to clogging at high HLR (50-80 cm/d); foam media biofilters are not prone to clogging (Jowett & McMaster, 1995).

Kondo *et al* (1992) found that the most wear-resistant materials for foam media were polyethylene and ether polyurethane. High ductility ether polyurethane was selected for use over other foam media.

Table 2.5.4 shows a comparison between sand and foam media. Calculations were made by Jowett & McMaster (1995), based on data from Robert & Chenu (1992) and Shutov (1981). Jowett & McMaster (1995) recommend that a foam media biofilter for a typical household would require up to 3.3 m^2 surface area.

Table 2.5.4: Properties of sand and foam media (Jowett & McMaster, 1995).

Media	Bulk Density	Specific Area	
	(kg/m^3)	(m^2/kg)	(m^2/m^3)
Silty Sand	1700	100	1.7E+05
Plastic Foam	60	1000	6.0E+04

The specific surface area is lower for foam media because a significant amount of void space exists, as seen above.

Waterloo Biofilter Systems Inc reports that effluent TN of less than 20 mg/L is possible from a foam media biofilter (50-60 % TN removal). A Waterloo biofilter operates at 50 % recirculation and with hydraulic loading rates 10 times larger than those possible for a sand filter. Loomis *et al* (2001a) reported 10-23 % TN removal in a foam media biofilter, to produce an effluent concentration of 28-61 mg/L.

2.5.2 Aerated Treatment Plants

Some OWTS have been designed with mechanical aeration to create an aerobic zone. For example, the EnviroServer range of aerated treatment plants (from Earthwell Environmental Systems Inc) incorporate two suspended-growth chambers, with plastic media and membrane air diffusers. Nitrified effluent from these chambers is returned to the septic tank for denitrification.

Edvardsson & Spears (2000) observed 79 % removal of TN in an EnviroServer 600 OWTS (Table 2.5.5).

Table 2.5.5: Performance of EnviroServer 600 aerated plant (Edvardsson & Spears, 2000).

Parameter	Concentration (mg/L)	
	Influent	Effluent
NH_3-N	20.0	0.1
NO_3-N	1.1	2.1
Organic N	23.0	6.9
TN	44.1	9.1

However, Särner (1980) stated that trickling filters for OWTS are preferred to aerated systems, because of lower operating costs.

2.5.3 Peat Filters

Peat beds have been used to treat septic tank effluent where local soil conditions do not favour direct disposal to land. Peat is used as a growth media to enable biological nitrogen removal. Peat is an absorbent medium, and has potential due to its high absorbency and air permeability. However, the properties of peat vary considerably with geography, age and decomposition (Jowett & McMaster, 1995).

Figure 2.5.3 shows a comparison of effluent from sand filters and peat filters (Winkler & Veneman, 1991):

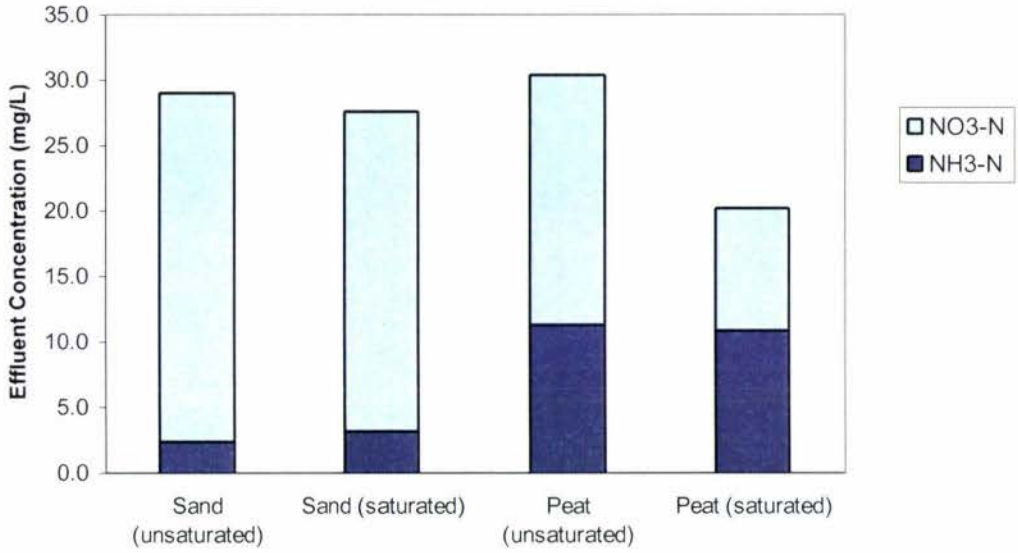

Figure 2.5.3: Effluent nitrogen, sand filters vs peat filters (Winkler & Veneman, 1991).

It is clear from Figure 2.5.3 that the peat filters studied did not achieve as much nitrification as the sand filters. Of the four systems studied, only the saturated peat filter achieved overall TN removal. Overall TN gains were observed in the other three systems. Possible reasons given for this were: (1) variations in STE concentration not detected during sampling, (2) mineralisation of nitrogen retained from prior application, or (3) fixation of atmospheric N_2 by microbes.

Boyle *et al* (1994) also observed high TN concentrations in effluent from peat filters (35-50 mg/L). Nitrogen and phosphorus removed by a peat filter can in some cases be subsequently leached out (Jowett & McMaster, 1995 after Heathwaite, 1990).

McKee & Brooks (1994) reported that peat filters could produce effluent TN concentrations less than 10 mg/L, provided that influent concentration was low.

2.5.4 Rock Media

Denitrification stages constructed from rock media have been used successfully by several researchers. Rock media is used to promote growth of denitrifying organisms. This technology is used following a separate stage in which nitrification is achieved.

Anderson *et al* (1998) constructed a lined bed after a septic tank in an OWTS. The top layer of the lined bed was unsaturated media for nitrification (depth 1.5 feet); the bottom layer was saturated media for denitrification (depth 1.0 feet). Three media were used: crushed red brick, silica sand and an expanded clay aggregate from Norway. This arrangement produced effluent with a TN concentration of 20.2 mg/L, from an influent concentration of 38.6 mg/L (47 % removal).

Lamb *et al* (1990) used an above-ground RSF as an aerobic environment for nitrification and a buried anaerobic rock tank for denitrification. This arrangement removed 36 % more TN than a conventional RSF when the carbon source used was STE. When the carbon source used was methanol or ethanol, the system removed 78 % more TN than a conventional RSF.

2.5.5 Plant Uptake

Planting of OWTS effluent disposal areas has been recommended to provide further removal of nutrients. Nitrate removal can occur through plant uptake or microbial action in the upper soil stratum (Ball, 1994b after Degen *et al*, 1991); however, nitrates are extremely soluble and mobile, and can pass readily through the soil without being adsorbed (Burks & Minnis, 1994).

Ball (1994) observed up to 55 % removal of TN in the top 30 cm of the soil below disposal areas at two locations. Ball also reported that soil type, ground cover, moisture and other conditions vary widely. In cases where groundwater is shallow, or the disposal area is close to surface water, nitrogen removal should occur before effluent is disposed to land.

Plant uptake can help to mitigate the impact of nitrogen discharges on the environment. Regulatory limits placed on discharge from OWTS, however require a high degree of treatment prior to discharge. Plant uptake, where utilised does not avoid the need for a high level of treatment within the system itself.

2.5.6 Anaerobic Upflow Filters (AUF)

Anaerobic upflow filters have been used as denitrification stages by several researchers. Ball (1994) found that the addition of an upflow filter to a septic tank and biofilter arrangement reduced effluent TN concentration to 5.4 mg/L (Table 2.5.6).

Table 2.5.6: Effect of upflow filter on effluent quality (Ball, 1994).

Arrangement	Effluent Conc (mg/L)			
	TN	NH_3-N	NO_3-N	Org-N
Septic Tank (ST)	68.0	54.0	2.0	14.0
ST + Trickling Filter (TF)	14.8	2.4	7.1	5.3
ST + TF + Upflow Filter	5.4	1.2	2.5	1.7

Boyle *et al* (1994) reported that the addition of an AUF after an RSF lowered effluent TN concentration from 26 to 12 mg/L.

Clearly a high quality effluent was obtained by passing wastewater through an AUF. However, this technology is not deemed appropriate for the current study, due to the assumed increases in capital and operating costs for homeowners.

2.6 Factors Affecting BNR

2.6.1 Dissolved Oxygen (DO)

As described above, there is a minimum DO requirement for nitrification (aerobic), and a maximum allowable DO for denitrification (anoxic). This means that DO is an extremely important parameter for any BNR system. DO concentration was recognised as the limiting factor in BNR by Yoo *et al* (1999), Schramm *et al* (1996), Gullicks & Cleasby (1986) and Okey & Albertson (1989a, 1989b).

Okey & Albertson (1989a) believed that the effluent DO concentration was not representative of concentrations within a biofilter, and that there was great uncertainty over what DO concentrations within a biofilter were. Overall, this implies that accurate measurement of the DO concentration within a trickling filter is essential to optimise performance, but is difficult to achieve.

DO Concentration

Yoo *et al* (1999) studied SND in an intermittently aerated single reactor (anoxic and aerobic phases). Optimum nitrogen removal was observed at maximum DO concentration of 2.00 to 2.50 mg/L, and median DO of 1.20 to 1.40 mg/L. The minimum DO concentration for nitrification was reported as 1.00 mg/L.

Jang *et al* (2002) studied the effect of DO concentration on nitrifiers in biofilms from an activated sludge plant. It was found that at low DO concentration (2 mg/L), nitrifiers constituted only a small fraction of the microbial population. The biofilm was slow-growing and only 400 μm thick. When a high DO concentration (10 mg/L) was maintained, nitrifiers made up more than 50 % of the microbial population, and dominated at greater biofilm depth. At high DO, the biofilm was 1000 μm thick, and fast-growing.

It is generally accepted that denitrification will be inhibited by the presence of molecular oxygen (e.g. Burks & Minnis, 1994). However, Ball (1994) after Meiklejohn (1940) reported that denitrification can occur in aerobic environments. Similarly, Schramm *et al* (1996) detected nitrifiers in the anoxic zone, as well as at the bottom of a biofilm.

Okey & Albertson (1989a) reported that the nitrification rate increased with bulk oxygen concentration as shown in Figure 2.6.1:

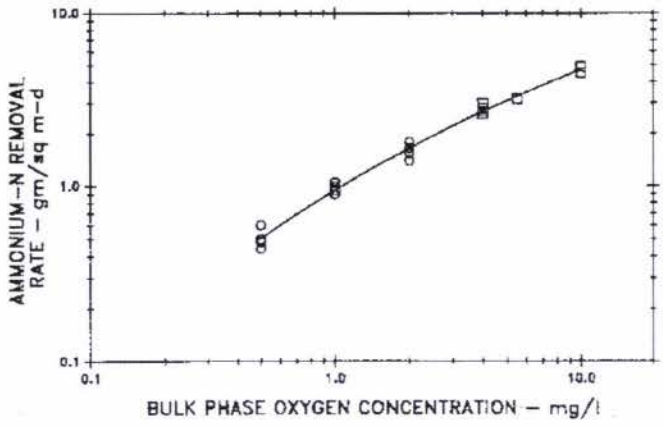

Figure 2.6.1: Nitrification rate vs bulk oxygen concentration (Okey & Albertson, 1989a).

Effect on Reaction Kinetics

Nitrification can be zero-order, half-order or first-order with respect to ammonia concentration. The reaction order changes depending on the ammonia concentration. Okey & Albertson (1989a) reported that nitrification is first-order below an ammonia concentration of 3-4 mg/L, and that the reaction order can vary according to depth in a trickling filter. When nitrification is zero-order for ammonia, it is half-order for oxygen concentration, and the nitrification rate can be calculated using Equation 2.6.1 (Okey & Albertson, 1989a):

$$r_{an} = \frac{1}{v_n}(K_{ao})(S_o)^{0.5} \qquad (2.6.1)$$

where r_{an} = nitrification rate ($g/m^2.d$)

K_{ao} = half-order rate constant ($g^{0.5}/m^{0.5}.d$)

S_o = bulk oxygen concentration (g/m^3)

v_n = 3.94 mg-O_2/mg-NH_4-N

Gullicks & Cleasby (1986) showed that above an ammonia concentration of 3.5 mg/L (15 °C) or 4.0 mg/L (20 °C), oxygen concentration is the limiting factor for nitrification. These observations agree with the reaction orders reported by Okey & Albertson (1989a).

Competition and DO Consumption

Consumption of DO by competitors can significantly inhibit nitrification. This effect is higher for wastewaters with high oxygen demand (BOD or COD), and has been referred to by Harremoës (1982), USEPA (2002) and Winkler (1981) to name a few.

Tchobanoglous *et al* (2003) reported that 0.44 g of oxygen is consumed for every 1 g COD removed from wastewater. Harremoës (1982) found that when oxygen can penetrate deeper into a biofilm than organic matter can, nitrifiers will get sufficient time for growth to such numbers that conversion of ammonia becomes significant; it was recommended that the filtered BOD of influent be less than 20 mg/L for every 3 mg/L DO.

Harremoës (1982) stated that biofilters have a maximum organic loading rate (OLR), measured in terms of g-BOD/m^3.d, which they should not be operated above. It was reported that operating at higher OLR will encourage heterotrophic bacteria and decrease the amount of nitrification occurring. When oxygen can penetrate to a greater depth than organic matter, nitrifiers will have time for sufficient growth, and significant nitrification can occur.

Wik (2000) stated that nitrifiers are affected by competition from heterotrophs. However, a study by Anderson *et al* (1994) showed very little competition from heterotrophs.

2.6.2 Carbon Availability

Carbon is essential for denitrification, and is either present in the wastewater, or in the form of additives such as methanol and ethanol. A comparison of denitrification achieved by Lamb *et al* (1990) achieved using various carbon sources is shown in Table 2.6.1. The use of additives (methanol or ethanol) instead of septic tank effluent (STE) resulted in a greater C:N ratio with a much lower addition, and a greater extent of denitrification.

Table 2.6.1: Effects of carbon source on denitrification in rock tanks (Lamb *et al*, 1990).

Carbon Source	TKN (mg/L)	Source:Effluent (vol:vol)	C:N Ratio	Denitri-fication	Effluent TN (mg/L)
STE	48.9	1:4	0.7:1	25%	39.2
Methanol	0.0	1:2000	4:1	99%	11.2
Ethanol	0.0	1:7000	2:1	99%	13.1

However, Piluk & Hao (1989) after Sikoro *et al* (1977) stated that the use of an external carbon source can be too complicated and costly for a small treatment system.

Lamb *et al* (1990) suggested a minimum C:N ratio of 3:1 for denitrification. Okabe *et al* (1996) reported that no denitrification occurred below a ratio of 1.5:1 (Table 2.6.2). Observations were made by Okabe *et al* (1999) of denitrification occurring without any carbon source. It was believed that NH_4^+ or organic matter derived from biomass decay may have acted as electron donors in this case.

Table 2.6.2: N recovery at various C:N ratios (Okabe *et al*, 1999).

C:N Ratio	Nitrogen Recovery
0:1	105 %
0.25:1	103 %
1.5:1	89 %

USEPA OWTS Technology Fact Sheet 9 states that for greater than 85 % nitrification, trickling filters must not be loaded above 3-6 g-BOD/m^3.d (rock media) or 6-12 g-BOD/m^3.d (plastic media). Harremoës (1982) recommended that the concentration of filtered BOD be less than 20 mg/L for every 3 mg/L DO.

2.6.3 Other Wastewater Constituents

Temperature of Wastewater

The rates of all metabolic reactions, and of transport processes such as diffusion, are affected by temperature to some extent.

The rate constant (k) for a reaction increases with increasing temperature, as shown in Equation 2.6.3:

$$k_{T^\circ C} = k_{20^\circ C} \cdot \theta^{T-20} \qquad (2.6.3)$$

where θ = usually given as 1.035

Most literature sources agree that nitrification is significantly affected by temperature. In some cases, temperature can also affect denitrification. The effects of temperature on the nitrification rate and the extent of nitrification are shown in Figure 2.6.2:

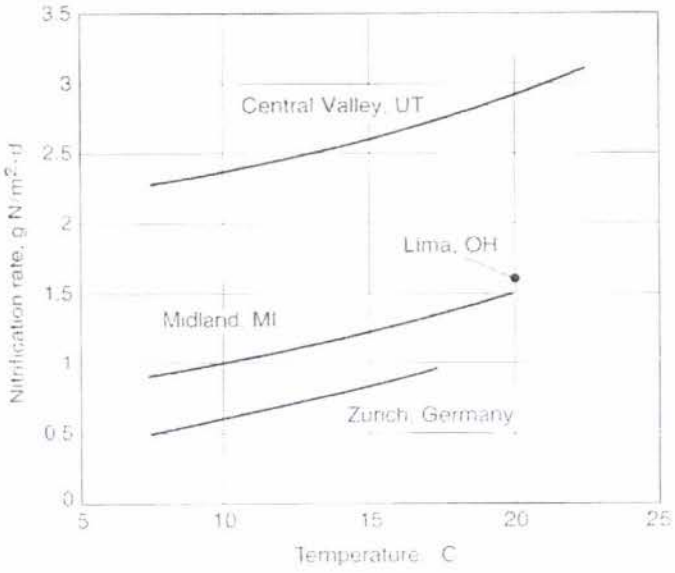

Figure 2.6.2: Effect of temperature on nitrification rate for tower trickling filters. (Tchobanoglous *et al*, 2003 after Parker *et al*, 1990).

Literature sources generally agree that the optimum temperature range for nitrification is 18-36 °C. Optimum temperatures within this range were reported by Osesek *et al* (1994) after Shammas (1986), Yoo *et al* (1999) after Ford *et al* (1980), and USEPA (1973).

Inhibition of nitrification below a temperature of 10-15 °C was reported by Lamb *et al* (1990), Gold *et al* (1992), and USEPA (1973). Gold *et al* (1992) observed that during winter, above-ground treatment systems were more adversely affected by temperature than buried systems.

However, Osesek *et al* (1994) showed that nitrification was not severely inhibited by low temperature: at 3.1 °C, the minimum NO_2^-/NO_3^- concentration detected was 10 mg/L. Welander *et al* (1997) also found that nitrification showed a weak temperature dependence: the nitrification rate at 5 °C was 77 % of the rate at 20 °C.

Welander *et al* (1997) after Knox (1985) stated that nitrification in attached-growth systems was less to susceptible to temperature effects (compared with suspended-growth systems). Okey & Albertson (1989a) stated that the effect of dissolved oxygen (DO) concentration on nitrification was more significant than temperature.

Osesek *et al* (1994) after Crites *et al* (1981) suggested that the minimum temperature for denitrification was 2-5 °C.

pH

All microorganisms have an optimum pH range, outside which their growth or metabolic activity is inhibited. Table 2.6.3 shows the reported values of optimum pH for BNR.

Table 2.6.3: Optimum pH reported for nitrification and denitrification.

Source	Optimum pH
Nitrification	
Osesek *et al* (1994) after Gaudy & Gaudy (1980)	8.0
Yoo *et al* (1999)	7.5 - 8.6
Denitrification	
Osesek *et al* (1994) after USEPA (1975)	7.0 - 7.5
Yoo *et al* (1999)	7.0 - 8.0

The optimum pH varies slightly depending on the bacterial population (Yoo *et al*, 1999). The minimum pH for nitrification is reported as 5.5 (Lamb *et al*, 1990 after Haug & McCarty, 1972; USEPA, 1975). Below the minimum pH, the nitrification rate decreases. However, the nitrification rate can recover after an acclimatisation period, or if the pH is restored to optimum levels (USEPA, 1993). Gold *et al* (1992) reported substantial TKN reductions under acidic conditions.

Wastewaters with high pH may have concentrations of NH_3 that are inhibitory to nitrification (see below).

Alkalinity

Stoichiometrically, 7.14 g of HCO_3^- is removed per 1 g of N nitrified (Lamb *et al*, 1990; Burks & Minnis, 1994). Measurements of alkalinity before and after treatment can confirm that nitrification is occurring. Osesek *et al* (1994) observed that as nitrate concentration increased to 15.3 mg/L (65 % of TN), alkalinity decreased from 267 to 172 mg/L. Alkalinity consumption was measured as 7.8 to 8.3 g per 1 g of N nitrified.

Lamb *et al* (1990) found that alkalinity became a limiting factor for BNR in a sand filter. Wastewater alkalinity was reduced to 0 mg/L, with only 80 % nitrification achieved.

Table 2.6.4: Alkalinity consumption and pH decrease across sand filter (Lamb *et al*, 1990).

Sample	pH	Alkalinity (mg/L)
Feed	7.0 - 7.5	200-300
Effluent	3.8	0

Suspended Solids

Parker *et al* (1995) showed that an increasing influent concentration of suspended solids decreased nitrification rates. It was believed that the effect of suspended solids was due to the development of heterotrophic microorganisms that competed with nitrifiers for oxygen.

Other researchers have also reported that soluble substrate removal in trickling filters is impeded by suspended solids or colloidal particles (Gullicks & Cleasby, 1986 after Särner, 1981; Gullicks & Cleasby, 1986 after Zimmerle *et al*, 1982).

Inhibitory Compounds

Anthonisen *et al* (1976) found that significant concentrations of free ammonia (NH_3) inhibit nitrification, as shown in Table 2.6.5. Inhibitory NH_3 concentrations for nitratation varied from 0.1 to 1.0 mg/L, above which nitrite accumulation occurred.

Above the inhibitory concentration for nitritation (10.0 to 150.0 mg/L), no nitrification took place.

Table 2.6.5: NH_3 concentrations inhibiting nitrification (Anthonisen *et al*, 1976).

Reaction	Inhibitory NH_3 Conc (mg/L)
Nitratation	0.1 - 1.0
Nitritation	10.0 - 150.0

Similarly, other researchers found that NH_3 concentrations up to 5 mg/L inhibited nitratation but not nitritation (Yoo *et al*, 1999 after Abeling & Seyfried, 1992; Gieseke *et al*, 2003).

Anthonisen *et al* (1976) reported that free nitrous acid (HNO_2) inhibits nitrification at concentrations above 0.2 to 2.8 mg/L.

Yoo *et al* (1999) after Yang & Alleman (1992) reported that hydroxylamine (NH_2OH/NH_3OH^+), an intermediate in nitritation, can inhibit nitratation.

Certain inorganic compounds such as heavy metals inhibit the growth of a wide range of microorganisms, including nitrifiers (De Renzo, 1978).

De Renzo (1978) after Painter (1970) reported a range of organic compounds that inhibit nitrifiers, including amino acids.

2.6.4 Growth of Microorganisms

It should be noted that the following information was derived from papers dealing with fixed growth processes that were not related to OWTS. It is assumed that the particular details of biofilm thickness, competition, acclimatisation and nitritation vs nitratation will also apply in OWTS.

Biofilm Thickness

Terada *et al* (2003) after Casey *et al* (2000) reported a reduction in nitrogen removal when biofilm thickness was greater than 1000 μm. Schramm *et al* (1996) observed that nitrification was restricted to a narrow zone of 50 μm on the top of a biofilm.

However, Terada *et al* (2003) reported a high nitrogen removal rate (4.48 g-N/m^2.d) in a membrane aerated biofilm reactor, despite a mean biofilm thickness of 1600 μm. Utilisation of extracellular substances in a thick biofilm could lead to increased nitrifier populations and a high nitrification rate (Terada *et al*, 2003 after Tsuneda *et al*, 2000).

Some researchers have reported the existence of nitrifiers deep within a biofilm, where it was expected that they could not survive because of low oxygen availability (Okabe *et al*, 1996; Schramm *et al*, 1996; Jang *et al*, 2002). In each case, it was thought that wastewater flowed directly into these depths because of heterogeneities in the biofilm. This would have set up oxic microniches, allowing consumption of oxygen by nitrifiers at the linings of the water channels.

Competition and Predation

Nitrifier populations can be adversely affected by competition from other microorganisms. Okabe *et al* (1996) reported that heterotrophs dominated nitrifiers at a C:N ratio of 1.5:1, whereas nitrifiers dominated at a C:N ratio of 0:1.

Decreases in performance due to the predation of nitrifiers by filter flies, larvae, worms and snails have been reported (Parker *et al*, 1997; Parker *et al*, 1995 after Boller & Gujer, 1986). Parker *et al* (1997) achieved an immediate improvement in NTF performance using an alkaline backwash to remove predators. Full recovery to expected effluent ammonia levels, however, took 4 months; full recovery of the nitrification rate took 7 months. Where macroorganisms are predominantly worms rather than filter flies, flooding does not improve performance (Parker *et al*, 1995).

Acclimatisation (Start-Up)

Estimates of the acclimatisation period required to reach steady-state nitrification vary between researchers: 2 weeks (Jowett & McMaster, 1995), 1 month (Welander *et al*, 1997), 2 months (Loomis *et al*, 2001a).

Gold *et al* (1992) stated that the long-term nitrogen removal of a sand filter cannot be assessed until after 12 months of operation. During the first 6-12 months of operation,

significant nutrient removal can occur through adsorption to particles, or assimilation into biomass.

Nitritation vs Nitratation

The reaction rates of nitritation and nitratation can vary under certain conditions. Okabe *et al* (1999) observed accumulation of NO_2^- at increasing bulk DO concentration, due to the limitation of NOB growth.

Some researchers have found that denitrification can occur via NO_2^-, without complete oxidation to NO_3^- (Terada *et al*, 2003; Yoo *et al*, 1999 after Abeling & Seyfried, 1992). This can lead to significant cost savings for a wastewater treatment plant, as the oxygen requirement for nitrogen removal is less. Yoo *et al* (1999) effectively inhibited nitratation, resulting in energy savings of 40 %.

2.6.5 Hydraulic Flow Effects

Distribution and Wetting

Effective distribution of wastewater over the trickling filter media is necessary to optimise treatment. Increasing the wetting rate (by increasing the hydraulic loading rate) increases the rate of nitrification, as more biofilm develops (Parker *et al*, 1997).

In non-wetted areas of a gas-phase biofilter (Figure 2.6.3), transfer of gases directly to the biofilm can occur, without first dissolving into the liquid phase (Zhu *et al*, 2001). Figure 2.6.4 shows that in wetted areas, the DO concentration drops substantially before contacting the biofilm:

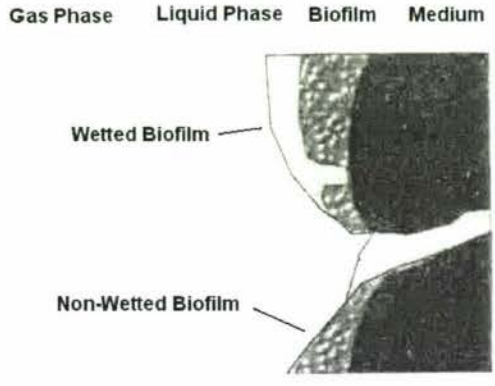

Figure 2.6.3: Wetted and non-wetted areas of biofilm (adapted from Zhu *et al*, 2001).

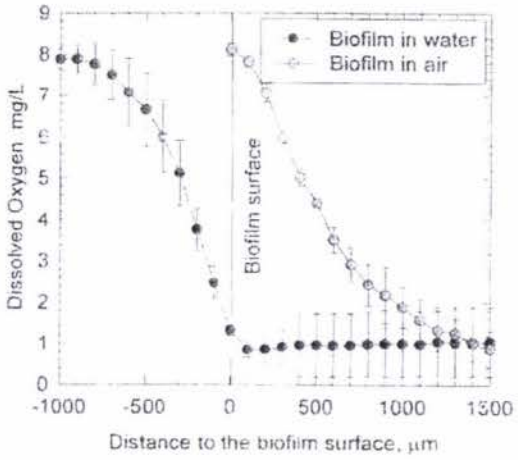

Figure 2.6.4: DO concentration in wetted vs non-wetted biofilm (Zhu *et al*, 2001).

Zhu *et al* (2001) concluded that when the limiting reactant is in the gas phase, and biofilm mass transfer resistance is significant, less wetting leads to increased performance. Conversely, if the limiting reactant is in the liquid phase, more wetting leads to increased performance.

Hydraulic Loading Rate (HLR)

The HLR determines the volume of media required to treat a given flow of wastewater. Jowett & McMaster (1995) after various researchers reported that a soil absorption field requires 80-400 m^3 of media (unsaturated soil); a sand filter requires 25-30 m^3 (sand and gravel), and a peat filter approx 50 m^3 (peat and gravel). To reduce the volume requirement to a reasonable level (3-4 m^3) and treat wastewater in a single pass, HLR would have to increase significantly (Jowett & McMaster, 1995).

Hydraulic Retention Time (HRT)

HRT in a trickling filter is proportional to depth, and can be estimated using Equation 2.6.4 (Särner, 1980):

$$t = k\frac{H}{Q^n} \qquad (2.6.4)$$

where t = HRT
k = constant
H = filter depth

Q = flow rate

n = a function of media geometry

At low flow, HRT is independent of flow rate. At higher flows, the exponent n becomes equal to 1. Above a certain flow rate, the exponent increases to 2.5, as water flows not only over the biological film, but also percolates through the medium (Särner, 1980 after Rincke & Wolters, 1971). The exponent n also varies greatly depending on the medium, and HRT can be significantly affected by biological growth.

The actual contact time of wastewater with biofilm can be longer than the HRT (Särner, 1980; Wik, 1999). Hold-up can be caused by diffusion of substances into and out of the biofilm, or adsorption of substances onto the biofilm.

Recirculation

Särner (1980) gives the potential benefits of recirculation as:

- further treatment of a portion of effluent
- dilution of pollutants entering the biofilter with effluent
- increasing the surface load and wetting
- operation of pumps at constant flow

Table 2.6.6 shows the TN removal achieved in RSFs run at various recirculation ratios:

Table 2.6.6: Effect of recirculation ratio on nitrogen removal.

Source	Recirculation Ratio	TN Removal
Bruen & Piluk (1994)	3:1	66%
Gold *et al* (1992)	4:1	20%
Mote *et al* (1991)	3.9:1	77%
Mote *et al* (1991)	7.3:1	83%

Mote *et al* (1991) observed that TN removal improved at higher recirculation ratios. However, the low removal observed by Gold *et al* (1992) shows that increased recirculation does not necessarily give a high level of treatment.

High recirculation ratios also reduce the amount of wastewater that can be treated. If a system has an HLR of 195 L/m^2.d and a recirculation ratio of 5:1 is used, the forward flow would be only 39 L/m^2.d (Lamb *et al*, 1990).

2.6.6 Mass Transfer

Trickling filter performance can be limited by the rate of mass transfer as well as by the rates of biological reactions. From the bulk liquid, oxygen and other substrates must diffuse through a laminar boundary layer and a stagnant liquid layer to reach the biofilm (Okey & Albertson, 1989b; Gullicks & Cleasby, 1986; Särner, 1980 after Harremoës, 1976).

The mass transfer rate of a reactant is proportional to its bulk concentration and its diffusivity in the solution (which is in turn dependent on temperature). This is represented by Equation 2.6.5 (Gullicks & Cleasby, 1986):

$$J = -A D_w \frac{dS}{dz} = -A D_w \frac{(S_S - S_0)}{(L_1 + L_2)} \qquad (2.6.5)$$

where J = mass transfer rate (mg/d)
A = area perpendicular to mass transfer (cm^2)
D_w = diffusivity of limiting reactant (cm^2/d)
S = concentration of limiting reactant (mg/cm^3)
S_0 = concentration in the bulk liquid
S_S = concentration at the biofilm-liquid interface
L_1 = thickness of laminar boundary layer (cm)
L_2 = thickness of stagnant liquid layer (cm)
z = distance in the direction of mass transfer (cm)

Särner (1980) after Matson (1976) stated that performance is limited by oxygen transfer in the upper regions of a biofilter, with substrate transfer limiting in the lower

regions. Gullicks & Cleasby (1986) also calculated that oxygen may be the limiting reactant through a substantial depth of the filter, or in some cases the entire depth.

2.7 Summary

Nitrogen discharges to the environment can have significant adverse impacts on the environment and human health. 25 % of homes rely on on-site wastewater treatment systems. The effluent total nitrogen concentration from a traditional OWTS varies greatly, and is generally greater than 50 mg/L.

Sand filters and recirculating sand filters have been used successfully for secondary treatment in OWTS. However, there are problems associated with these systems, including clogging and low hydraulic loading rates. More recently, expanded polyurethane foam has been used as a growth media for nitrification and denitrification in a single stage. Foam media biofilters allow greater aeration, higher hydraulic loading rates, and smaller volume requirements. However, the effluent total nitrogen concentration from foam media biofilters can vary significantly.

Literature on biological nitrogen removal in large-scale municipal trickling filters and suspended growth systems, as well as OWTS was reviewed. The dissolved oxygen concentration has been identified as the limiting factor by a large number of researchers. While the effluent DO concentration can be easily measured, there is often a great deal of uncertainty over DO concentrations within a trickling filter.

Trickling filter performance is also affected by the hydraulic flow regime, rates of mass transfer and wastewater composition. Effective wastewater distribution and media wetting improve performance. The hydraulic residence time (HRT) of wastewater depends on filter depth, but contact time can in some cases exceed HRT. Recirculation of treated effluent can increase media wetting as well as providing further treatment.

2.8 Research Questions

Based on the findings of this literature review, an investigation followed based on these research questions:

- do nitrification and denitrification occur in a foam media biofilter
- is a single stage adequate for both nitrification and denitrification to occur
- what are the mechanisms of nitrogen removal in a foam media biofilter, and their relative importance
- what are the factors limiting nitrogen removal

3 Methods

3.1 Introduction

The methods used to study on-site wastewater treatment systems and foam media biofilters are described in this chapter. The configuration of full-scale systems studied in the field is explained, as is the set-up of the bench-scale biofilter. Methods used for sampling wastewater and determining the concentration of key parameters are given. The methods developed to allow sampling and measurement of dissolved oxygen concentration in foam media are described in Chapter 4.

3.2 Field Configurations

3.2.1 General Description

Three different configurations of foam media biofilter were studied in the field. Overall, there were some similarities between the configurations, which are discussed here. The first stage of treatment was an arrangement of septic tank(s). Effluent from the septic tank(s) was filtered, then passed into the distribution pump chamber. The distribution pump was triggered by a float switch. Once wastewater reached a certain level, the pump distributed it over the foam media biofilter(s). Effluent from the biofilter(s) drained into the final pump chamber, also triggered by a float switch. Once a certain level was reached, the pump activated and effluent was pumped to drip lines for irrigation in the soil absorption field. 20 % of effluent was recirculated to the distribution pump chamber (giving a recirculation ratio of 0.2:1). This had the effect of flushing out the drip lines, as well as returning wastewater for further treatment.

Figure 3.2.1 shows the construction of the treatment system for configuration F1. The system is contained within a single concrete tank, with stages divided by concrete walls and connected with PVC pipes. Risers (not shown) provide access to the pump chambers and filters. Configurations F2 and F3 differed slightly, in the arrangement

of septic tanks and biofilters. For reasons of commercial sensitivity, more detailed diagrams of the treatment systems are not presented.

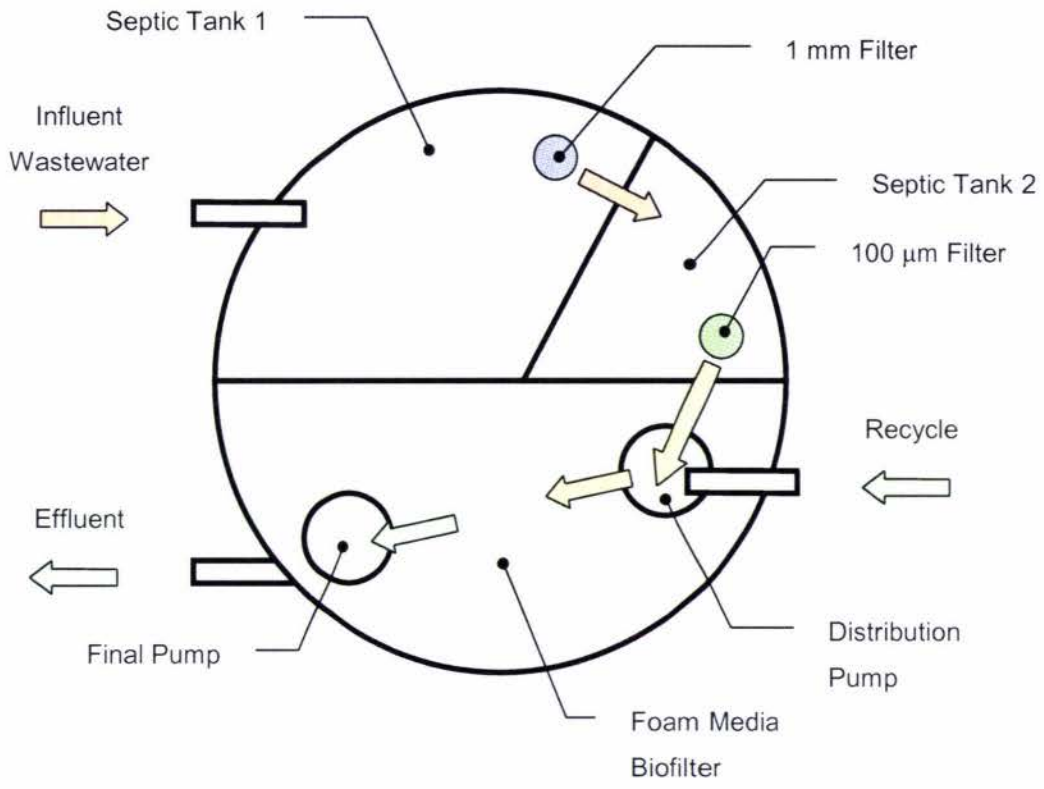

Figure 3.2.1: Cutaway plan view of configuration F1, showing division into treatment stages.

3.2.2 Septic Tank Arrangement

Configuration F1 had a two chamber septic tank, with disc filters on the outlets of each tank. Configurations F2 and F3 each had only one septic tank of larger volume, also with a disc filter on the outlet (Table 3.2.1).

Table 3.2.1: Septic tank details for each configuration.

Configuration	Septic Tank 1		Septic Tank 2	
	Vol (L)	Filter	Vol (L)	Filter
F1	4000	1 mm	1400	100 µm
F2	6000	1 mm	-	-
F3	6000	1 mm	-	-

3.2.3 Foam Media Biofilter Arrangement

The media used for supporting microbiological growth was expanded polyurethane foam with a density of 21 kg/m^3. No CFCs were used in the production of foam media for these treatment systems. Configurations F1 to F3 used unique sizes and arrangements of foam media, as described below. Table 3.2.2 shows the dimensions of the biofilter and the amount of foam media in each configuration. The total surface area of foam media available was calculated based on 6.00 x 10^4 m^2/m^3 (Jowett & McMaster, 1995). For configuration F3, the total volume and foam media area from both biofilters are shown.

Table 3.2.2: Biofilter dimensions in each configuration.

Configuration	Biofilter		Foam Media	
	Height (m)	Area (m^2)	Volume (L)	Area (m^2)
F1	1.50	0.76	768	46,080
F2	0.75	1.17	960	57,600
F3	1.10	0.33 x 2	643	38,570

Configuration F1: Medium Foam, Random Packing

The system consisted of two septic tanks in series, followed by a foam media biofilter. The first septic tank had a volume of 4000 L, followed by a septic tank of 1400 L. The biofilter has a volume of 1300 L, depth of 1.50 m and surface area of 0.759 m^2.

Effluent from the first septic tank passed through a 1 mm disc filter. Effluent from the second septic tank passed through a 150 μm disc filter. Wastewater was distributed over the biofilter through a moving high velocity nozzle known as a 'wobbler'.

Foam media used in the biofilter was medium size (200 x 160 x 60 mm), with a total volume of 1.920 L per block. The foam media was randomly packed in the biofilter. The biofilter contained approx 400 foam blocks, giving a total foam volume of 0.768 m^3 (Figure 3.2.2).

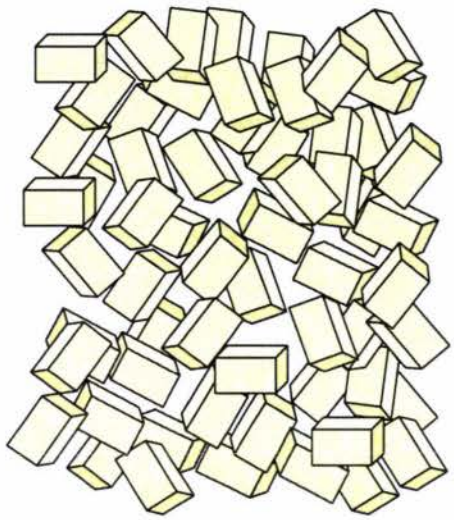

Figure 3.2.2: Arrangement of foam blocks in biofilter (configuration F1).

Configuration F2: Large Foam, Structured Packing

The system consisted of one 6000 L septic tank, with effluent passing through a 1 mm disc filter, followed by a foam media biofilter. The biofilter had a volume of 1300 L, depth of 0.75 m and surface area of 1.1683 m^2.

Wastewater was distributed at low pressure through a network of drilled PVC pipes. Each dose distributed 16 L of wastewater over the top of the biofilter. An additional 4 L of wastewater was flushed through the distribution system at each dose.

Foam blocks in the biofilter were large size (200 x 160 x 150 mm), with a total volume of 4.800 L per block. The blocks were placed side-by-side in a square biofilter, 5 blocks deep (Figure 3.2.3). The biofilter contained 200 blocks, giving a total foam volume of 0.960 m^3.

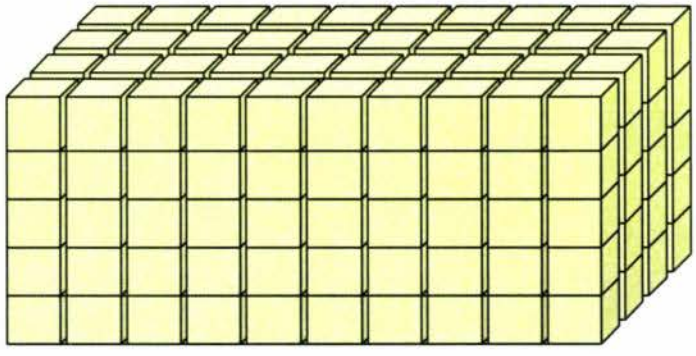

Figure 3.2.3: Arrangement of foam blocks in biofilter (configuration F2).

Configuration F3: Small Foam, Random Packing

The system consisted of a 6000 L septic tank, with effluent passing through a 1 mm disc filter, followed by two identical foam media biofilters operating in parallel. Each biofilter had a volume of 365 L, a depth of 1.1 m and surface area of 0.3318 m^2. This gave a total volume of 730 L and surface area of 0.6636 m^2.

Since the distribution pump had a high flow rate, wastewater was distributed evenly across both biofilters. Distribution was through a nozzle which gave a fine spray, reducing the amount of wastewater that 'bounced' off the top of the foam.

The top 600 mm of each biofilter was filled with randomly packed foam blocks, small size (60 x 60 x 60 mm), each block having a volume of 0.216 L. Each biofilter contained 720 of these, giving a total volume of 156 L of small foam blocks.

Underneath this were two large, round blocks of foam (each 250 mm height x 650 mm diameter) which filled the entire diameter of the chamber. Each of these blocks had a volume of 82.95 L. The total volume of foam in each biofilter (including small and large blocks) was therefore 321 L. This gave a total foam volume of 642 L (Figure 3.2.4).

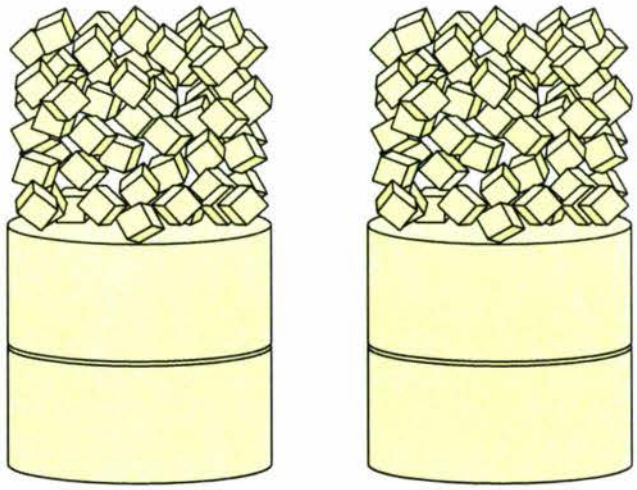

Figure 3.2.4: Arrangement of foam blocks in biofilters (configuration F3).

3.3 Bench-Scale Biofilter

Bench-scale studies were carried out to determine the effect of feed composition on nitrogen removal, and to test the hypothesis that nitrification and denitrification occur in a single foam block. The biofilter constructed consisted of one medium size block (200 x 160 x 60 mm) held horizontally in a perspex container (Figure 3.3.1). The foam block contacted the perspex walls on four sides, with air gaps at the top and bottom surfaces. The foam block used was taken from a system in the field (configuration F1) in which nitrogen removal was already occurring.

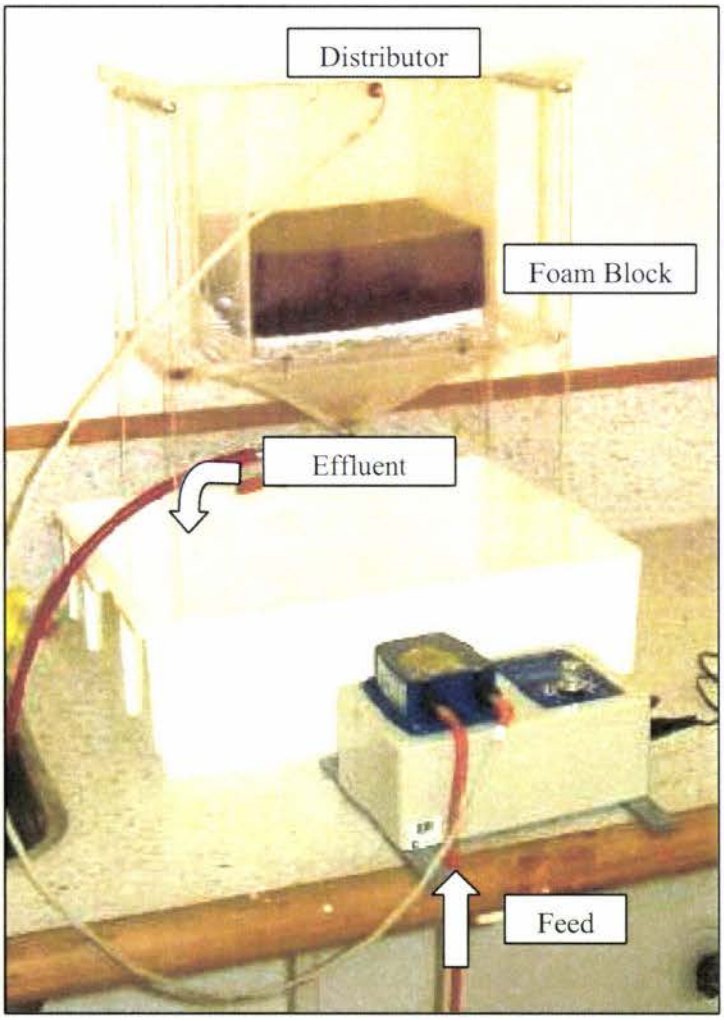

Figure 3.3.1: Bench-scale biofilter.

The bench-scale biofilter was fed from a 20 L container using a variable speed peristaltic dosing pump (TPS easyFLOW-VS with SED-24500S AC-DC adaptor).

Synthetic wastewater was pumped through a length of 4 mm diameter tubing, with pinholes at regular intervals to distribute wastewater over the foam block.

Dosing was controlled by a timer (HPM D817/2) and took place at 30 minute intervals from 10:00 am to 3:30 pm daily (12 doses). Dosing times were chosen to provide adequate time for preparation before sampling runs, and for analysis afterwards. The dosing volume was 180 mL and total loading was 2.2 L/d (69 $L/m^2.d$). Loading rate was selected so that a 20 L container of synthetic wastewater would last for one week.

Macronutrients were present in the synthetic wastewater as CH_3COONa, NH_4Cl, Na_2HPO_4 and $NaH_2PO_4.2H_2O$ (Table 3.3.1). Micronutrient solution was added to the synthetic wastewater in the ratio 0.6 mL/L (composition as given by Smolders *et al*, 1994). Temperature in the bench-scale study was controlled at 24.0 °C (± 2.6 °C), and feed pH was buffered to 7.2.

Table 3.3.1: Synthetic wastewater composition (macronutrients).

Study	Description			Average Feed Conc (mg/L)			
				Amm-N	Ac^-	DO	PO_4^{3-}-P
L1	High N	Low C	Med DO	163.8	65	4.03	18.3
L2	Med N	High C	Low DO	72.6	220	2.44	19.5
L3	Med N	High C	Med DO	73.2	228	5.16	19.3
L4	Med N	Zero C	High DO	70.1	3	6.57	18.6
L5	Med N	High C	Low DO	70.6	259	3.01	21.2

Although up to 5 m of tubing was used, it was determined that no losses of Amm-N, COD or sCOD occurred between the feed container and the biofilter. DO concentrations reported in Table 3.3.1 were measured immediately after the distributor.

Low DO Feed

DO was stripped from feed for study L2 by bubbling N_2 gas through a beaker containing 200 mL synthetic wastewater. The DO concentration was monitored using a YSI Model 5775 electrode (with Model 57 meter). Once the DO concentration in the beaker was 0.00 mg/L, the N_2 bubbler was taken out of the liquid and placed in the headspace; the gas flow rate was then reduced to avoid entrainment of excess N_2

in the feed. DO concentration increased from 0.00 mg/L in the beaker to 2.44 mg/L after the distributor (Table 3.3.1).

Sterilisation

During study L3, the DO concentration in each batch of feed decreased over time. This may have been due to microbial growth in the feed container, despite the fact that the container was stored at 4 °C.

For studies L4 and L5, the feed container and tubing were autoclaved at 15 atm for 30 minutes. The feed container was sealed, with air entering through a 0.45 μm filter. After autoclaving, feed was aerated to the desired DO concentration.

During study L4, DO concentration in the feed did not decrease. In study L5 the DO concentration decreased as before; this may have been because air used to aerate the feed was not filtered during study L5 (as it was during study L4).

This shows that attention must be paid to the sterilisation of equipment when control of the feed DO concentration is desired.

3.4 Sampling Methods

3.4.1 Field Sampling Method

Several sampling sites were chosen for each of the configurations studied. Each system treated wastewater from a single household of 4-6 persons. The total number of systems studied, and the dates on which samples were taken, are given in Table 3.4.1. Concentrations of various constituents (Section 3.5) were determined at each site and averaged for each configuration (Chapter 5). Where data from a system was not representative of normal operating conditions, it was not included in averages. Reasons for excluding particular systems are given in the Appendices.

Table 3.4.1: Details of systems sampled.

Site	Date	Configuration	Age (wks)	Data Used
Run 1				
1	29 Jan 04	GT8000RPF	13	✓
2	29 Jan 04	GT8000RPF	9	✓
3	4 Feb 04	GT8000RPF	11	×
4	19 Feb 04	GT8000RPF	19	×
5	5 Apr 04	EnviroClear™ SQ	10	✓
Run 2				
6	10 Aug 04	EnviroClear™ SQ	21	×
7	16 Aug 04	EnviroClear™ SQ	22	×
8	16 Aug 04	EnviroClear™ SQ	17	✓
10	10 Aug 04	Gould EnviroClear™	12	✓
Run 3				
7	21 Oct 04	EnviroClear™ SQ	31	×
11	19 Oct 04	Gould EnviroClear™	20	×
12	21 Oct 04	Gould EnviroClear™	12	✓
13	9 Nov 04	Gould EnviroClear™	18	✓
14	9 Nov 04	Gould EnviroClear™	19	×
15	9 Nov 04	Gould EnviroClear™	24	×
16	9 Nov 04	Gould EnviroClear™	11	×
Run 4				
12	7 Dec 04	Gould EnviroClear™	19	×

Usually, a single grab sample was taken of wastewater at 3 or 4 positions in the treatment system. On two occasions, effluent samples were also taken at several different positions for comparison. The sampling locations used were:

(1) septic tank 1

(2) septic tank 2

(3) distribution pump chamber

(4) final pump chamber

(5) drain from biofilter into final pump chamber

(6) line recirculating effluent to distribution pump chamber

Sample times varied between 10:00 am and 3:30 pm on weekdays. Most sites were sampled only once during the project (Table 3.4.1). Samples were taken by dipping a sample grabber with glass bottle 100-200 mm below the liquid surface. Sample was

then transferred to a plastic bottle for storage. The glass bottle was rinsed with deionised water between samples. 500 mL of unfiltered sample was collected from each location using this method. For each sample taken, 10 mL was immediately filtered to 0.45 μm (using a disposable syringe and syringe filter) and stored in a separate container. Samples were stored in coolers with ice packs until returning to the laboratory, where they were frozen for subsequent analysis.

Variation with Time

Samples were taken from a septic tank every hour from 9:00 am to 3:00 pm. Concentrations of COD, sCOD, Ac^-, Amm-N and Nit-N were determined to check the variation with sampling time.

Variation with Position

On one occasion, samples were taken from the same depth at two different positions in a septic tank. Concentrations of TSS, COD, sCOD, Ac^-, Amm-N, Org-N and Nit-N were measured. The differences in concentration between each position were not statistically significant.

Also, one study of the effect of depth was performed. Samples were taken from various depths in a septic tank. Analysis of COD, sCOD, Ac^-, Amm-N, Nit-N and Org-N was conducted to determine how these parameters changed with depth in the septic tank.

Effluent Sample Position

On two occasions, effluent samples were taken from three different positions, as indicated above (Positions 4, 5 and 6). Overall, there was no statistically significant difference in the effluent quality between these positions. This shows that sampling wastewater from the final pump chamber was representative of the effluent from the system, for the two cases studied.

3.4.2 Laboratory Sampling Method

Samples of the feed were taken by removing the distributor from the bench-scale reactor, placing it in a sample container and activating the pump. Effluent samples were collected by placing a sample container under the effluent drain from the bench-scale reactor.

Generally, effluent samples were collected at 10:00 am, 1:00 pm and 3:00 pm on several days within each study. Feed samples were generally collected between 10:00 am and 1:00 pm. Only one feed sample was taken on each day sampled; it was assumed that feed composition did not vary significantly during the course of a day.

Nodes in Foam Media

The foam block was divided into nodes, as shown in Figure 3.4.1. The foam block had a permanent liquid level up to a height of 20-30 mm, allowing the extraction of liquid samples from the nodes pictured (at heights of 0 and 15 mm). Liquid samples could not be taken above a height of 30 mm, so the bottom nodes were selected for study. When required, samples were extracted using a disposable syringe and custom-made syringe needle (as described in Chapter 4). These samples were taken immediately after DO measurements were performed.

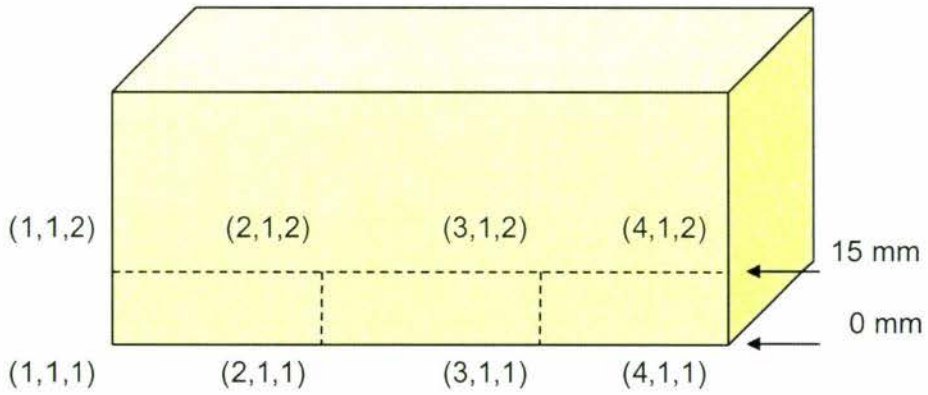

Figure 3.4.1: Division of foam block into nodes.

Sample volume from each node was approx 1.5 mL for DO measurement (see Chapter 4), 1.5 mL for anion analysis (Section 3.5.5) and 1.5 mL for Amm-N analysis

when required (Section 3.5.4). This meant that the sample taken would have been drawn from a small area around each node. Reporting that samples taken were from a single, infinitesimal point is therefore not completely accurate.

3.5 Analytical Methods

3.5.1 Total Suspended Solids (TSS)

TSS was determined by APHA Standard Method 2540 D (Clesceri *et al*, 1998). As specified, Whatman 934-AH glass microfibre filter papers were prepared and used (pore size 1.5 μm). After filtration, papers were dried to constant weight in a Contherm Series Five digital drying oven at 110 °C. Filters were weighed before filtration and after drying using a Mettler AE200 balance, accurate to 0.1 mg.

The sample volume used was 100 mL. Tests were performed in duplicate. Above a TSS concentration of 20 mg/L, the average error between duplicates was 13 %. Below 20 mg/L, the average error was 67 %.

Checking of TSS concentrations against results from another laboratory was performed for 8 samples. On average, results obtained independently were 24 mg/L higher than results reported in the present study. The independent laboratory used Whatman GF/C filter papers (pore size 1.2 μm), which could possibly explain the reported differences. Deviations would have occurred if samples had a high proportion of solids between 1.2 μm and 1.5 μm diameter.

3.5.2 Chemical Oxygen Demand (COD)

COD was determined using closed reflux digestion and colorimetry, according to APHA Standard Method 5220 D (Clesceri *et al*, 1998). Absorbance was measured at 600 nm using a Philips PU 8625 UV/VIS spectrophotometer.

A calibration curve was constructed using potassium hydrogen phthalate standards at COD concentrations of 0, 100, 200, 300, 400 and 500 mg/L. The linear relationship between COD and absorbance is represented by Equation 3.5.1. The same equation was given by two separate calibrations, 7 months apart (R^2 values 0.9850, 0.9599).

$$y = 0.0003\,x \qquad (3.5.1)$$

where y = COD concentration (mg/L)

x = absorbance at 600 nm

The sample size used was 2.5 mL. Tests were performed in triplicate. Undigested blanks were used as a zero reading in the spectrophotometer. Blanks were also carried through the digestion procedure to determine the effect on absorbance (this was subtracted from the final sample readings).

Soluble COD (sCOD) was determined by filtering the sample to 0.45 μm (as reported in Section 3.4.1) and following the procedure described above.

3.5.3 Total Kjeldahl Nitrogen (TKN)

The sum of organic nitrogen and ammonia nitrogen is referred to as total Kjeldahl nitrogen (TKN). TKN concentrations were determined using the macro Kjeldahl method, APHA Standard Method 4500-N_{org} B (Clesceri *et al*, 1998).

Thompson & Capper Kjeltabs W were used in place of digestion reagent. Each digestion was carried out until all samples had become transparent (usually 2-3 hours). Following digestion, samples were distilled using a Büchi 323 Distillation Unit. TKN concentration was then determined using a Mettler DL25 titrator (with Mettler DG111-SC electrode).

Sample volume used was 25 mL. Tests were performed in triplicate. The average error between replicate samples was 14 % when samples were fully digested. Blanks carried through the digestion procedure gave readings of 0.0 mg-N/L.

3.5.4 Ammonia (Amm-N)

The concentration of NH_3/NH_4^+ (Amm-N) in samples was measured using distillation and titrimetric analysis according to APHA Standard Methods 4500-NH_3 B and C (Clesceri *et al*, 1998). Distillation was performed using a Büchi 323 Distillation Unit;

Amm-N concentration was then determined using a Mettler DL25 titrator (with Mettler DG111-SC electrode).

The sample volume used was 50 mL. Tests were performed in duplicate. The average error between replicates was 4 %. An 80 mg/L standard was carried through the distillation and titration steps, and gave an average concentration of 80.4 mg/L ± 6 % (this also applies to the distillation and titration steps for TKN).

The sample volume from nodes within the foam block was too small for determination of Amm-N concentration by the above method. When determination of Amm-N concentration was required for these samples, they were sent to NIWA Inorganic Chemistry Laboratory in Hamilton. Concentrations were determined by flow injection analysis, following the proposed APHA Standard Method 4500-NH_3 H (Clesceri *et al*, 1998).

3.5.5 Anion Analysis

Concentrations of Ac^-, Cl^-, NO_2^-, NO_3^- and PO_4^{3-} were determined using a Dionex ICS-2000 Ion Chromatography System with AS50 Autosampler and Chromeleon software.

Samples were filtered to 0.45 μm before analysis (Section 3.4.1). The sample volume required was approx 1.5 mL.

Calibration curves were constructed automatically by the software, using four mixed standards at various concentrations. The relative errors observed with each standard are given in Table 3.5.1 (e.g. reported concentrations of the 75.0 mg/L standard for acetate were ± 6 % of 75.0 mg/L).

Table 3.5.1: Accuracy of ion chromatography at various concentrations.

Ion	Standard Concentration (mg/L)			
	5.0	**50.0**	**75.0**	**100.0**
Ac^-	11%	19%	6%	4%
PO_4^{3-}	12%	9%	1%	3%
	12.5	**25.0**	**37.5**	**50.0**
Cl^-	4%	1%	0%	1%
NO_2^-	1%	2%	2%	1%
NO_3^-	3%	3%	1%	1%

The use of an autosampler meant that samples were stored at room temperature for up to 24 hours before analysis was completed. The effect of long-term room temperature storage on the concentrations of each ion was assessed (Table 3.5.2). Concentrations of Ac^- and PO_4^{3-} decreased markedly over a period of 1 month. Concentrations of Cl^-, NO_2^- and NO_3^- were not significantly affected.

Table 3.5.2: Decrease in anion concentration after 1 month storage at 25 °C.

Ion	Decrease (%)
Ac^-	100%
Cl^-	1%
NO_2^-	0%
NO_3^-	0%
PO_4^{3-}	22%
SO_4^{2-}	0%

This shows that samples intended for the analysis of Ac^- and PO_4^{3-} should not be kept at room temperature for an extended period of time, but that room temperature storage does not affect the determination of Cl^-, NO_2^- or NO_3^- concentrations.

3.5.6 Temperature, Dissolved Oxygen (DO)

In the field, wastewater temperature and DO concentration were recorded with a YSI Model 5775 membrane electrode and YSI Model 57 meter.

3.5.7 pH

pH of wastewater samples was measured in the laboratory, up to 3 days after collection, using an Orion Model 230A meter. The pH meter was calibrated with buffer solutions at pH 4.00 and 7.00.

3.5.8 Foam Media

Samples of clean foam of each size used were obtained (small, medium, large but not the large round blocks from configuration F3). These were measured and weighed as controls.

Various samples from the field were taken at biofilter depths of 0.0 to 0.2 m. These were stored in water-tight plastic bags. The total weight of each foam block plus the water retained on it was measured using a Mettler Toledo SB16001 Delta Range balance (accurate to 0.1 g). Foam blocks were then dried to constant weight in a Contherm Series Five digital drying oven at 110 °C. Tests on controls showed that the foam did not experience any mass loss at this temperature over a period of several days.

The difference between weight before and after drying was used to determine the amount of water retained on each block. The difference between the dry weight of a foam sample from the field, and a control of the same size, was taken to be the weight of biomass on the sample.

4 Method for DO Measurement in Foam Media

4.1 Introduction

As reported in Chapter 2, dissolved oxygen (DO) concentration has been identified as a limiting factor in biological nitrogen removal (BNR) systems. Aerobic zones for nitrification and anoxic zones for denitrification must be present to achieve overall nitrogen removal. This means that an understanding of DO concentrations at various points within a BNR process is essential for optimisation of performance.

A preliminary investigation of various methods for DO measurement has been carried out. Miniature membrane polarographic electrodes proved to be the most suitable method of DO measurement in a foam media biofilter. A sampling technique was developed that enabled extraction of small volumes of liquid samples from a block of foam media. This technique was developed to minimise errors resulting from oxygen transfer between the sample and the environment. Temporary storage in glass tubes meant that samples could be taken from a number of different points in the foam block and subsequently analysed, to determine the spatial DO profile.

The accuracy of the DO measurement method was checked against a commonly used membrane electrode. The accuracy of the sampling technique was assessed by comparing with results from *in situ* measurements. Validation of the method is described in Section 4.5. Further improvements that could be made are also discussed.

4.2 DO Measurement Techniques

4.2.1 Dissolved Oxygen (DO)

All gases are soluble in water to some extent. The saturation concentration of a component in solution is determined by the partial pressure of that component in the

gas phase. An equilibrium is maintained by diffusion of oxygen between the gas and liquid phases. Henry's Law (Equation 4.2.1) describes this relationship:

$$p_g = \frac{H}{P_T} x_g \qquad (4.2.1)$$

where p_g = mole fraction of gas in air (mol/mol)
H = Henry's Law constant for the gas (atm) (41,100 for oxygen)
P_T = total pressure (usually 1 atm)
x_g = mole fraction of gas in water (mol/mol)
= mole gas (n_g) / (mole gas (n_g) + mole water (n_w))

Since the partial pressure of a gas is equal to the total pressure multiplied by the mole fraction of that gas, Henry's Law may also be written in the form shown by Equation 4.2.2:

$$P_g = H\, x_g \qquad (4.2.2)$$

where P_g = partial pressure of gas in air (atm)

The Henry's Law constant is specific to the gas and liquid under investigation. Gas solubility decreases with increasing concentration of salts in the liquid, so a value of H that applies for pure water will not apply for water with high concentrations of salts. Values of H vary with temperature according to Equation 4.2.3:

$$\log_{10} H = \frac{-A}{T} + B \qquad (4.2.3)$$

where T = temperature (K)
A, B = empirical constants (595.27, 6.644 for oxygen)

Values for the saturation DO concentration (C^*) determined from Henry's Law are not in exact agreement with experimental data for air-water systems (e.g. sources such as Metcalf & Eddy, 2003 or Hammer & Hammer, 2004). Winkler (1981) gives two

empirical relationships (Equations 4.2.4 and 4.2.5) which can be used in air-water systems to estimate C^*:

$$C^* = \frac{468}{31.6 + T} \tag{4.2.4}$$

where C^* = saturation DO concentration (mg/L)
T = temperature (0-50 °C)

$$C^* = \frac{468}{31.6 + T} - \frac{0.0036\,J}{21.2 + T} \tag{4.2.5}$$

where C^* = saturation DO concentration (mg/L)
T = temperature (0-30 °C)
J = Cl^- concentration (0-20,000 mg/L)

Equilibrium DO concentrations can be determined using any of the relationships described above (Henry's Law, tables or empirical relationships). However, for effective wastewater treatment it is necessary to measure DO in samples that are not at equilibrium. Aerobic bacteria consume oxygen, while algae produce it, which means that accurate measurement of DO concentration must be possible over a range of concentrations to enable optimisation of wastewater treatment processes.

Solute Transport Processes

Several measurement techniques discussed in this chapter rely on the movement of oxygen through the sample solution to a measurement surface. Three main processes are responsible for the transport of solute in a liquid: migration, convection and diffusion (Hitchman, 1978). Migration is the movement of ions due to an electric field. Convection is the physical movement of solute particles by fluid movement, caused by density or pressure gradients within the solution. Diffusion occurs as a result of concentration gradients within the solution. Solute particles will diffuse from areas of high concentration to areas of low concentration. Ficks Law (Equation 4.2.6) shows that the flux (J) or flow of particles per unit area is proportional to the concentration gradient (dC/dx) and a diffusion coefficient (D):

$$J = D \frac{dC}{dx} \tag{4.2.6}$$

As solution temperature increases, diffusion becomes more rapid. This is accounted for by using the following expression to modify the diffusion coefficient (Equation 4.2.7):

$$D = D_0 \exp\left(-\frac{E_D}{RT}\right) \tag{4.2.7}$$

where E_D = activation energy required for diffusion

D_0 = diffusion coefficient or diffusivity at temp T

4.2.2 Method 1: Winkler Titration

The Winkler titration (or iodometric method) was introduced in 1888, and is still the standard chemical method for DO measurement. Divalent manganese solution and strong alkali is first added to the sample. Manganese (II) hydroxide precipitates are formed and subsequently oxidised to hydroxides of higher valency by DO in the sample. Manganese is converted back to Mn (II) in the presence of I^- ions in acidic solution, releasing I_2 gas in the process. The amount of I_2 released is determined by titration against a thiosulphate standard; this is equivalent to the DO concentration of the sample.

Accuracies of ± 50 µg/L are possible with visual end-point determination, or ± 5 µg/L with electrometric end-point detection (APHA Standard Methods, 1998). However, this method requires a significant amount of time and also a reasonable amount of experience with titrimetric techniques. The method has been reported as slow, tedious and demanding, especially to those unfamiliar with the process (Winkler, 1981). APHA Standard Methods (1998) suggests that a sample volume of 300 mL is required. Interferences from oxidising agents, reducing agents, NO_2^- or Fe^{2+} must be compensated for using one or more of the modifications described in APHA Standard Methods (1998).

4.2.3 Method 2a: Standard Membrane Electrodes

A membrane electrode for DO measurement consists of an electrochemical cell built into a probe, with an oxygen-permeable membrane fitted over the end. The electrochemical cell consists of an anode (positively charged), a cathode (negatively charged) and an electrolyte solution to connect the two electrically. Maintaining a negative potential at the cathode can be achieved in two ways. When a voltage is applied from an external source, the system is referred to as a 'polarographic' or 'voltammetric' detector. When the electrode potential (E^0) between the anode and the cathode is used, the system is called a 'galvanic' detector, and operates on the same principle as a battery or fuel cell. Membrane electrodes are also referred to as Clark-type electrodes, since they were first patented in the United States by L Clark (1959).

In polarographic membrane electrodes for DO measurement, the cathode is usually gold or platinum, and acts as a source of electrons for reduction of oxygen (Equation 4.2.8):

$$O_2 + 2\,H_2O + 4\,e^- \rightarrow 4\,OH^- \qquad (4.2.8)$$

The hydroxide ions produced react with the electrolyte (most commonly KCl, as shown in Equation 4.2.9):

$$4\,OH^- + 4\,KCl \rightarrow 4\,KOH + 4\,Cl^- \qquad (4.2.9)$$

The chloride ions resulting from this react with the anode, usually silver (Equation 4.2.10). This Ag/AgCl system is known as the 'reference couple'. The silver anode also acts as a 'reference electrode' maintaining a stable potential.

$$Ag + Cl^- \rightarrow AgCl + e^- \qquad (4.2.10)$$

It can be seen from the cathodic reaction (Equation 4.2.8) that the current produced is proportional to the amount of oxygen consumed. Oxygen diffuses through the permeable membrane to the cathode, so the current produced by a membrane electrode is ultimately proportional to sample DO concentration. More accurately, it is

the activity of oxygen in the sample solution that controls diffusion and current. Activity is related to concentration by an activity coefficient which varies depending on the substance and environmental conditions (Equation 4.2.11):

$$a_c = f_c \times C \qquad (4.2.11)$$

where a_c = activity
f_c = activity coefficient
C = concentration

For pure water or solutions with low dissolved salt concentrations, the activity coefficient is equal to 1, and concentration may be used instead of activity. In solutions with high salt concentrations, the activity coefficient is greater than 1, and activity is greater than concentration. This means that for a given electrode current, the DO concentration is lower than expected (Hitchman, 1978).

For practical reasons, the electrochemical cell is always placed in a plastic housing of some type. The physical design of the DO probe is important, as it can affect the rate of diffusion of oxygen to the cathode. Figure 4.2.1 and Figure 4.2.2 show a typical oxygen probe designed for field measurement of DO:

Figure 4.2.1: YSI Model 5775 electrode and Model 57 meter.

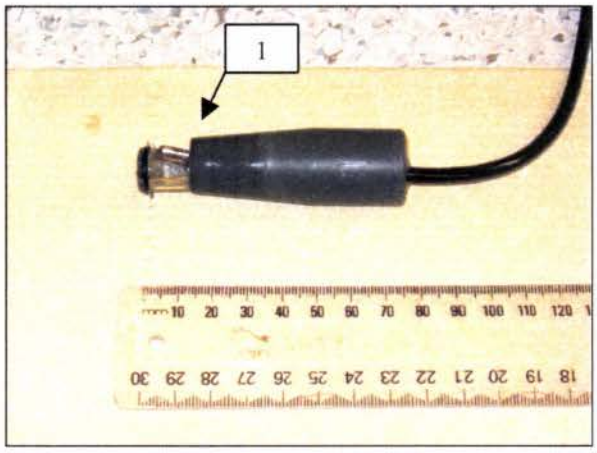

Figure 4.2.2: YSI Model 5775 electrode.

The stainless steel temperature sensor that can be seen at the tip of the probe provides temperature compensation (1). This enables the DO concentration to be read instantly from the meter. Probes mounted with a stirrer are also available. Movement of the sample with respect to the electrode is of high importance for accurate DO measurements. If the sample solution is not moving, oxygen will be consumed by the electrode over time, resulting in a negative interference (Hitchman, 1978).

4.2.4 Method 2b: Miniature Membrane Electrodes

Miniature oxygen electrodes are also available, such as the Diamond General 733 (Figure 4.2.3). This electrode has a length of 86 mm and a body diameter of 6 mm. Membranes used are teflon, and each membrane is fixed to an acrylic housing for easy attachment or removal.

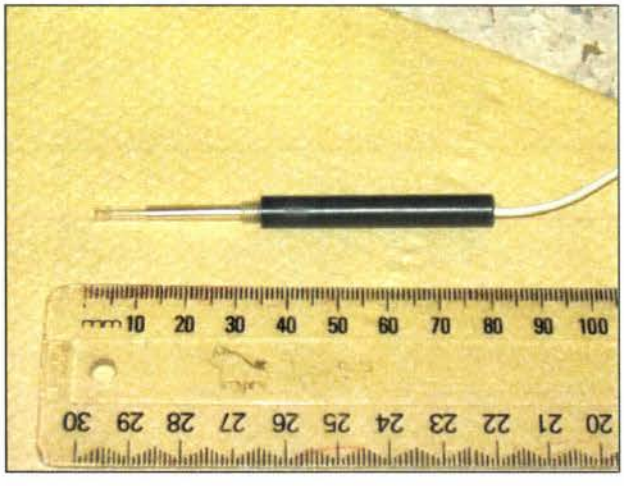

Figure 4.2.3: Diamond General 733 electrode.

Some precision equipment is required to operate a Diamond General 733 electrode. The power source used must be able to supply a precise and stable voltage. Figure 4.2.4 shows the characteristic curve for the electrode. The applied voltage must be between -0.60 and -0.80 V (on the 'plateau') so that slight changes in voltage have no effect on the current. The electrode also requires a picoammeter to read current output, which varies from approx 2-1800 pA.

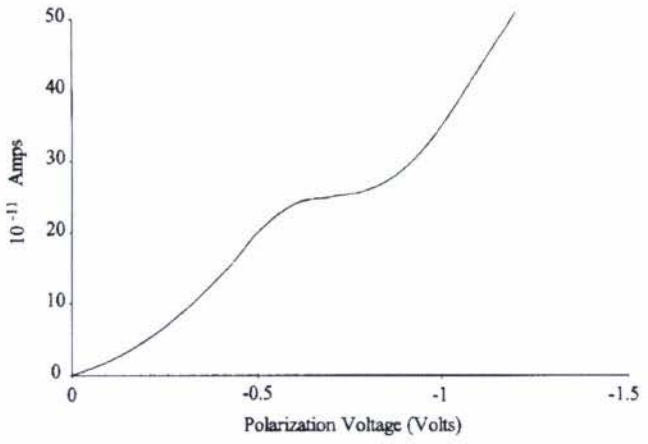

Figure 4.2.4: Characteristic curve of Diamond General 733.

The major advantages of this electrode are the small sample volume required, and the low DO consumption rate. The depth of immersion required for a reading is only 0.1 mm; the electrode consumes just 2.5 x 10^{-7} mL of oxygen per hour (in air at 25 °C).

4.2.5 Method 3: Microelectrodes

Oxygen microelectrodes work on the same principles as the membrane electrodes described above. The major difference is the size of the sensors, which determines the applications for which they are or are not suitable. The construction of a microelectrode such as that described by Revsbech (1989) involves a series of precise and complicated steps. Etched platinum wires are inserted into glass capillaries of Schott 8533 glass; these capillaries are then fused with shafts of soda-lime glass. Epoxy resin must be used to create a seal between the glass capillary and silver wire (Figure 4.2.5). The exposed platinum tip of the cathode is electroplated with gold. The microelectrode shown below has a guard cathode which removes all oxygen diffusing

towards the tip from the internal electrolyte reservoir, resulting in a more stable signal:

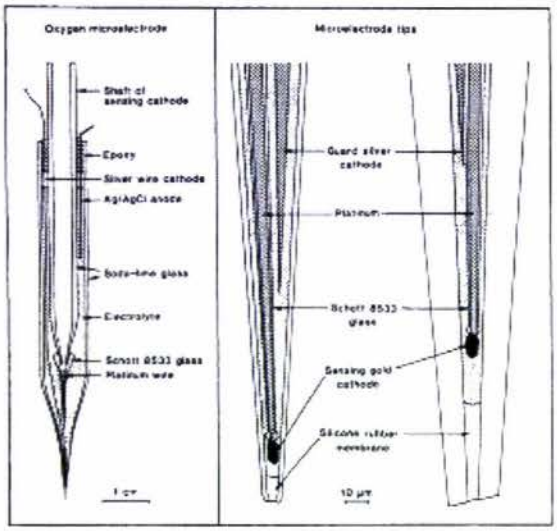

Figure 4.2.5: Oxygen microelectrode construction (Revsbech, 1989).

Revsbech (1989) stated that oxygen microsensors were already used extensively in limnological and oceanographic research. The key application in this area is to measure the oxygen profile in water and sediment, several mm either side of the interface. Several researchers have used microelectrodes to examine the DO profile in biofilms with thicknesses of only 2-3 mm (de Beer *et al*, 1997; Jang *et al*, 2002; Terada *et al*, 2003). The use of a micromanipulator, microscope and oxygen microelectrode allows increments as small as 25 µm. Microsensors for NO_2^-, NO_3^- and pH have also been developed. Data from de Beer *et al* (1997) shown in Figure 4.2.6 illustrates the usefulness of microelectrode measurements in determining concentration profiles:

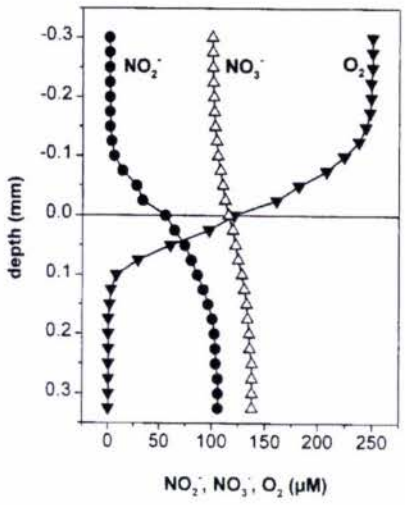

Figure 4.2.6: NO_2^-, NO_3^- and O_2 in aggregate from fluidised bed reactor (de Beer *et al*, 1997).

The construction of microelectrodes appears complicated and would consume a significant amount of time. Also, precise control of the microelectrode is necessary to obtain data such as that shown in Figure 4.2.6. A micromanipulator and microscope are essential, as is a measurement location that will not be affected by vibrations or air movement. This is an important aspect of microelectrodes, as it significantly limits their range of application. In addition, microelectrodes would be too fragile to insert into a block of foam media (Hart, prs com).

4.2.6 Alternative Methods

Method 4: Paramagnetic Detectors

When exposed to a magnetic field, oxygen gas draws magnetic lines of force into itself such that the magnetic field in oxygen is greater than in free space. A paramagnetic detector can be used to measure the concentration of oxygen in a sample, which is proportional to the degree of rotation of a sample chamber.

However, this method requires oxygen in gaseous form. When determination of DO in liquid samples is required, oxygen must first be scrubbed from the water using nitrogen. This oxygen-nitrogen mixture is then passed through the instrument, which determines the amount of oxygen present (Lipták, 1974). This procedure makes the paramagnetic method inconvenient for liquid DO determination.

Method 5: Fluorescence and Optodes

Incident light of an appropriate frequency on a molecule forces electrons into an excited energy state. When these excited electrons return to their ground state, photons or 'packets' of light are emitted. When molecules with the appropriate stereospecific configuration (such as oxygen) are nearby, energy can be absorbed through collisions, reducing the intensity of light emitted. The concentration of oxygen in a sample can be determined in this way, as it is proportional to the reduction in intensity.

This method is known as measurement by fluorescence. It requires a sample chamber containing a fluorescent dye; optical fibres and connectors which conduct light to and from the sample; the optical system; a probe (optode) containing photodiodes; a microprocessor to process instrument data; a display module, and a calibrating system.

Mahutte (1998) reported optode methods as superior to miniature electrodes because: no electrical connections to the sensor are necessary, no electrical drift is observed, and oxygen is not consumed. Similar methods have also been used in medical applications by Liu *et al* (1994) and Kostov *et al* (2000). Results from the method of Liu *et al* (1994) agreed with the Winkler titration method ± 0.25 mg/L.

The range of equipment necessary can make this method prohibitively expensive. Mahutte (1998) identified the following problems with the optode technique: low signal levels, high signal to noise ratio, unstable sensor chemistry (photobleaching of the fluorescent dye), sophisticated optics and electronics required, and technical obstacles to cheap and reliable mass manufacture of the technology.

Method 6: Electrochemical Oxygen Reactor

An electrochemical oxygen reactor is a type of galvanic cell, as described above. The equipment required consists of an air-tight chamber into which gaseous samples are injected by syringe, N_2 carrier gas, current detection equipment and a microprocessor. Over a period of time, the current output is recorded. By integrating this current, the

oxygen concentration of the sample can be determined. Sample volumes can be as low as 70 μL, but the sample volume taken must be accurately known.

This method is easy to use, and the equipment required is relatively inexpensive and easy to construct. However, processing times can be up to several hours per sample, and determination can only be carried out on gaseous samples (Bronlund, prs com).

4.3 Use of Miniature Membrane Electrode

4.3.1 Equipment Setup

Based on a preliminary investigation of DO measurement techniques, a miniature membrane electrode was selected as the most appropriate technique for DO profile determination in a foam block. As described above, a stable voltage source must be connected to the electrode, and a picoammeter is required to read the current output. The equipment setup used is shown in Figure 4.2.1. A stable voltage source was built to supply a potential difference to the electrode; this was checked regularly using a digital multimeter (Fluke 23) and was constant at -0.749 V. An autoranging picoammeter (Keithley 485) was connected in series to the electrode to measure current output. The picoammeter was connected to a chart recorder (Sekonic SS-250F) to determine when a stable current reading was reached. Conversion factors for the chart recorder were calculated so that time and current could be calculated from the chart. All DO measurement equipment was located in a temperature-controlled room, next to the bench-scale biofilter constructed for experimental work.

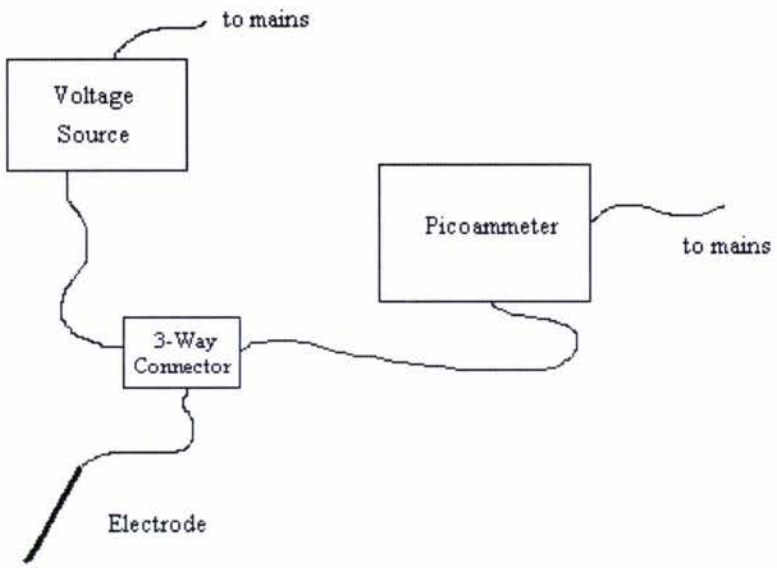

Figure 4.2.1: Schematic of electrode setup.

4.3.2 Electrode Preparation

Electrode membranes are built into the end of an acrylic housing, which was screwed onto the body of the electrode after filling with electrolyte (Figure 4.2.2):

Figure 4.2.2: Diamond General 733 electrode and membrane housing.

When filling with electrolyte, the tip of the filler was placed as close as possible to the internal surface of the membrane. The bulb of the filler was squeezed gently, taking care not to introduce any air bubbles. The membrane housing was filled almost to the top with electrolyte, shaken to remove air bubbles from the electrolyte and screwed onto the electrode. The housing was screwed on as tight as reasonably possible, since any gap between the electrode and the membrane would slow the response time (Redding, prs com). When properly attached, the membrane bulged slightly due to the position of the electrode, as recommended by Diamond General. Care was taken not to invert the electrode at any time during calibration or measurement, as this could

have resulted in air bubbles becoming trapped at the tip of the electrode (Harding, prs com). When not in use, the electrode was stored vertically at room temperature in a retort stand.

After each day of operation, electrolyte was refilled and left to equilibrate overnight, and the membrane was cleaned by immersing in pepsin solution (5 % in 0.1 M HCl) for 5 minutes, then rinsing with deionised water. Electrolyte was also refilled whenever the electrode response was found to be slow or current reading was low (in which case, equilibration took approx 40 min). When refilling the electrolyte did not result in improved electrode performance, the membrane housing was replaced. When refilling the electrolyte and changing the membrane housing had no effect, the face of the electrode was polished using the polishing paper provided.

4.3.3 Electrode Calibration

Two calibration chambers were constructed (Figure 4.11). Air was bubbled through water in one chamber to equilibrate DO at saturation concentration. Nitrogen was bubbled through water in the other chamber, leaving water with zero DO concentration. This enabled a two-point calibration of the electrode to be carried out within 20 minutes as necessary. Before each run of measurements, calibration at saturation DO concentration was performed to check current reading, followed by calibration at zero DO concentration to check response time. This two-point calibration is valid assuming that a linear relationship exists between current and DO concentration (as indicated by the manufacturer and the literature review).

The two calibration chambers each consisted of a 50 mL glass beaker sealed with a rubber stopper (Figure 4.2.3). Two holes were drilled in each stopper to accommodate the electrode and a length of 3 mm tubing. Tubing was connected to either compressed air (from a compressor located outside the laboratory) or N_2 gas (BOC Gases Code 152). A 2.1 x 51 mm needle (Monoject 2006-10) was inserted into each rubber bung to allow for pressure release. Each beaker was filled with approx 15 mL deionised water (Millipore Mill-Q Plus). The electrode could be seated with the membrane was either in the headspace or the liquid, depending on the calibration required. Pinholes were made in the end of each tube to produce a fine dispersion of bubbles. Bubbling rate was high enough for adequate mixing and fast response, but

low enough to avoid water droplets on the membrane when in the headspace, or air bubbles when immersed in water.

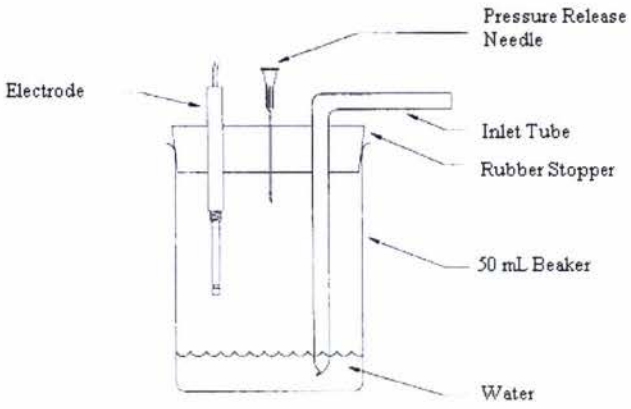

Figure 4.2.3: Calibration chamber.

At constant temperature, current (I) produced by the electrode is directly proportional to the concentration of oxygen in the sample (Co_2). This is shown in Figure 4.2.4 and represented by Equation 4.3.1:

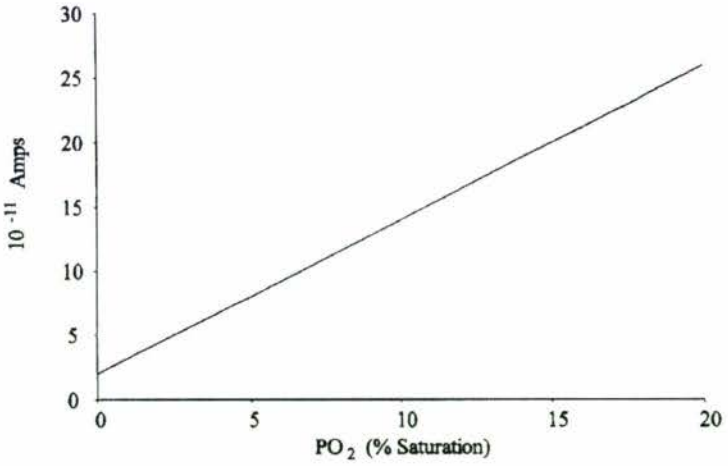

Figure 4.2.4: Standard curve for Diamond General 733.

$$I = k C_{O_2} \tag{4.3.1}$$

Two-point calibrations were performed at various temperatures, and the value of the proportionality constant (k) for each calibration was determined. Water temperature in the air calibration chamber was measured with thermocouple wire attached to a digital

thermometer (Yokogawa Model 2455); temperature varied since the air compressor was located outside the laboratory. It was observed that as temperature increased, a steeper calibration curve was obtained (Figure 4.2.5):

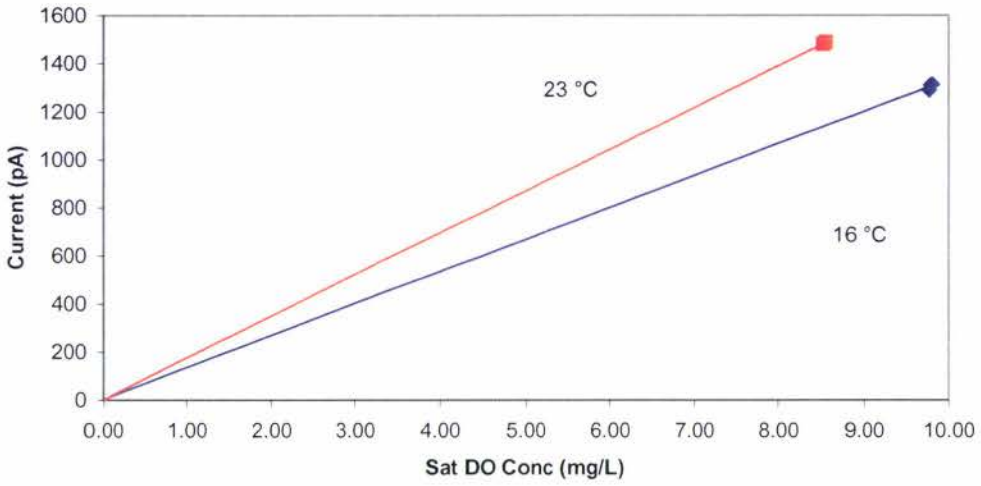

Figure 4.2.5: Effect of temperature on current readings.

Figure 4.2.5 shows that the proportionality constant k changes with temperature. By performing calibrations at a range of temperatures and plotting values of k, a linear temperature dependence was observed (Figure 4.2.6):

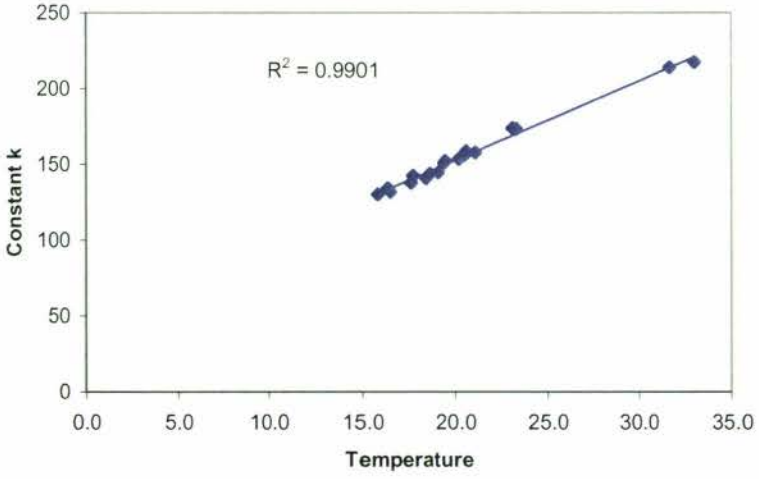

Figure 4.2.6: Proportionality constant at various temperatures.

This enabled prediction of k for a given temperature, which in turn led to an empirical equation for DO concentration based on electrode current and sample temperature (Equation 4.3.2). This equation was used throughout the laboratory study to calculate the measured DO concentration. Validation showed that the equation was accurate to within ± 2.9 % (Section 4.5.2).

$$C_{O_2} = \frac{I}{5.2512\ T + 47.604} \qquad (4.3.2)$$

4.3.4 Factors Affecting C^*

The calibration procedure developed relied on accurate data for the saturation DO concentration (C^*). This meant that sample conductivity (salinity) and atmospheric pressure had to be considered, as both these factors can affect C^*.

Salts (predominantly chlorides) and other dissolved solids lower the solubility of oxygen in water. Calibrations were performed using deionised water, whereas samples were domestic wastewater (either field samples or synthetic feed). Specific conductivity and salinity were measured (using a YSI Model 30 conductivity probe) to determine whether the effect on calibration accuracy would be significant (Table 4.2.1):

Table 4.2.1: Specific conductivity and salinity of test solutions.

Sample	Spec Cond (µS)	Salinity (ppm)
Tap Water	258	100
RO Water	6.7	0
Milli Q Water	1.7	0
Reactor Feed	398	200
Reactor Effluent	1276	700
Field Sample (1.5.4)	1198	700

Lipták (1974) reported a difference in saturation DO concentration of 0.009 mg/L for every 100 mg/L of chloride at 20 °C (0.017 at 0 °C). A salinity of 700 ppm would lower the saturation DO concentration at 20 °C from 9.09 to 9.03 mg/L (less than 1 % error). The effect of conductivity (salinity) was considered negligible.

The effect of atmospheric pressure on gas solubility is shown by Henry's Law, Equation 4.2.1. Data given by YSI indicates that saturation DO concentration changes by 1 % for a change in atmospheric pressure of 7-8 mm Hg. The effect of pressure was considered negligible.

4.4 Method Development

4.4.1 Sampling Method

A needle syringe arrangement was used to extract liquid samples from the foam block. Three arrangements were tested: (1) a gas-tight syringe with needle attached (Hamilton 100 μL), (2) a disposable plastic syringe (Terumo 10 mL luer lock) with an animal biopsy needle (Becton Dickinson 14 gauge x 133 mm luer slip), and (3) a disposable plastic syringe (Terumo 10 mL luer lock) with a custom-made small diameter needle (Hamilton 23 gauge x 80 mm luer lock). Performance criteria were: (a) the amount of liquid sample that could be easily extracted from a foam block, (b) air tightness, and (c) amount of 'deadspace'. Deadspace is the volume of air held between the tip of the needle and the plunger seal at rest. Air in the deadspace of a needle syringe can cause contamination of a sample. When measuring DO, minimal deadspace is essential to reduce oxygen transfer between ambient air and the sample.

Air tightness of the three arrangements was tested with the syringe inverted and immersed in water, with the needle tip in air. The plunger was drawn up to get a sample of air. No water entered the syringe in any case, showing that the arrangements tested were air tight. This meant that samples could be taken by placing the point of the needle at the area of interest, without the concern that water or air was entering through the plunger seal or needle fitting.

It was found that the disposable syringe and custom-made needle arrangement was able to extract the largest volume of water from a foam block sample from the field. In addition, the large diameter animal biopsy needle had too much deadspace, and the gas-tight syringe only had a volume of 250 μL. The 10 mL barrel of the disposable syringe meant that large sample volumes could be collected when necessary.

Deadspace was minimised due to the small diameter needles, and the tight seal formed between the plunger and barrel of the disposable syringe.

Sample Storage

1 mL samples were taken from nodes of interest 10-20 minutes after the reactor was fed. When sampling, the plunger was drawn very slowly, and care was taken not to allow air into the syringe. It was observed that any air entering the syringe would bubble through the liquid sample and increase DO concentration. Samples were stored in 1 mL glass Durham tubes (used for gas collection in microbiological experiments). Sample was filled to the top of the tube (ensuring no headspace), and the tube was covered with Parafilm (American National Can Parafilm M).

Collecting and storing samples from 8-12 nodes took approx 10 minutes. Following sampling, DO concentrations were measured using the technique described in Section 4.4.3.

Bulk Samples

Samples of synthetic wastewater stored in the fridge, and exiting the distributor were also taken for DO measurement. Samples of wastewater exiting the distributor were taken by placing a storage tube under the outlet. Wastewater from the fridge was sampled using a volumetric pipette, taking care not to alter DO by mixing or aerating. Sample was slowly drawn up, then gently expelled onto the side of the Durham tube for storage, and allowed to fill to the top. Sample was covered with Parafilm (American National Can Parafilm M), then stored until temperature equilibrated before measurement (approx 30 mins).

4.4.2 DO Measurement Method

A disposable syringe and custom-made needle (as described above) was used to extract samples from storage when ready for DO measurement. A plunger was constructed with a hole drilled down the centre to allow for seating of the miniature electrode (Figure 4.3.1). This meant that when a sample was drawn into the barrel of the syringe, DO concentration could be measured rapidly without exposure of the sample to the atmosphere. A rubber seal (from a disposable plunger) with a hole drilled was fitted over the end of the plunger. The electrode protruded approx 1.5 mm to allow immersion of the membrane in the sample. When the plunger was depressed, a good seal was still formed (as the tip of the electrode fitted into the syringe nozzle) and deadspace was minimised.

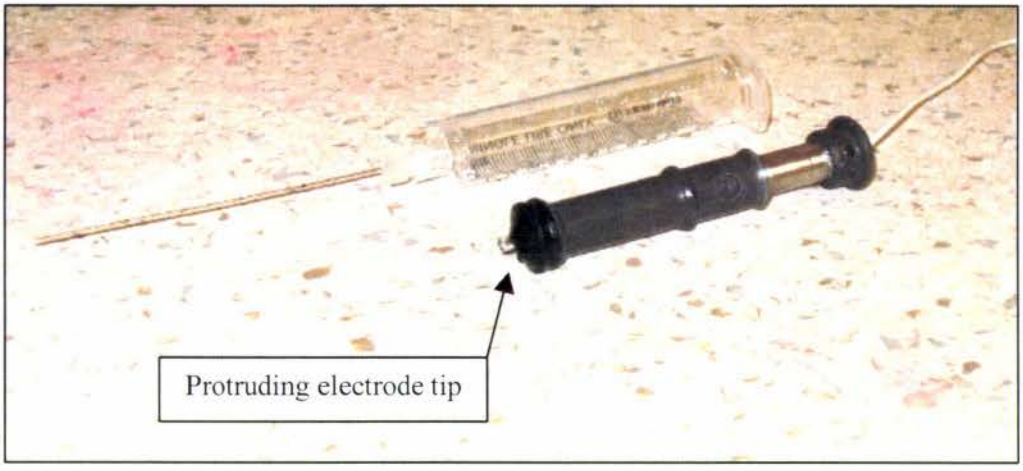

Figure 4.3.1: Plunger/electrode apparatus with needle syringe.

Samples were extracted from storage in the Durham tubes by inserting the needle through the parafilm cover. Sample was drawn up with the needle tip resting on the flat bottom of the tube. Care was taken not to draw up any air, since this would have bubbled through the sample and increased DO concentration. Deadspace in the syringe and needle meant that a very small amount of air contacting the sample was present.

The arrangement of syringe, sample and electrode was suspended vertically in a retort stand while measurement was carried out. After a current reading had been taken (1-2 min), the electrode was removed and thermocouple wires inserted to allow

measurement of sample temperature with a digital thermometer (Yokogawa Model 2455).

4.5 Validation of Method

4.5.1 Accuracy and Repeatability

A comparison of DO measurement with data for saturation concentration showed that the method used was reliable for deionised water samples with DO concentrations at saturation or zero. To test the validity of the method on wastewater samples, measured concentrations were compared with those obtained using a YSI Model 5775 membrane electrode.

The accuracy of the miniature electrode and empirical equation were checked against calibrations at saturated DO concentration (saturation concentrations from YSI data). Saturation DO concentration changed with temperature, allowing a range of concentrations to be tested. Figure 4.4.1 shows the fit of concentrations calculated from the empirical equation vs saturation concentrations given by YSI.

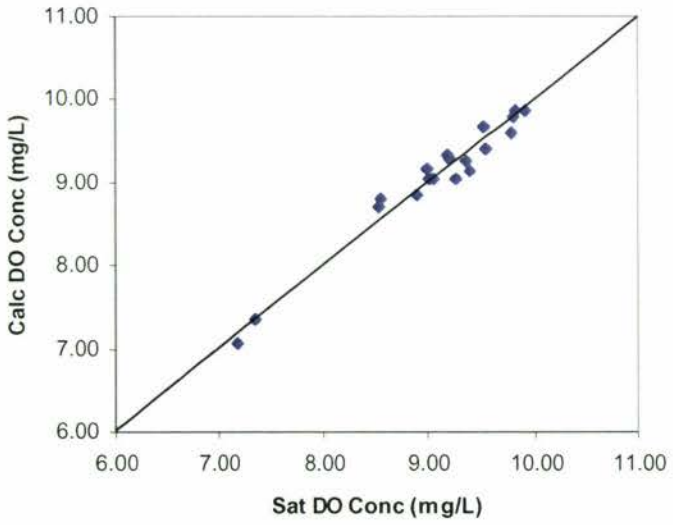

Figure 4.4.1: DO concentration: miniature electrode/empirical equation vs actual.

The close fit of measurements to the $y=x$ line shows that Equation 4.3.2 agrees well with saturation DO data given by YSI for calibrations at saturation DO concentration. The average deviation was 0.11 mg/L (1.3 %); maximum was 0.25 mg/L (2.9 %).

DO measurement using the electrode and empirical equation was also checked in samples of wastewater and tap water, against measurements given by a YSI Model 5775 electrode and Model 57 meter. Samples with a range of DO concentrations were tested, including reactor feed, reactor effluent, tap water and a wastewater sample from the field. A comparison of the measured DO concentrations from each electrode is given in Figure 4.4.2:

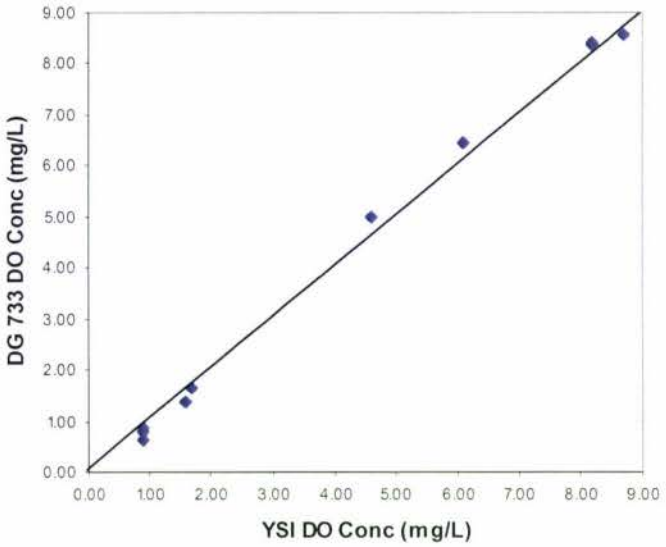

Figure 4.4.2: Comparison of electrodes.

The average difference over the 12 samples was 0.20 mg/L; the maximum difference was 0.39 mg/L. Repeatability of actual DO measurements was of a similar standard; the maximum variability observed throughout the project was ± 0.22 mg/L.

4.5.2 Sampling and Measurement Method

The sampling and measurement method used could have introduced additional sources of error resulting from: (a) oxygen transfer between sample and environment; (b) biological reactions in the sample; (c) temperature fluctuation in the sample; (d) a non-homogeneous sample, or (e) fouling of the membrane.

To assess the effect of sampling method on errors, a comparison was made between the following three methods (results shown in Table 4.4.1):

(1) *in situ* measurement as a control (electrode held in place in a sealed beaker of sample using a retort stand)

(2) sampling with no storage before measurement (extracting the sample and measuring DO using the plunger/electrode apparatus)

(3) sampling and storage before measurement (extracting the sample with a needle syringe, storing for 5 minutes, then extracting and measuring using the plunger/electrode apparatus)

Table 4.4.1: Validation of sampling method. Each value is an average of 2 replicates.

Method	Sample		
	Zero DO	Low DO	Sat DO
(1) Sealed Beaker	0.00	1.63	7.78
(2) Syringe (No Storage)	0.82	2.08	7.62
(3) Syringe (Storage)	1.34	2.30	7.62

For both methods (2) and (3) significant positive interferences were observed with the zero DO and low DO samples (i.e. the method gave a higher concentration than actual). This was expected, as the driving force for oxygen transfer into the sample from the environment would be greatest at zero DO concentration (Winkler, 1981). The larger interference observed for method (3) was likely due to additional oxygen transfer during the storage period. A small negative interference (i.e. slightly lower concentration than actual) was observed with the saturated DO sample, but no further error was introduced by storage of the sample for 5 minutes.

Several medical researchers have expressed concern over the permeability of plastic syringes used for blood gas analysis. Scott *et al* (1971) and Bryant (1977) showed that oxygen transfer into the sample can occur from the plastic of a syringe (due to gases stored in the plastic) and from ambient air (depending on permeability of the plastic). Scott *et al* (1971) reported changes up to 6 % in 2 minutes, and 16 % in 60 minutes

(depending on the plastic type), and suggested that all-glass syringes should be used. However, Bryant (1977) found that of six plastics tested, the worst took 96 minutes to show a 1 % change in concentration.

Since 100 % response was usually achieved within 1-2 minutes, the use of plastic syringes was considered acceptable. Glass syringes (Popper & Sons) were considered, but the type investigated did not form a good seal between barrel and plunger. This resulted in a reasonably large amount of deadspace, and it was believed that this could introduce more error than the use of a plastic syringe.

Mixing of Sample

Having a well-mixed sample is widely recommended (Winkler, 1981; Hitchman, 1978; Fraher & Clarke, 1998) to reduce fouling, and to prevent localised decreases in DO concentration resulting from consumption by the electrode.

During calibrations, solutions were mixed through the action of gas bubbles. However, measurement of sample DO using the plunger/electrode apparatus meant that mixing of the sample could not easily be achieved. However, it was noticed that no significant fouling occurred, since drop-offs in current were not observed. Also, the electrode was cleaned regularly with Pepsin solution, and test solutions had almost zero suspended solids.

Consumption of DO by the electrode should be negligible, since the Diamond General 733 electrode consumes only 2.5×10^{-7} mL of oxygen per hour (in air at 25 °C). Overall, the effects of having umixed samples were considered as minor.

Temperature Stability

Sample temperature affects the current response given by an electrode such as the Diamond General 733, which does not have temperature compensation built in. This means firstly that the sample temperature as well as the current reading must be known, and secondly that the sample temperature is constant while the DO measurement is performed.

A controlled temperature room was used to house the bench scale reactor and to perform all DO measurements. Sample temperatures were constant during DO measurement. The temperature of different samples varied by ± 1.2 °C during any one day of DO measurements. A jacketed or insulated measurement chamber (see below) was considered to ensure constant sample temperature. However, since temperatures in the foam block did vary somewhat throughout the course of the project (21.4 - 26.6 °C), the use of such a chamber may have meant heating or cooling of the sample. This may in turn have had an effect on the sample DO concentration.

4.5.3 Discussion of Method

A miniature membrane electrode was used for measurement of DO concentration. A sampling and measurement method was developed to allow extraction of samples from nodes of interest within a foam block. Samples were stored and subsequently analysed using a plunger/electrode apparatus in a needle syringe. The sample volumes required were only 1 mL, and this method provided quick and reliable determination of DO concentration without a great deal of specialised equipment.

The electrode used was tested against a YSI Model 5775 electrode, and agreed to within an average of ± 0.20 mg/L. The repeatability of measurements was ± 0.22 mg/L. The sampling and measurement method used introduced positive interferences in samples with low DO concentration.

Several further improvements to the method could be made. The picoammeter could be connected to a PC to allow instantaneous readings of DO concentration, if simultaneous logging of temperature was available. Oxygen transfer to the sample could be reduced using a glass respiration cell for measurement instead of the plunger/electrode apparatus. A three-point calibration could have been performed using a gas mixture such as 5 % oxygen in nitrogen, to confirm linearity.

5 Results

5.1 Introduction

Chapter 3 described the field sampling regime and the bench-scale biofilter used to examine foam media biofilter performance. This chapter summarises the key findings of the field sampling programme and laboratory tests. The overall performance of foam media biofilters is assessed with respect to removal of nitrogen, carbon and suspended solids. The effects of hydraulic flow on performance are also reported.

Results from a detailed investigation of the foam media are presented. Using the method developed for sampling and measurement of DO concentrations (Chapter 4), microenvironments within the foam media were examined. This meant that it could be determined whether simultaneous nitrification and denitrification was occurring, and that the effects of DO concentration on biofilter performance could be assessed.

5.2 Wastewater Composition in Septic Tank

5.2.1 Septic Tank Samples

The average composition of wastewater in the septic tank for each configuration is shown in Figure 5.2.1 and Figure 5.2.2. For configuration F1, results shown are from the second septic tank chamber. In all cases, samples were taken from a depth of 0.1-0.2 m.

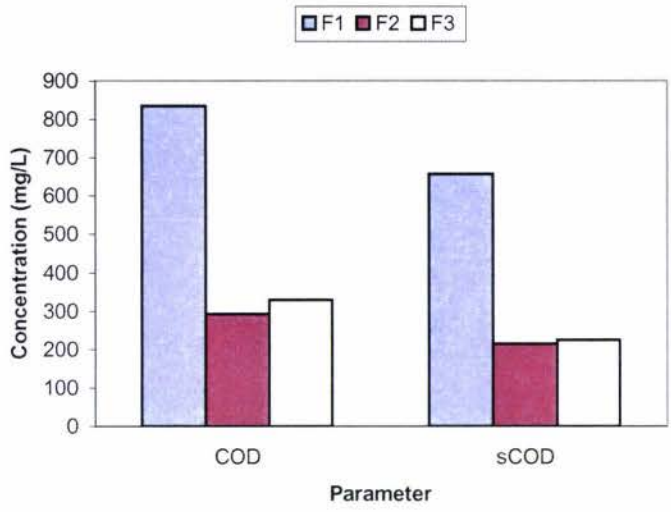

Figure 5.2.1: Average COD and sCOD concentrations in septic tanks.

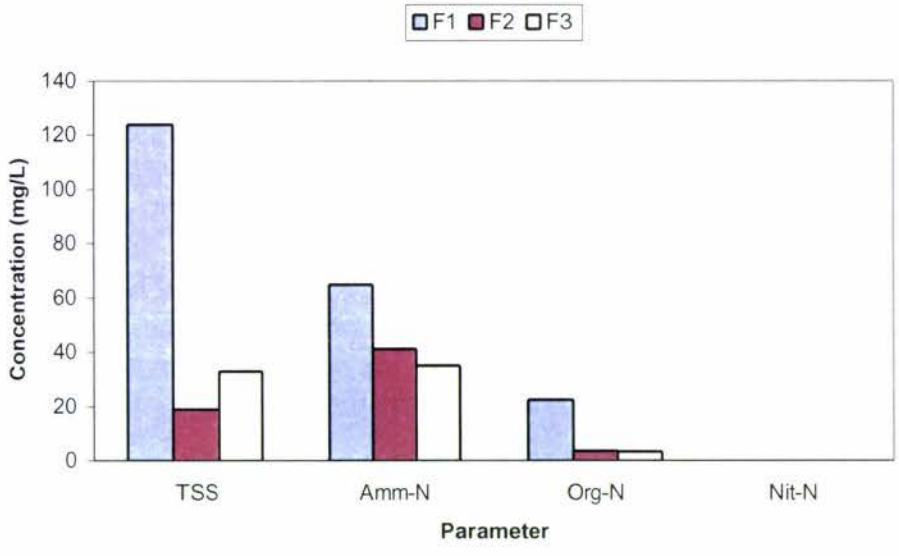

Figure 5.2.2: Average TSS, Amm-N, Org-N and Nit-N concentrations in septic tanks.

Samples taken from the septic tank are not necessarily representative of domestic wastewater. Also, as explained below, sample composition varies significantly with depth, and samples from near the surface of the septic tank may not be representative overall. Concentrations of all parameters were significantly higher in the septic tank of configuration F1 than other configurations.

Variation with Time

Samples were taken from a septic tank (configuration F3) every hour from 9:00 am to 3:00 pm. Concentrations of COD, sCOD, Ac^-, Amm-N and Nit-N were determined to check the variation with sampling time. During the sampling period there were no inputs to the system from the household.

COD showed the most variability of the parameters tested, with concentrations from 145 to 235 mg/L during the sampling period (62 % variation). sCOD varied from 138 to 169 mg/L, Ac^- from 14.5 to 19.6 mg/L, Amm-N from 7.0 to 9.1 mg/L and Nit-N from 0.1 to 0.6 mg/L. There was no general trend over this time period. Variations appeared to be random.

Results from this test showed that there is a degree of variability inherent in taking samples from the septic tanks. However, no general trend was observed over time. This shows that, provided there are no inputs made to the treatment system, the time at which samples are taken should not have an effect on the results.

Variation with Depth

Samples were taken from various depths in a septic tank (configuration F3) to determine how composition changed with depth (Figure 5.2.3 and Figure 5.2.4):

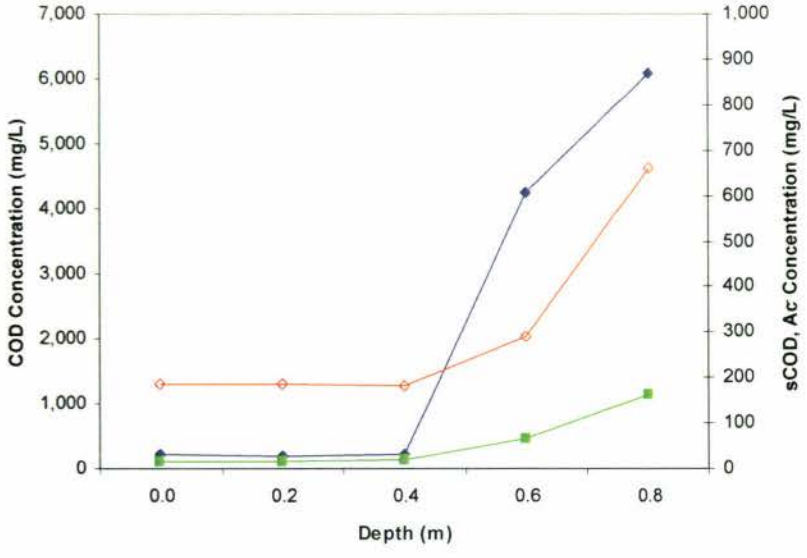

Figure 5.2.3: Variation of COD (♦), sCOD (◊) and Ac^- (■) with depth in septic tank.

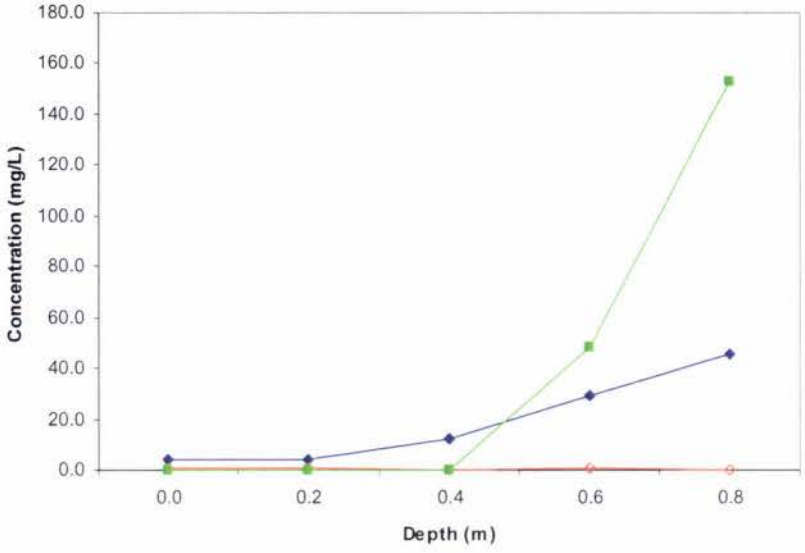

Figure 5.2.4: Variation of Amm-N (♦), Nit-N (◊) and Org-N (■) with depth in septic tank.

Concentrations of all constituents increased with depth in the septic tank (apart from Nit-N concentration, which was below 1 mg/L in all cases). The greatest increases were in concentrations of COD (from 222 to 6,090 mg/L) and Org-N (from 0.0 to 153.1 mg/L). This was expected, as a high proportion of COD and Org-N would be present as solids near the bottom of the septic tank. More surprisingly, the concentration of soluble constituents increased e.g. Amm-N from 4.1 to 45.3 mg/L. TSS concentrations were not determined; it is expected that these would follow the same trend as COD and Org-N.

5.2.2 Septic Tank Effluent

The average composition of septic tank effluent (sampled from the distribution pump chamber) is shown in Figure 5.2.5 and Figure 5.2.6:

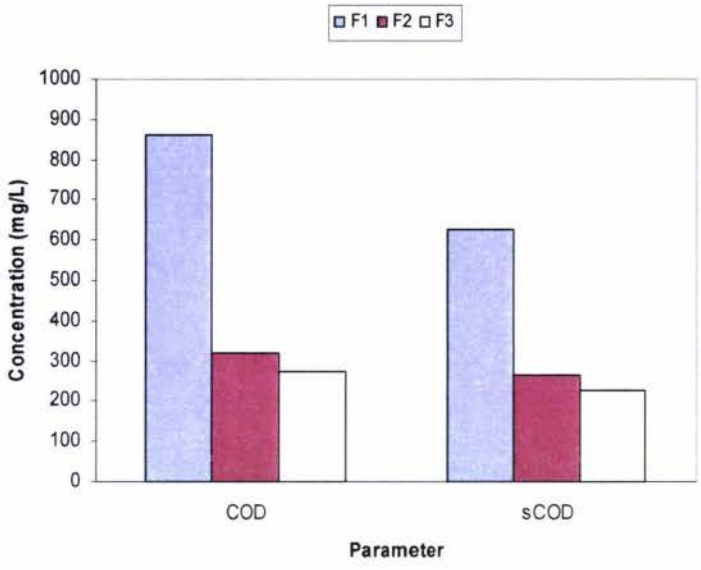

Figure 5.2.5: Average COD and sCOD concentrations in STE.

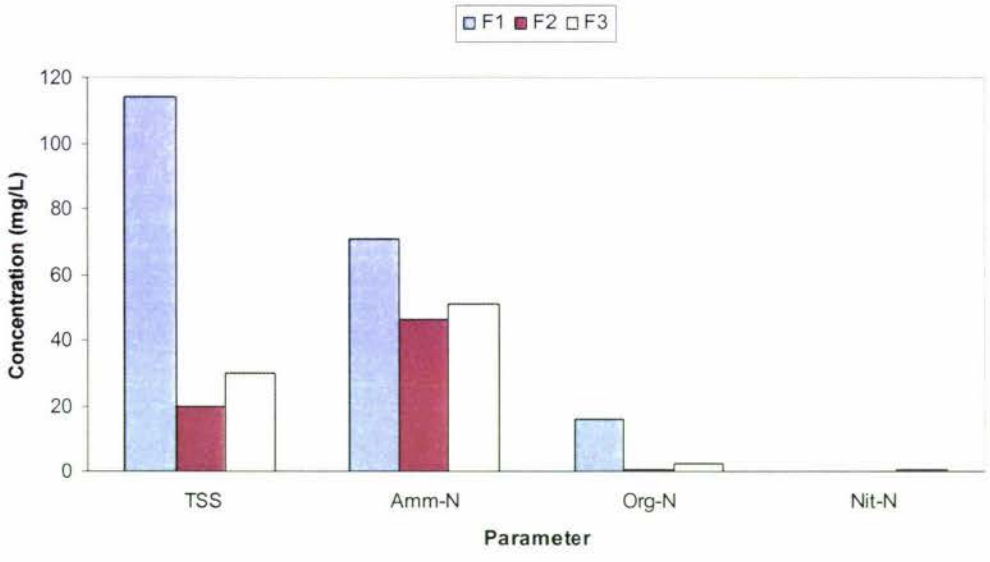

Figure 5.2.6: Average TSS, Amm-N, Org-N and Nit-N concentrations in STE.

Org-N was the only parameter for which concentration in the septic tank effluent (distribution pump chamber) was significantly lower than in the septic tank. In configuration F1, the concentration of Org-N decreased from an average of 22.4 mg/L in the septic tank to 16.1 mg/L in septic tank effluent.

5.3 Biofilter Performance

5.3.1 Carbon and Suspended Solids Removal

Field Samples

Chemical oxygen demand (COD) was used as a measure of the amount of carbon present in field samples. Figure 5.3.1 shows the concentrations of COD before and after the biofilter for each configuration:

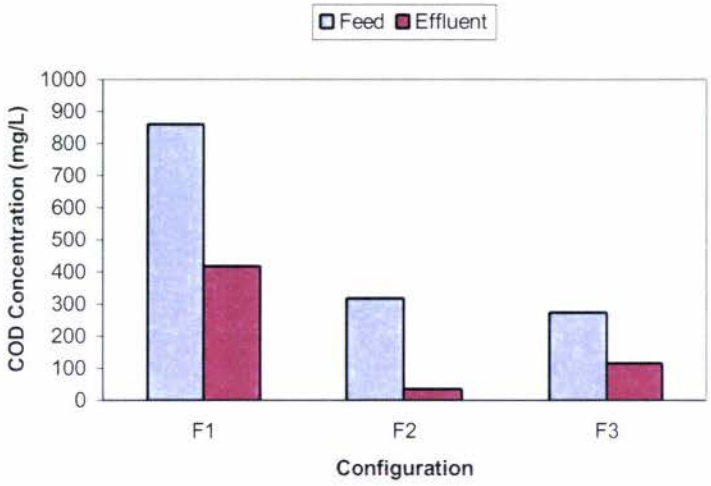

Figure 5.3.1: COD concentrations in feed to and effluent from biofilters in field.

Feed to the biofilter had a higher COD concentration in configuration F1 than in others (861 mg/L compared to 319 for F2 and 275 for F3). Configuration F2 showed the best COD removal in the biofilter (89 % to give 36 mg/L effluent concentration).

Figure 5.3.2 below shows the concentrations of TSS in the feed to and effluent from the biofilter:

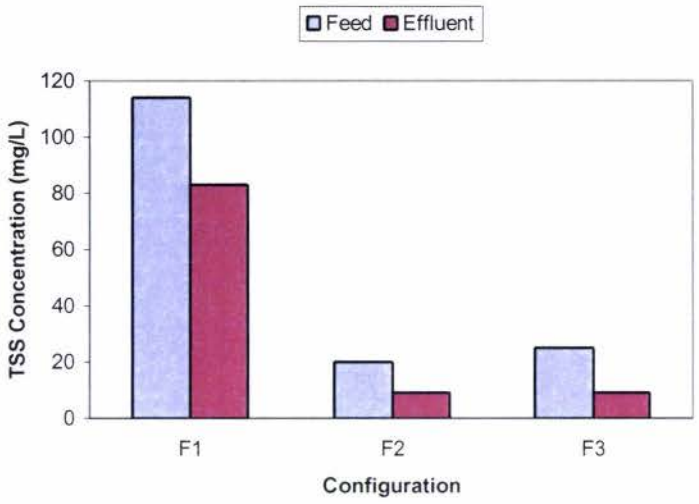

Figure 5.3.2: TSS concentrations in feed to and effluent from biofilters in field.

TSS removal followed the same trends as COD removal. Feed to the biofilter had a significantly higher TSS concentration in configuration F1 than in others (114 mg/L compared to 20 mg/L for F2 and 25 mg/L for F3). The biofilter removed only 27 % TSS in configuration F1, but 55 % in F2 and 64 % in F3 (effluent concentration of 9 mg/L from F2 and F3).

Bench-Scale Biofilter

Sodium acetate (NaAc) was the sole carbon substrate fed to the bench-scale biofilter. Removal of acetate (Ac^-) was determined as the difference between feed and effluent concentrations, which are shown in Figure 5.3.3:

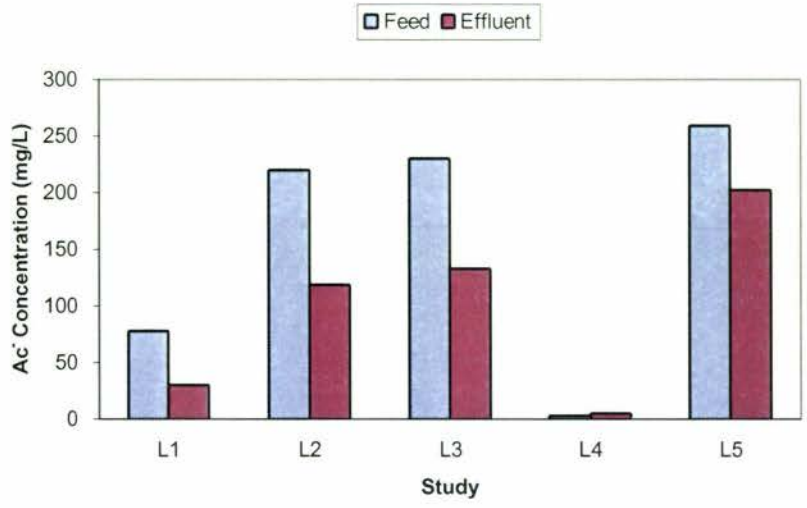

Figure 5.3.3: Ac^- concentrations in feed and effluent for bench-scale biofilter.

Ac^- removal in the bench-scale biofilter varied from 35 to 101 mg/L (an average of 46 % removal).

5.3.2 Nitrogen Removal

TN can be considered as the sum of Amm-N and Nit-N for the bench-scale biofilter, and as the sum of Amm-N, Nit-N and Org-N for the field systems. TN removal was considered as the difference between feed and effluent concentrations.

Average concentrations of TN in the feed and effluent for each study are shown in Figure 5.3.4. For laboratory studies (L1 to L5) effluent concentrations given are steady-state values; concentrations differed when not at steady-state (Chapter 6). For field studies (F1 to F3) samples from the distribution pump chamber are referred to as the biofilter feed. Studies L1 to L5 below represent treatment from a single foam block in the bench-scale biofilter; F1 to F3 are actual treatment systems in the field. Accordingly, there are differences between biofilter depths and hydraulic loading rates, which are discussed in Chapter 6.

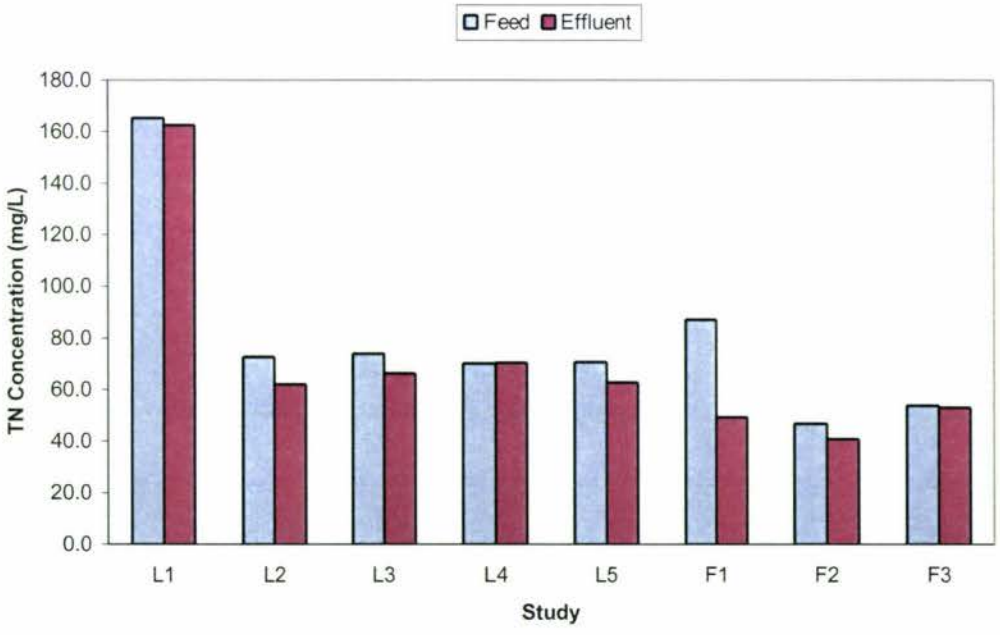

Figure 5.3.4: Average TN concentration in biofilter feed and effluent.

Figure 5.3.4 shows that while results from the bench-scale biofilter varied widely depending on feed composition, TN removal up to 10.7 mg/L was achieved in a single foam block (Study L2).

In the field, configuration F1 removed an average of 38.0 mg/L TN; F2 removed an average of 6.2 mg/L, and F3 removed an average of 0.8 mg/L. Effluent TN concentrations in the field varied from 30.9 to 67.5 mg/L. The fractions of Amm-N, Nit-N and Org-N in the effluent are shown in Figure 5.3.5:

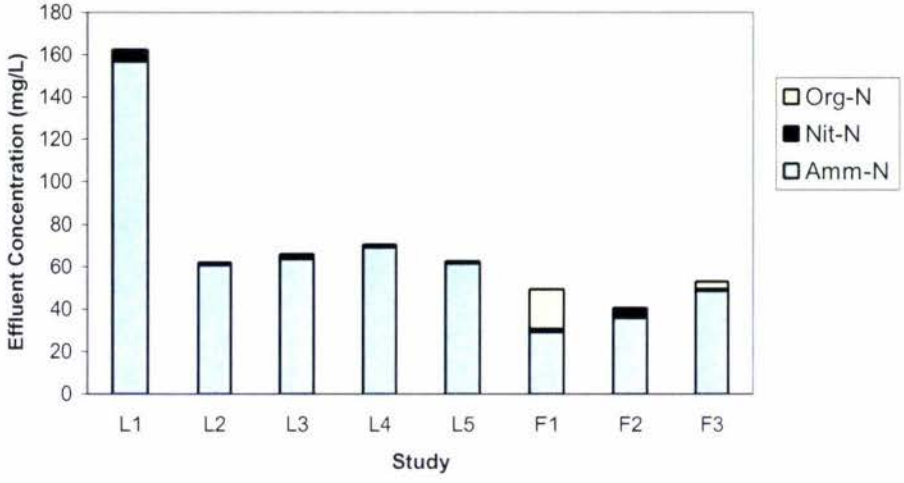

Figure 5.3.5: Concentrations of Amm-N, Nit-N and Org-N in effluent.

The proportion of Nit-N in the effluent from the bench-scale biofilter was low (maximum 4 %). In the field, the highest concentrations of Nit-N were observed in effluent from configuration F2 (average of 4.6 mg/L or 11 %).

Effluent from configuration F1 contained a high proportion of Org-N (an average of 18.4 mg/L or 37 %). Average effluent concentrations were low in the other configurations: 0.1 mg/L in F2 and 3.4 mg/L in F3.

Variation with Time

Effluent samples were taken from the bench-scale biofilter at various times to determine whether performance varied. Effluent concentrations of Amm-N and Nit-N

varied between samples taken in the morning and in the afternoon (Figure 5.3.6 and Figure 5.3.7):

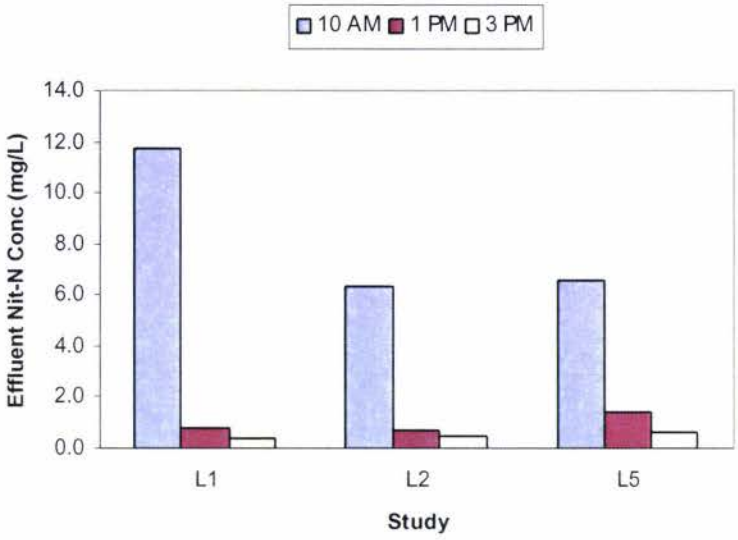

Figure 5.3.6: Effluent Nit-N concentration at 10 AM, 1 PM and 3 PM.

Figure 5.3.6 shows that effluent concentrations of Nit-N were higher in the morning than in the afternoon, with a maximum difference of 10.9 mg/L. Concentrations of Amm-N were lower in the morning than in the afternoon (Figure 5.3.7).

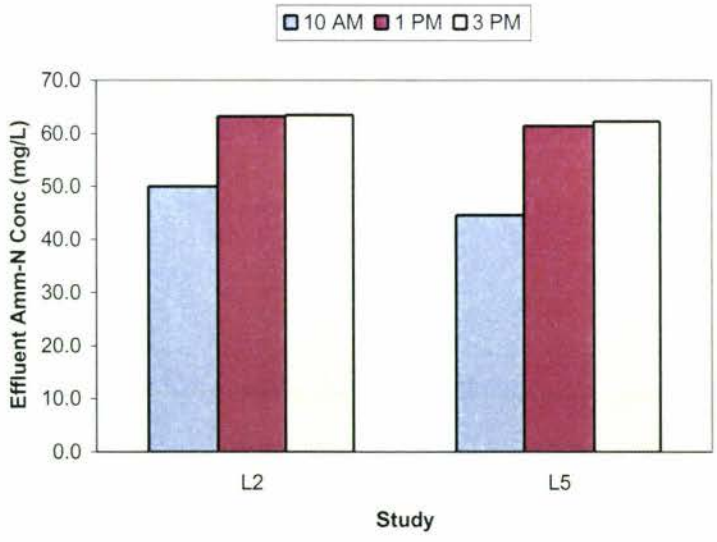

Figure 5.3.7: Effluent Amm-N concentration at 10 AM, 1 PM and 3 PM.

5.4 Hydraulic Flow

Variations in nitrogen removal with time suggested that the dosing regime used impacted on biofilter performance. Data given above showed that the extent of nitrification was greatest during the overnight rest period.

As well as studying the variation in performance with time, hydraulic residence time and distribution were investigated. Several studies were conducted to investigate hydraulic flow within the bench-scale biofilter and its effect on nitrogen removal.

5.4.1 Hydraulic Residence Time (HRT)

It was observed that a large proportion of wastewater applied to the bench-scale biofilter flowed through quickly, with very little time for treatment. Using a timer and measuring cylinder, the amount of wastewater applied and the amount of effluent collected over 30 minutes was measured. The volume of feed dosed and the volume of effluent collected are plotted against time in Figure 5.4.1:

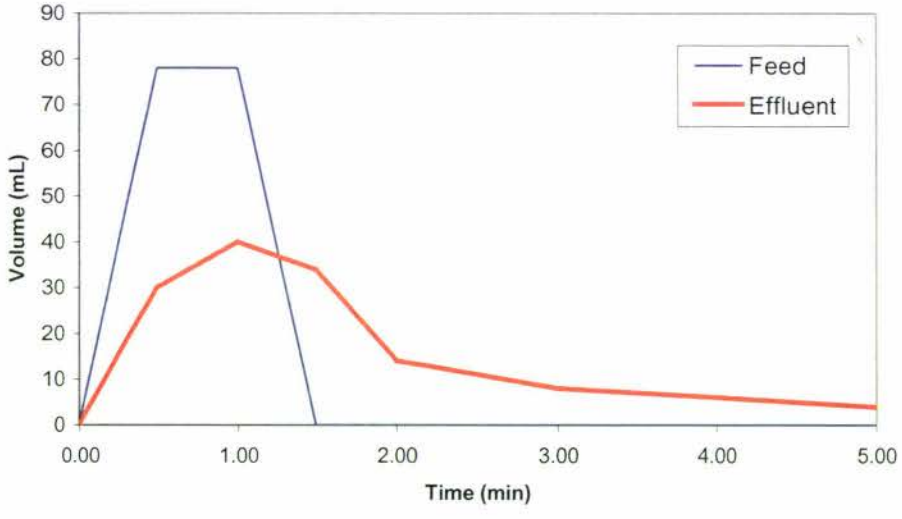

Figure 5.4.1: Hydraulic study.

The cumulative amount of feed dosed or effluent collected is given by the area under each line. The total amount of feed dosed was 156 mL. After 2 minutes, 118 mL effluent had been collected (76 % of the volume of feed dosed); after 5 minutes, 136 mL (87 %) was collected, and after 30 minutes 148 mL (95 %).

5.4.2 Flow Variation

Concentrations of Cl^- at nodes in the foam were analysed to investigate the hydraulic flow within the foam block. Since no overall Cl^- removal occurred in the biofilter, this ion was a suitable 'tracer'. A step change in feed concentration of Cl^- from 200 mg/L to 430 mg/L was introduced. Samples were taken from 8 nodes (2 different heights and 4 different horizontal positions) at 11:00, 1:00 and 3:00, and Cl^- concentrations determined to assess the effect of this step change (Figure 5.4.2):

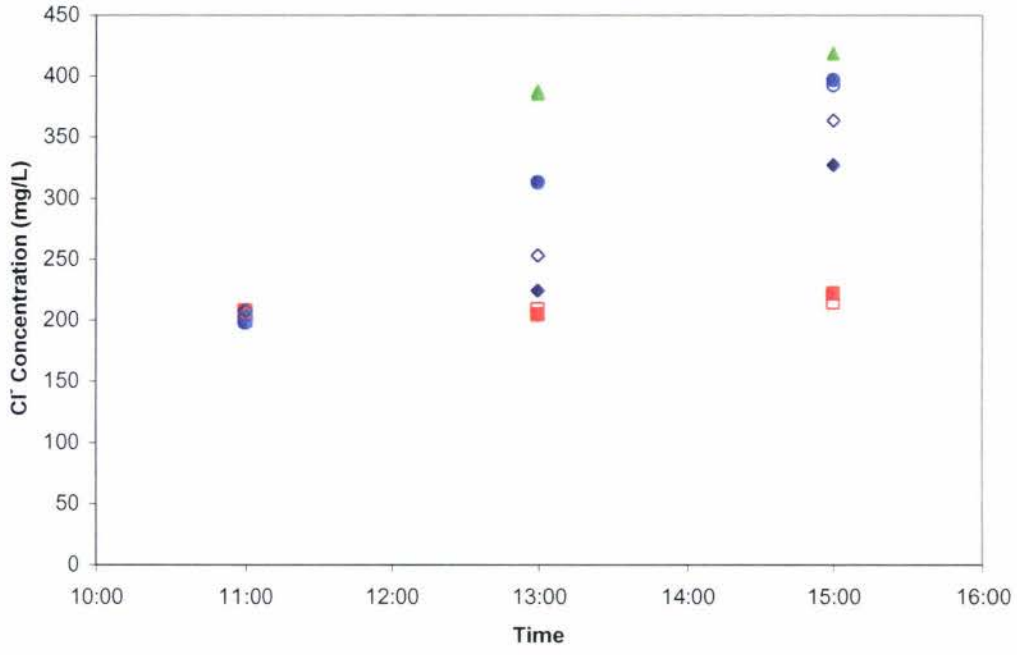

Figure 5.4.2: Cl^- concentrations in columns 1 (■), 2 (♦), 3 (▲) and 4 (●). Nodes at 0 mm height (bottom surface) shown by closed shapes. Nodes at 15 mm height shown by open shapes.

It can be seen that at each horizontal position (columns 1 to 4), concentrations did not vary greatly between the two heights. The maximum difference between heights was in column 2 (37 mg/L or 11 %). This shows that in general, flow was evenly distributed in the vertical direction. The extent of cross-flow can be considered as negligible compared to flow in the downward direction. This was expected since the foam media block was laid flat horizontally.

However, after the step change was introduced, the time taken for Cl^- concentration in each column to increase varied. Column 3 showed the fastest response; column 1 showed the slowest response; response times in columns 2 and 4 were somewhere in between. This shows that the flowrate of feed through each column varied, making it possible to qualitatively assess the flowrate and hydraulic retention time in each column (Table 5.4.1):

Table 5.4.1: Variations in flowrate and hydraulic retention time (HRT).

Column	Flowrate	HRT
1	Low	Long
2	Med	Med
3	High	Short
4	Med	Med

The most likely reason for these variations is the distributor design. It appears that the most wastewater was distributed to column 3, and the least to column 1. Comparing data from each of the four columns within the foam block enabled the effect of HRT on various parameters to be determined.

5.5 Microenvironments in Foam Media

To investigate the mechanisms responsible for nitrogen removal, detailed studies of the bench-scale biofilter were conducted. Simultaneous nitrification and denitrification (SND) in the bench-scale biofilter requires the existence of aerobic and anoxic microenvironments. Samples were taken from nodes within the foam block to determine the extent of nitrification and denitrification, and to confirm the existence of these microenvironments.

5.5.1 Nitrogen Concentration

NO_2^- and NO_3^- are both intermediates in biological nitrogen removal. Concentrations measured are referred to as 'accumulation', and represent nitrogen that was nitrified, without subsequent denitrification. Figure 5.5.1 and Figure 5.5.2 show typical Amm-N and Nit-N profiles from each study.

A wide variation in Nit-N accumulation occurred in the foam block. Nit-N accumulation was consistently higher in column 1 than in other columns. There was also some variation in the vertical direction, although neither height showed consistently higher Nit-N accumulation.

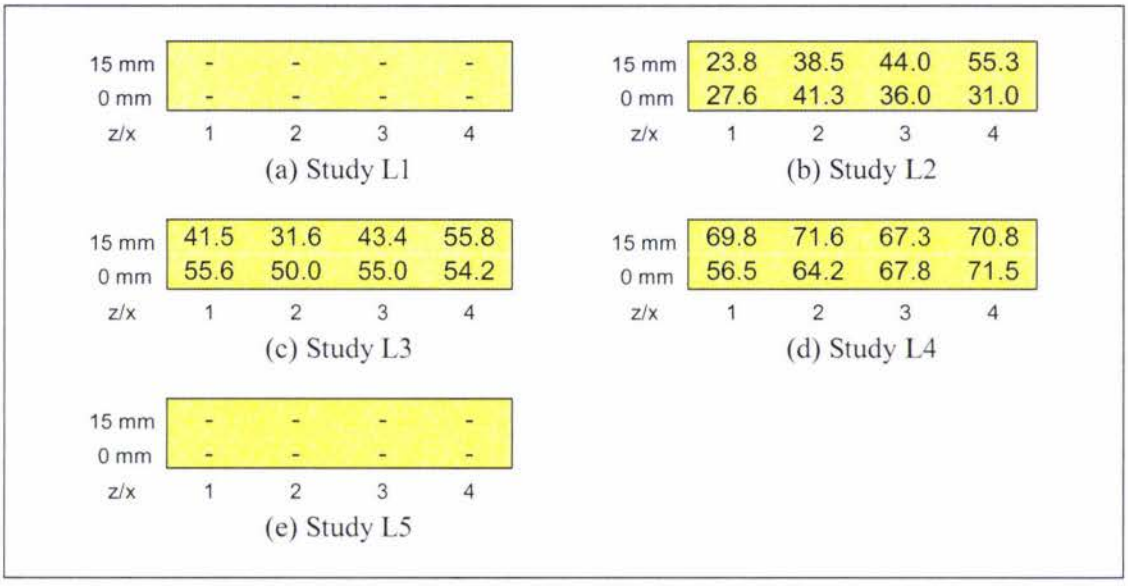

Figure 5.5.1: Frontal views of Amm-N concentration in nodes (mg/L).

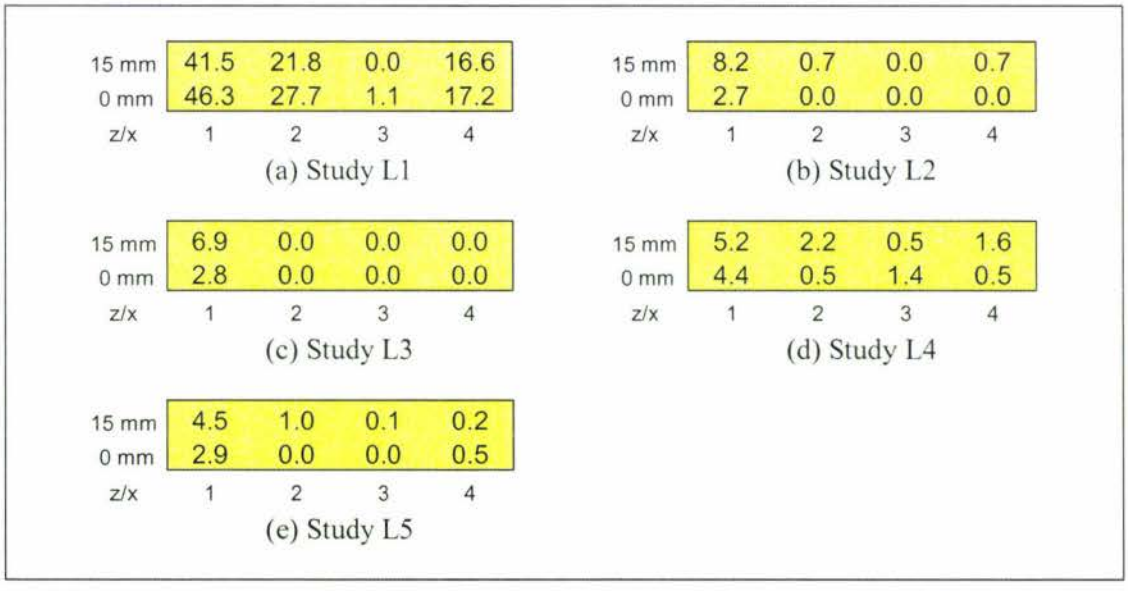

Figure 5.5.2: Frontal views of Nit-N accumulation in nodes (mg/L).

5.5.2 Ac^- Concentration

Typical Ac^- profiles from each study are shown in Figure 5.5.3:

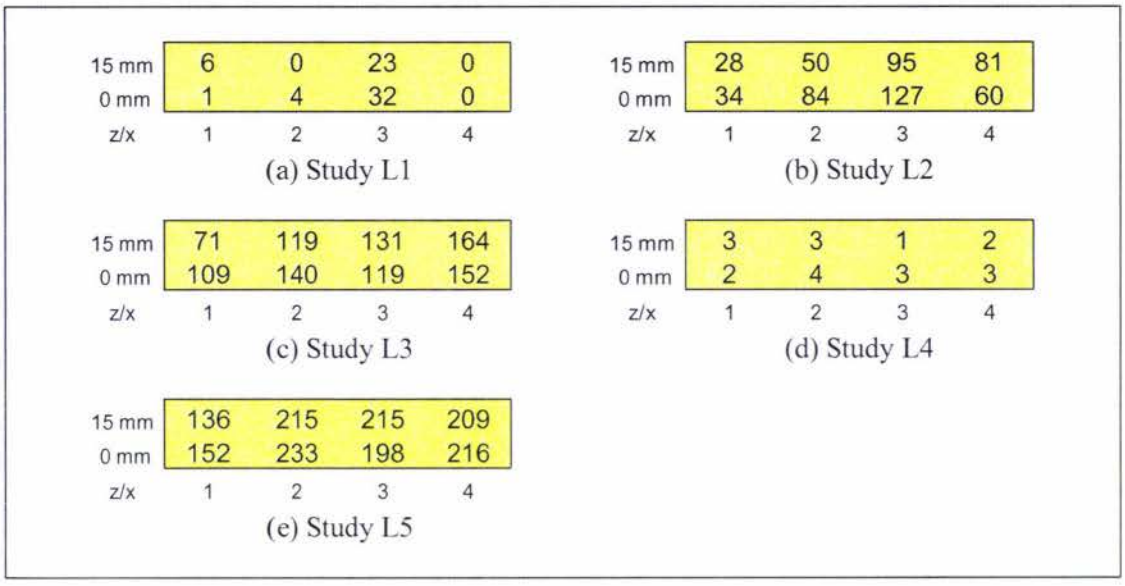

Figure 5.5.3: Frontal views of Ac^- concentration at nodes (mg/L).

As with Nit-N concentrations, Ac^- concentrations varied significantly in the horizontal direction, but variations in the vertical direction were not as large. Ac^- concentrations showed less variability than Nit-N concentrations.

5.6 DO Concentration

5.6.1 Feed Concentration

DO concentrations were measured before and after the distributor for each configuration in the field, and in the bench-scale biofilter (Figure 5.6.1):

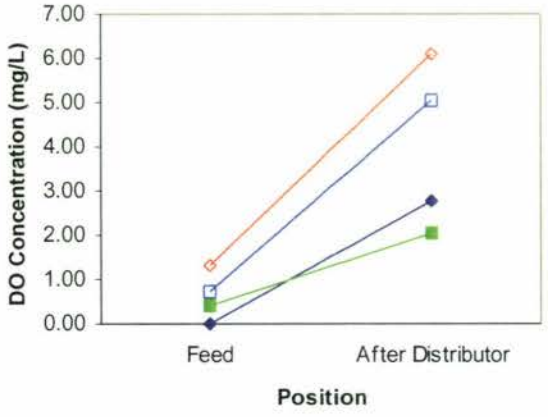

Figure 5.6.1: Effect of distributor on DO concentration. L2 (♦), F1 (◊), F2 (■) and F3 (□).

In all cases, the DO concentration increased after the distributor. This is not surprising given the low feed concentrations. The driving force for oxygen transfer into the liquid is highest at low DO concentrations.

It can be seen from Figure 5.6.1 that the DO increase achieved depends on the distributor design. The lowest increase in DO was observed in configuration F2 (1.65 mg/L). The distributor of the bench-scale biofilter achieved an increase of 2.79 mg/L. The distributors used in configurations F3 and F1 achieved DO increases of 4.30 and 4.80 mg/L respectively.

5.6.2 Concentration in Microenvironments

Figure 5.6.2 shows a typical DO profile for each study:

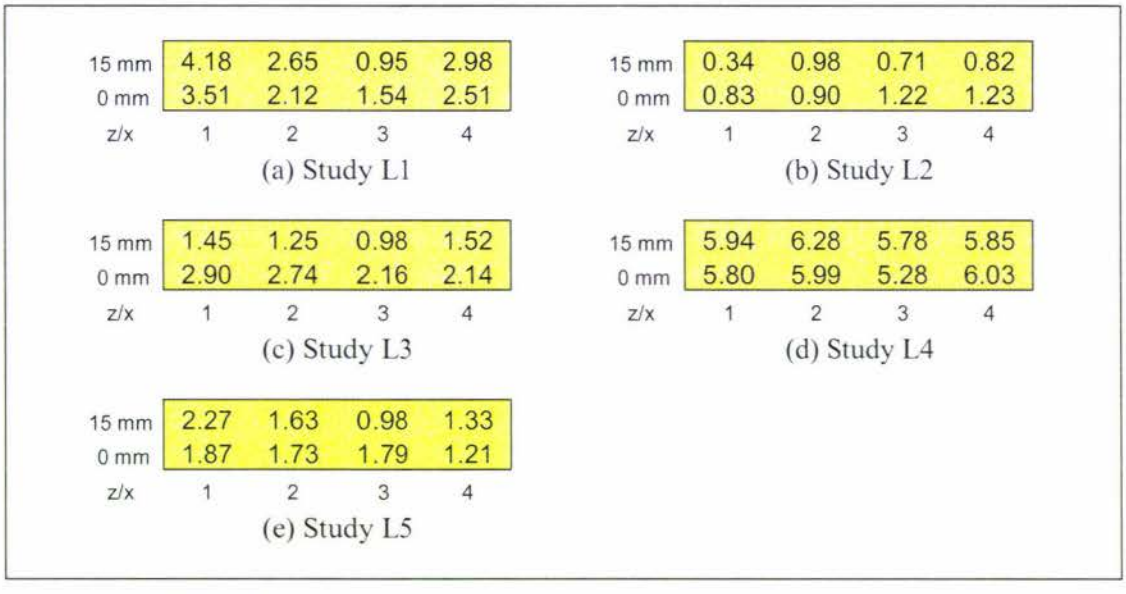

Figure 5.6.2: Frontal views of DO concentration in nodes (mg/L).

The average DO concentration at microenvironments within the foam varied between studies (from 0.88 to 5.87 mg/L).

In study L2, DO concentration at each node was within 0.54 mg/L of the average across the nodes. In study L4, variation was within 0.59 mg/L of the average.

In studies L1, L3 and L5, wider variations were observed, with differences of up to ± 1.62 mg/L of the average concentration across the nodes. In each of these three cases, column 1 (long HRT) had the highest DO concentration, and column 3 (short HRT) had the lowest DO concentration.

6 Discussion

6.1 Introduction

In this chapter, the results presented in Chapter 5 are discussed. The nitrogen removal mechanisms occurring in foam media biofilters are examined. The effects of factors such as DO concentration, hydraulic flow and biofilter configuration on performance are assessed. Nitrification and denitrification are discussed at length, and limiting factors identified for each process. Comparisons are made between the findings of this study and information from various literature sources. Chapter 7 then summarises the conclusions made from the project.

6.2 Field Configurations

6.2.1 Septic Tank Performance

Samples taken from the distribution pump chamber after the septic tank have been considered as septic tank effluent (STE). Due to recirculation, these samples would have been partially diluted with treated biofilter effluent (although dilution would not have been great since the recirculation ratio was only 1.67:1). Table 6.2.1 shows a comparison of STE from each configuration with average values from literature sources (Chapter 2):

Table 6.2.1: Comparison of septic tank effluent with averages from literature.

Parameter	Concentration (mg/L)			
	Lit	F1	F2	F3
TN	59.0	87.2	46.8	53.8
TSS	73	114	20	30
BOD_5	239	-	-	-
COD	-	861	319	275

STE from configuration F1 had higher concentrations of TN and TSS than average values reported in the literature. STE from configurations F2 and F3 had lower concentrations of TN and TSS than average literature values.

COD concentrations were not available directly from the literature, but using a BOD_5:COD ratio of 0.44:1 (Tchobanoglous *et al*, 2003) gives an average of 543 mg/L. Again, concentration is higher in STE from configuration F1 than from F2 or F3.

Higher quality STE was therefore achieved by using a larger septic tank, with longer HRT, despite the fact that 100 μm filters were not installed in configurations F2 or F3. The importance of septic tank HRT for solids removal is emphasised by Burks & Minnis (1994).

6.2.2 Biofilter Performance

As well as providing an environment for biological nitrogen removal, the foam media biofilters also further reduce concentrations of TSS and COD in wastewater. Overall removal of TSS, COD and TN by biofilters in the field is shown in Table 6.2.2:

Table 6.2.2: Overall performance of biofilters in field.

Configuration	TSS Removal		COD Removal		TN Removal	
	(mg/L)	(%)	(mg/L)	(%)	(mg/L)	(%)
F1	31	27%	443	51%	38.0	44%
F2	11	55%	283	89%	6.2	13%
F3	16	64%	159	58%	0.8	1%

Table 6.2.2 shows that the overall performance of biofilters in the field varied with configuration. The effect of key parameters on performance are discussed below.

Effect of Biofilter Layout

Effluent concentrations of TSS and COD were lower from configurations F2 and F3 than configuration F1. These improvements could be due to:

- changes to biofilter layout to reduce short-circuiting
- changes in distributor design to reduce short-circuiting

- reduction in influent concentrations through better septic tank performance

Nitrogen removal decreased from configuration F1 to F2 to F3. No visible correlation exists between biofilter dimensions or the amount of foam media available and nitrogen removal. However, there is some indication that nitrogen removal increased with increasing hydraulic retention time (HRT). Table 6.2.3 shows that configuration F3 had a higher areal dosing rate than configuration F1, but a shorter biofilter.

Table 6.2.3: Dimensions and dosing for each biofilter.

Configuration	Biofilter		Dosing	
	Height (m)	Area (m^2)	L/dose	L/m^2/dose
F1	1.50	0.76	16.0	21.1
F2	0.75	1.17	16.0	13.7
F3	1.10	0.33	10.0	30.3

While studies of HRT in field systems were not conducted, the above table gives some indication that HRT would have been higher in configuration F1 than F3 (although this does not take account of short-circuiting). If the areal dose is divided by the biofilter height, and the result is plotted against Amm-N removal, a relationship is observed (Figure 6.2.1):

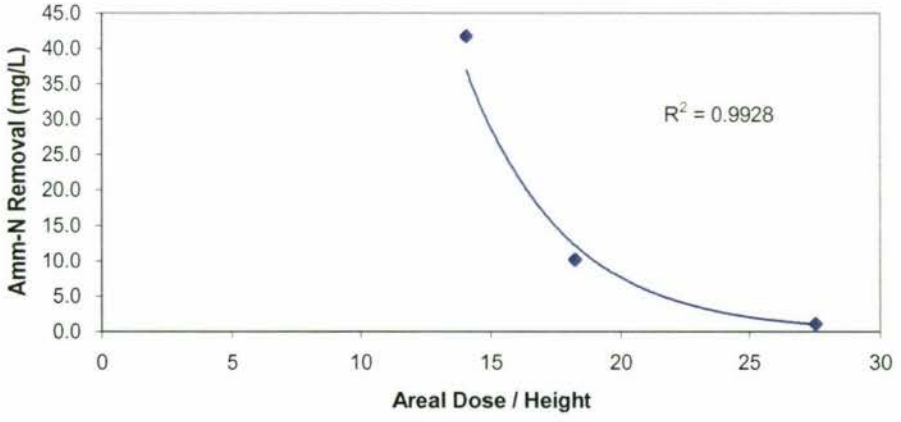

Figure 6.2.1: Effect of biofilter dimensions and dosing on Amm-N removal.

This suggests that dimensions and dosing rates may have impacted on nitrogen removal in biofilters in the field. The poor nitrogen removal performance of

configuration F3 may be attributable to its high areal loading rate and short biofilter depth. Further investigation of the HRT (for example using tracer studies) is necessary to determine the causes of poor nitrogen removal in configurations F2 and F3.

Effect of Foam Media Size

Three different sizes of foam media were used in the three different configurations. It was found that smaller blocks held a proportionately higher amount of water and biomass. Medium size blocks held 11 times their own weight of water, and biomass accounted for 16 % of the dry weight of field samples. Small blocks held 19 times their own weight of water, and biomass accounted for 31 % of the dry weight of field samples.

Analysis of several samples of small foam media from F3 systems showed that the amount of biomass growth on a particular block was directly proportional to the amount of water held by that block (Figure 6.2.2):

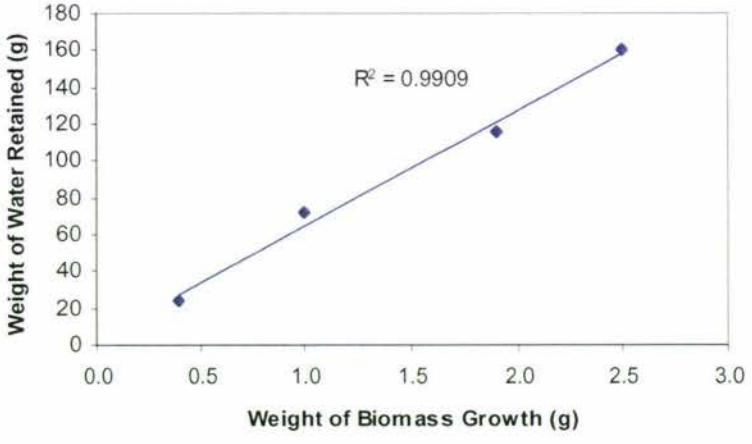

Figure 6.2.2: Weight of biomass growth and water held on small foam blocks.

Since the greatest proportion of biomass growth occurs on small foam blocks, it would be expected that removal of COD, Amm-N and Nit-N would be higher for small block sizes. However, this was not the case. The greatest amount of COD removal occurred in configuration F2, which had the largest size of foam media. The

least amount of Amm-N removal occurred in configuration F3, which had the smallest size of foam media.

Overall, the presence of a high proportion of biomass on the foam media, resulting from a smaller size of foam block, did not correlate strongly with improved performance.

Effect of DO Concentration

Nitrification depends on the availability of dissolved oxygen (DO). Table 6.2.4 shows the average biofilter feed DO concentration and Amm-N removal for each configuration.

Table 6.2.4: Effect of DO concentration in feed to biofilters on Amm-N removal.

Configuration	Feed DO Conc (mg/L)	Amm-N Removal (mg/L)
F1	6.10	41.7
F2	2.05	10.2
F3	5.05	1.1

Configuration F1 had the highest feed DO concentration and the greatest Amm-N removal; configuration F2 had the lowest feed DO concentration and less Amm-N removal. However, configuration F3 had the lowest Amm-N removal despite having a high feed DO concentration.

DO concentration is therefore not the only factor limiting nitrogen removal in foam media biofilters in the field.

Nitrogen Removal by Assimilation

Section 6.3.1 discusses the significance of assimilation as a nitrogen removal mechanism in foam media biofilters. To determine whether removal assimilation may have been significant in biofilters in the field, the concentration of sCOD in the feed was plotted against Amm-N removal (Figure 6.2.3). Each point represents a single system. There are two points for each of configurations F1, F2 and F3. There appears to be a strong correlation between sCOD concentration in feed to the biofilter and Amm-N removal in the biofilter.

While this does not prove that assimilation was the dominant mechanism of nitrogen removal, it does suggest that further research into its significance is necessary.

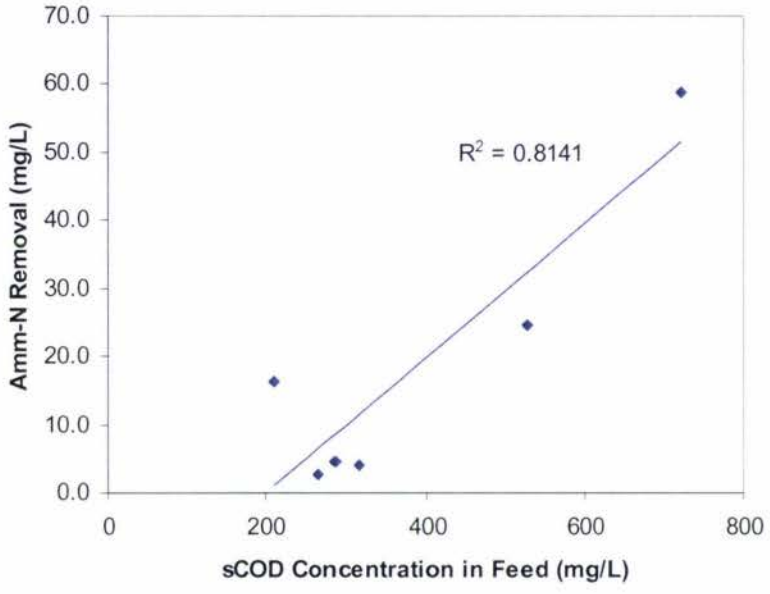

Figure 6.2.3: Correlation of sCOD concentration in feed with Amm-N removal for biofilters.

6.2.3 Effluent Quality

The overall effluent concentrations of key parameters from systems in the field are given in Table 6.2.5:

Table 6.2.5: Composition of effluent from field configurations.

Configuration	Effluent Concentration (mg/L)					
	TSS	COD	TN	Org-N	Amm-N	Nit-N
F1	83	418	49.2	18.4	29.3	1.5
F2	9	36	40.6	0.1	35.9	4.6
F3	9	116	53.0	3.4	48.6	1.0

Increasing the septic tank volume was effective at improving removal of TSS, COD and Org-N. The foam media biofilter contributed to overall removal of TSS and COD. The foam media biofilter achieved 44 % TN removal in configuration F1, but only 13 % in F2 and 1 % in F3. Effluent concentration of Nit-N from configuration F1 was low, indicating that denitrification as well as nitrification occurred in the foam media biofilter.

Table 6.2.6 shows a comparison between TN removal observed in the field, and values reported in literature:

Table 6.2.6: TN removal observed in field and from literature.

Configuration or Literature Source	TN Removal (%)	Effluent TN (mg/L)
F1	44%	49.2
F2	13%	40.6
F3	1%	53.0
Loomis *et al* (2001a)	10-23%	28.0-61.0
Waterloo Biofilter Inc	50-60%	20.0

Overall, both field sampling and literature review indicate that around 50 % TN removal can be achieved, but that removal varies. Effluent TN concentrations in the field were greater than the 20.0 mg/L reported by Waterloo Biofilter Inc.

Further investigation in the following areas is necessary in order to optimise biofilter performance in the field:

- measurement of HRT in biofilters in the field
- the effect of HRT on nitrogen removal
- relationship between biofilter dimensions and HRT
- significance of nitrogen removal by assimilation

6.3 Nitrogen Removal

This section discusses nitrogen removal achieved in foam media biofilters in the field and under laboratory conditions. Overall removal of nitrogen is then divided into removal of each individual fraction. The mechanisms of nitrogen removal which occurred are then evaluated. The following sections then look at the processes of nitrification and denitrification in greater detail.

6.3.1 Mechanisms of Nitrogen Removal

TN removal achieved varied both in the field (between configurations) and under laboratory conditions (depending on feed composition). TN removal achieved in the field was discussed above. In the bench-scale biofilter, up to 10.7 mg/L TN removal was achieved in a single foam block. Considering that the biofilter depth in the bench-scale biofilter was only 0.06 m, this is significant. Greater removal was achieved in a single foam block in the laboratory than full-scale treatment systems in configurations F2 or F3. This could have been due to:

- lower dosing rates (5.8 L/m^2/dose or 69 L/m^2/d)
- less variable feed composition
- absence of organic matter and suspended solids in feed
- absence of peaks in loading
- higher temperature in the laboratory than most field samples

For the bench-scale study, an analysis of the mechanisms of nitrogen removal occurring was performed.

Assimilation

In microbiological wastewater treatment systems, the concentrations of carbon and nitrogen in wastewater are reduced as they are assimilated into cells for growth. Heterotrophic bacteria have high yields and rapid cell growth rates compared with autotrophic bacteria. If a high proportion of heterotrophs are present, removal and assimilation of both carbon and nitrogen will be significant. Figure 6.3.1 shows that as carbon removal in the bench-scale biofilter increased, so did nitrogen removal, indicating that assimilation may have been an important removal mechanism:

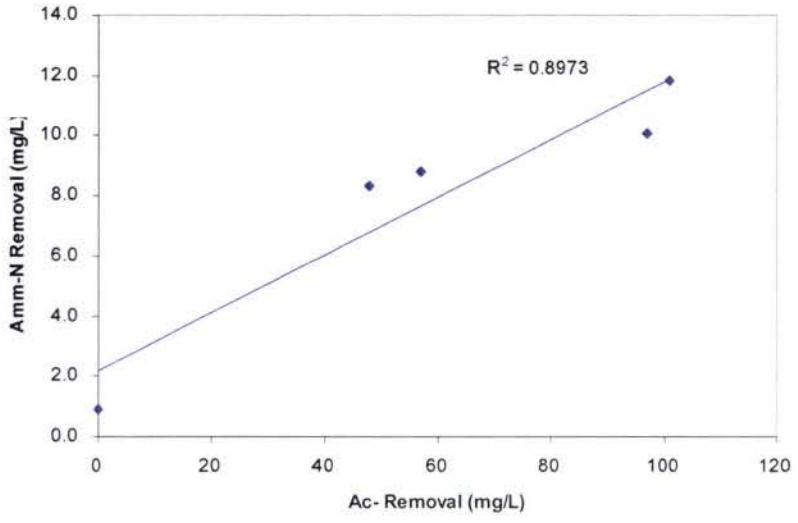

Figure 6.3.1: Amm-N removal vs Ac^- removal (studies L1 to L5).

To calculate the amount of assimilation occurring in each study, the COD of Ac^- was first estimated using Equation 6.3.1 (which shows that 64 g COD is removed for every 60 g Ac^- removed):

$$CH_3COOH + 2\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O \qquad (6.3.1)$$

The amount of cell growth is theoretically equal to COD removal multiplied by 0.39 (Tchobanoglous *et al*, 2003). The amount of nitrogen assimilated through cell growth is calculated based on 12 % nitrogen composition in bacterial cells (Tchobanoglous *et al*, 2003 after Madigan *et al*, 1997). The amount of Amm-N removal by assimilation can then be compared with the overall Amm-N removal observed (Figure 6.3.2):

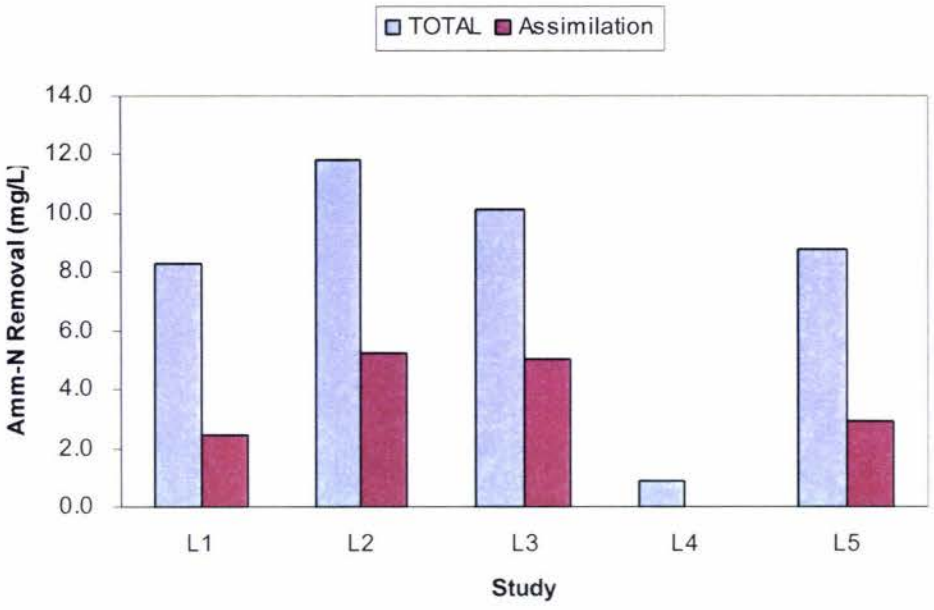

Figure 6.3.2: Amm-N removal due to assimilation (studies L1 to L5).

Assimilation accounted for an average of 31 % of total Amm-N removal in the bench-scale biofilter, up to a maximum of 49 %. This shows that assimilation is significant as a nitrogen removal mechanism, and must be accounted for when considering BNR systems. However, assimilation alone accounted for less than half of the observed Amm-N removal, indicating that nitrification was occurring.

Nitrification

Direct measurement of the extent of nitrification is difficult. NO_2^- and NO_3^- are intermediates in BNR, and can be consumed by denitrification shortly after production. Nitrification in the bench-scale biofilter was therefore calculated as the difference between total Amm-N removal and Amm-N removal by assimilation.

The bench-scale biofilter achieved an average nitrification of 4.9 mg-N/L. The maximum amount of nitrification occurring was 6.6 mg-N/L (study L2). Nitrification accounted for an average of 69 % of total Amm-N removal. Factors affecting the extent of nitrification are discussed in Section 6.4.

Denitrification

Nit-N produced by nitrification in the bench-scale biofilter would either be lost through denitrification, or leave the system in the effluent. Denitrification was therefore calculated as the difference between nitrification and the effluent Nit-N concentration (Table 6.3.1).

Denitrification of up to 86 % was achieved in the bench-scale biofilter. This gave the maximum amount of biological nitrogen removal as 5.5 mg/L. Factors affecting the extent of denitrification in each study are discussed in Section 6.5.

Ammonia Volatilisation

The concentrations of NH_3 in the feed to the biofilter were calculated for each laboratory study and field configuration. The average concentration was 0.90 mg/L, and the maximum was 1.85 mg/L (configuration F3). The highest pH value recorded in the field was 8.00. Feed to the bench-scale biofilter was buffered to a pH of 7.20.

At these low pH values and NH_3 concentrations, it is expected that ammonia removal by volatilisation was insignificant.

Summary

Table 6.3.1 shows the amount of nitrogen removal by assimilation, nitrification and denitrification occurring in studies L1 to L5:

Table 6.3.1: Nitrogen removal mechanisms (concentrations in mg/L).

Parameter	L1	L2	L3	L4	L5
Feed TN	165.2	72.6	73.8	70.1	70.6
Assimilation	2.5	5.2	5.0	0.0	2.9
Nitrification	5.8	6.6	5.1	0.9	5.9
% Nitrification	4%	9%	7%	1%	8%
Denitrification	0.3	5.5	2.7	0.0	5.1
% Denitrification	6%	83%	53%	0%	86%
Feed N	High	Med	Med	Med	Med
Feed C	Low	High	High	Zero	High
Feed DO	Med	Low	Med	High	Low

Biological nitrogen removal up to 5.5 mg/L was observed in the bench-scale biofilter, which had a depth of only 0.06 m. Nitrification and denitrification both occurred in a single foam block. When considering the results of the laboratory experiments, it should be remembered that the results given are for a single foam block. In the field systems there were in excess of 400 foam blocks. It can be expected that the removal achieved in the laboratory would be much greater when scaled up to replicate field conditions, in which each subsequent block in the plug flow arrangement should accomplish similar removal.

6.4 Nitrification in Foam Media Biofilter

6.4.1 Effect of Feed Composition

Nitrification should be greatest at low carbon concentration and high DO concentration (Chapter 2). Table 6.4.1 shows that low feed concentrations of carbon and high feed concentrations of DO did not result in increased nitrification. However, DO concentrations at microenvironments within the foam media differed significantly from feed concentrations (Section 6.4.4).

Table 6.4.1: Effect of feed composition on nitrification.

Study	Feed			% Nitn
	Carbon	DO	C:N Ratio	
L2	High	Low	10	9%
L5	High	Low	12	8%
L3	High	Med	10	7%
L1	Low	Med	1.3	4%
L4	Zero	High	0	1%

6.4.2 Effect of Hydraulic Residence Time (HRT)

Chapter 5 explained that HRT varied between different zones in the bench-scale biofilter. The concentration of Nit-N at nodes within the foam block increased with increasing HRT (Figure 6.4.1):

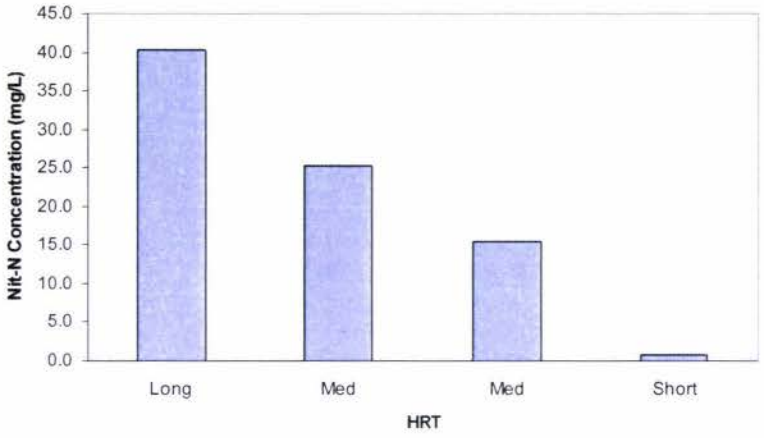

Figure 6.4.1: Effect of HRT on Nit-N accumulation (study L1).

This trend was observed in all bench-scale biofilter studies. The concentration of Amm-N at nodes within the foam block decreased with increasing HRT (where determined). This shows that the extent of nitrification increases at longer HRT. Literature sources such as Jang *et al* (2002) mention the low yields and slow growth rates of nitrifiers, implying that they would dominate only at longer HRT.

It should also be mentioned that significant hold-up occurred, as shown by high concentrations of Nit-N within nodes, even when effluent concentrations were low. For the example shown, the effluent concentration of Nit-N was 5.5 mg/L. This is similar to the observations of De Beer (1997), who reported that significant concentrations of nitrite may be present in a biofilm even when effluent concentration was low. The fact that proportionately more wastewater flowed through the columns with shorter HRT may also have contributed to the comparatively low effluent concentrations.

Effect of Rest Period

The bench-scale biofilter was dosed between 10:00 am and 3:30 pm each day. It was observed that samples taken immediately after the overnight rest period (at 10:00 am) showed the greatest extent of nitrification (Figure 5.3.6 and Figure 5.3.7). By calculating TN balances, it was determined that the additional Nit-N had been produced during the overnight rest period, and flushed out with the first feed at 10:00 am. These observations show that nitrification increased with increasing HRT.

Effect on Carbon Removal

Carbon removal also increased at long HRT, as seen by lower Ac^- concentrations at nodes within the foam block of the bench-scale biofilter. Data from study L2 shows this pattern in Figure 6.4.2; the same trend was observed in all other bench-scale studies (L1, L3, L4 and L5).

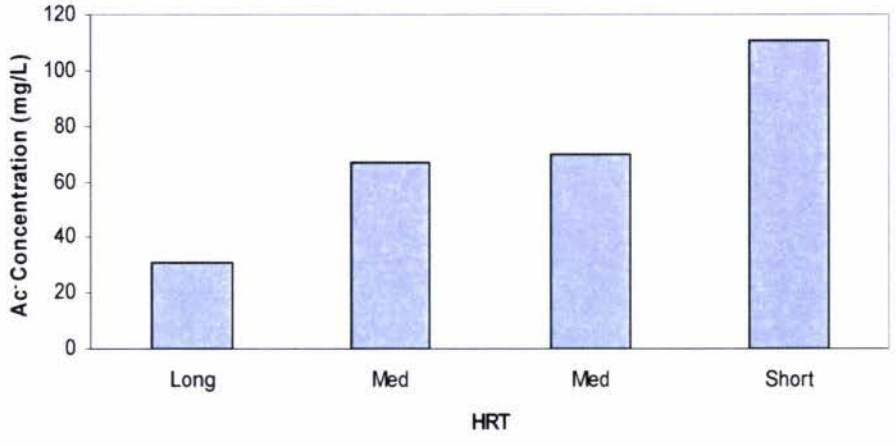

Figure 6.4.2: Ac^- concentration according to HRT (study L2).

This shows that a longer HRT at nodes within the foam block allowed time for more complete oxidation of carbon.

6.4.3 Effect of DO Concentration

Nitrification was not completely inhibited by feed DO concentrations as low as 2.44 mg/L (Table 6.4.1). The effect of DO concentration at nodes within the foam block on nitrification is shown in Figure 6.4.3:

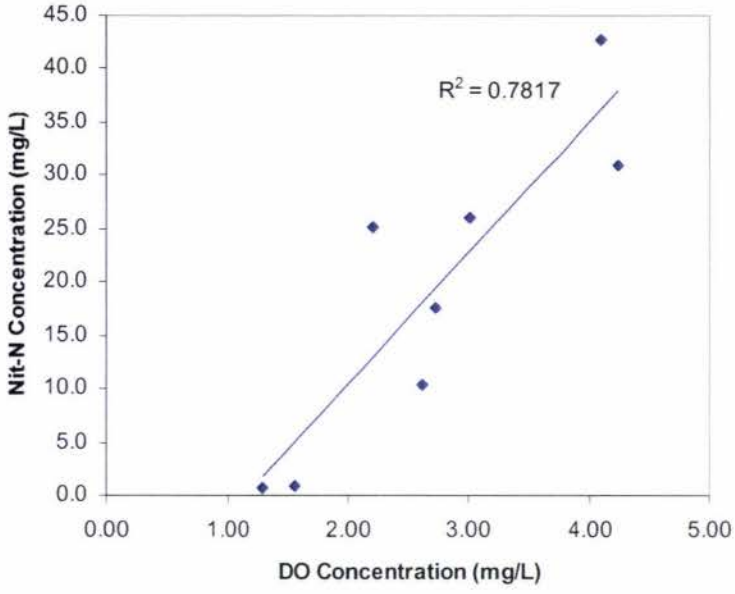

Figure 6.4.3: Concentrations of Nit-N and DO at each node (study L1).

The greatest Nit-N accumulation was observed at nodes with high DO concentration, low Ac^- concentration and long HRT. Nit-N accumulation could be due to increased nitrification, inhibited denitrification, or both. Figure 6.4.3 alone does not prove that a correlation existed between DO concentration and nitrification at nodes within the foam block.

While study L5 showed the same trend as the above figure, no relationship between DO concentration and Nit-N accumulation was observed in studies L2, L3 or L4. Nitrification occurred even when DO concentrations at nodes within the foam block were low. In study L2, nitrification of 6.6 mg-N/L occurred, even though the average DO concentration at the nodes was only 0.88 mg/L. Nit-N accumulation of 8.2 mg/L was observed at one node even when the DO concentration was 0.34 mg/L.

DO concentration alone had no noticeable effect on nitrogen removal in the field (Table 6.2.4).

Overall, it appeared that DO concentration alone did not have a great influence on the extent of nitrification. Nitrification still occurred at DO concentrations less than 1 mg/L.

6.4.4 Factors Affecting DO Concentration

DO concentrations at nodes within the foam block varied considerably. This appeared to have been due to several factors.

Effect of Feed DO

Feed DO concentration strongly influenced the average DO concentration at nodes within the foam (Figure 6.4.4):

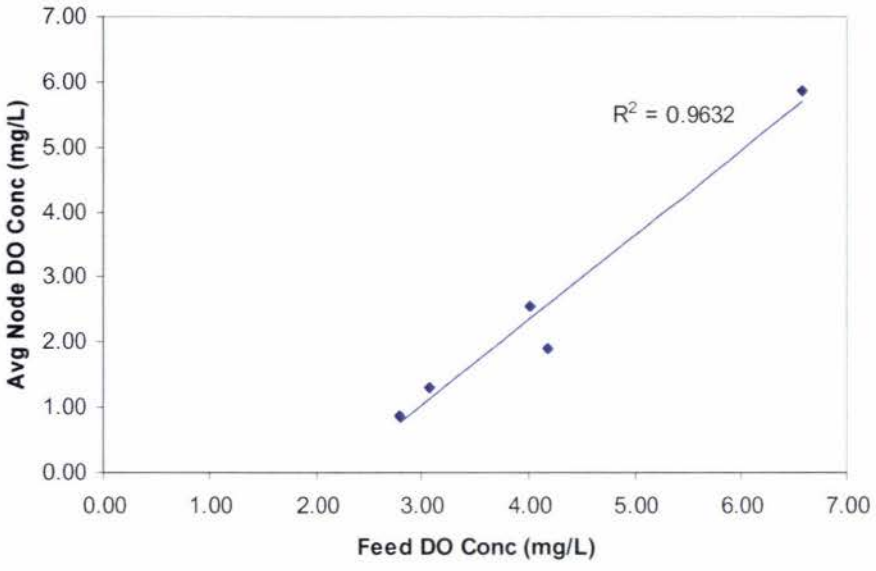

Figure 6.4.4: Feed DO concentration vs average node DO concentration (studies L1 to L5).

However, it was observed that DO concentration within the foam was always lower than the feed concentration.

Effect of DO Consumption

Heterotrophic and autotrophic aerobic bacteria consume DO, reducing concentration at nodes within the foam block below that of the feed. Carbon removal gives an indication of the activity of heterotrophs. Figure 6.4.5 shows that as carbon removal in the bench-scale biofilter increased, so did the average DO removal:

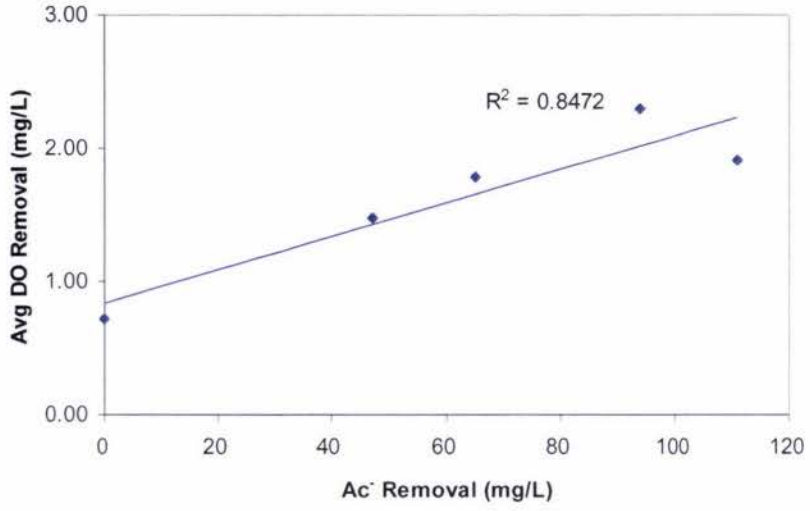

Figure 6.4.5: Average DO removal vs Ac^- removal (studies L1 to L5).

Between 0.017 and 0.031 mg-DO/L was removed per 1 mg-Ac^-/L removed. DO consumption by heterotrophs significantly affected the DO concentration at nodes within the foam block.

Effect of Position

DO concentrations varied widely across the 8 nodes studied. The nodes studied were at four different horizontal positions, and at heights of 0 mm (bottom surface of foam, in contact with ambient air) and 15 mm (inside the foam block).

Figure 6.4.6 shows the average DO concentrations applied to the biofilter (measured at the surface of the foam), and the average DO concentration across the nodes at the 2 heights studied (15 mm and 0 mm). Wastewater flowed downward, passing first through the 15 mm height, and subsequently the 0 mm height (bottom surface) before exiting the bench-scale biofilter.

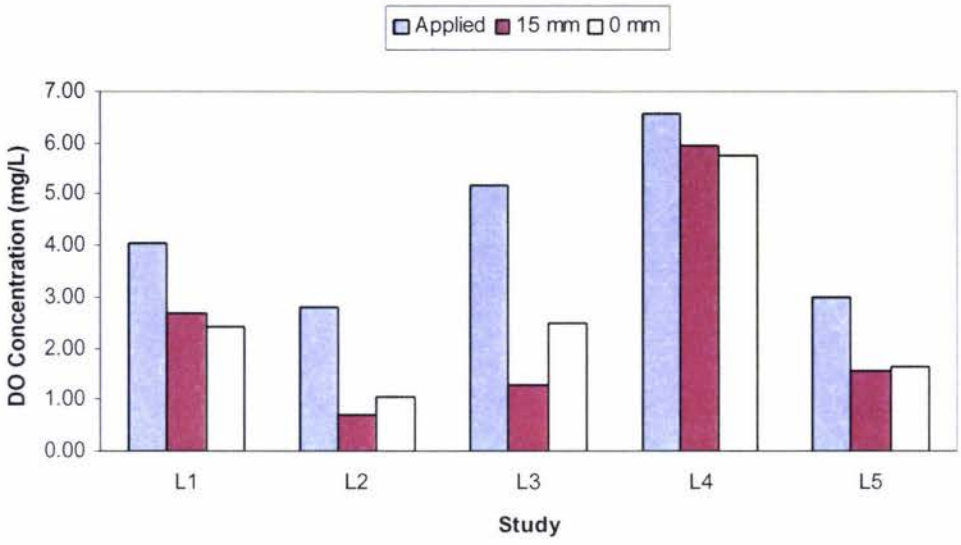

Figure 6.4.6: Average DO concentrations in bench-scale biofilter.

In all cases, average DO concentration within the foam was lower than the applied DO concentration. A significant amount of DO was removed, up to an average of 3.86 mg/L (study L3).

Where DO concentrations at nodes within the foam block were 2.70 mg/L or greater (studies L1 and L4), DO concentration decreased from 15 mm to 0 mm. This may have been due to extra consumption of DO by aerobic microorganisms as wastewater flowed downward through the foam.

Where DO concentrations at nodes within the foam block were 1.60 mg/L or less (studies L2, L3 and L5), DO concentration increased from 15 mm to 0 mm. This may have been due to reaeration, since the driving force for oxygen transfer would have been higher (Chapter 4).

6.4.5 Significance of Other Factors

Effect of Carbon Concentration

Figure 6.4.7 shows that nitrification in the bench-scale biofilter appeared to increase as the amount of available carbon increased. It was not expected that this would be the

case. As carbon concentration increases, the proportion of heterotrophs should increase, and out-compete nitrifiers.

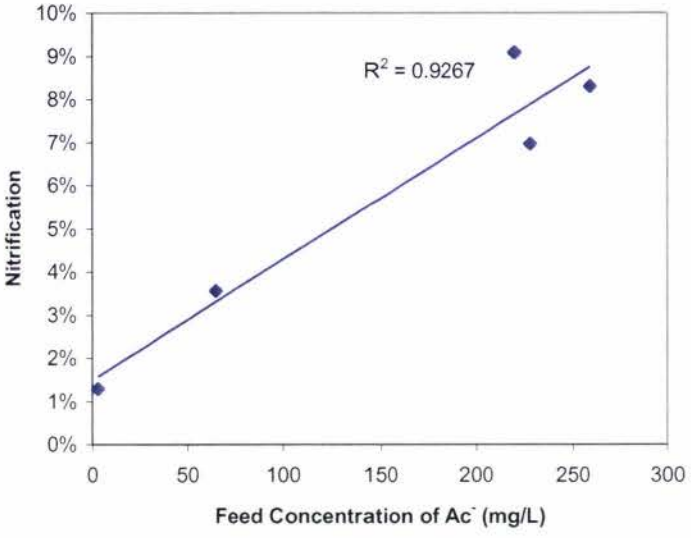

Figure 6.4.7: Nitrification at various feed concentrations of Ac^- (studies L1 to L5).

These findings may indicate the presence of heterotrophic nitrifiers, as described by Stevens *et al* (2002). Alternatively, CO_2 produced by oxidation of carbon may have provided a substrate for increased autotrophic nitrification.

Competition from Heterotrophs

As discussed above, higher concentrations of carbon in a particular study did not reduce the amount of nitrification occurring in the bench-scale biofilter. Results presented in Section 5.5 also showed that the greatest amounts of both nitrification and carbon removal occurred in column 1 of the foam block. This indicates that competition from heterotrophs did not limit nitrification in the bench-scale biofilter.

Nitrite Accumulation

In the bench-scale biofilter, nitrite effluent concentrations up to 0.6 mg/L were observed in the studies where feed DO concentration was lowest (L2 and L3). No nitrite accumulation occurred in other laboratory studies. This pattern is expected, as nitrification can be incomplete at low DO concentrations (Chapter 2).

In the field, average effluent concentrations in configurations F1, F2 and F3 were 0.0, 2.8 and 0.8 mg/L respectively. Nitrite accounted for 61 % of effluent Nit-N from configuration F2, and 80 % from F3. This may indicate that limited DO was available in the lower part of the biofilters for these configurations.

NH_3 Inhibition

Nitratation is inhibited starting at NH_3 concentrations of 0.1-1.0 mg/L; nitritation and nitratation are both inhibited from concentrations of 10-150 mg/L (Anthonisen *et al*, 1976). Feed concentrations of NH_3 were reported in Section 6.3.1. At the concentrations observed, no inhibition of nitritation would have occurred. The absence of nitrite accumulation indicates that in most cases, nitratation was not inhibited either. Overall, nitrification was not inhibited by NH_3.

Temperature of Wastewater

Due to seasonal variations, wastewater samples taken from configuration F1 had a higher temperature than samples from F2 or F3 (Table 6.4.2). The highest Amm-N removal was observed where the wastewater temperature was highest.

As shown in Chapter 5, nitrogen removal in the bench-scale biofilter was greater in some cases than in configurations F2 or F3. This may have been partly due to temperature differences; temperature in the bench-scale biofilter was 24.0 ± 2.6 °C throughout the experiment.

Table 6.4.2: Effect of temperature on Amm-N removal (configurations F1 to F3).

Configuration	Amm-N Removal (mg/L)	Temp (°C)
F1	41.7	23.5
F2	10.2	19.0
F3	1.1	14.7

Lower temperatures possibly reduced the amount of Amm-N removal in configurations F2 and F3, but would have only been one contributing factor. Overall, not enough data was collected on the effect of temperature for any definite conclusions to be drawn.

6.5 Denitrification in Foam Media Biofilter

6.5.1 Effect of Feed Composition

The greatest amount of denitrification in the bench-scale biofilter was observed in studies with high feed concentrations of carbon (Table 6.5.1). For studies with similar feed concentrations of carbon, more denitrification occurred in studies with lower feed DO concentration. Both of these trends were expected; denitrification requires a carbon source and an anoxic environment (Chapter 2).

Table 6.5.1: Effect of feed composition on denitrification.

Study	Feed			Denitrification
	Carbon	DO	C:N Ratio	
L4	Zero	High	0	0%
L1	Low	Med	1.3	6%
L3	High	Med	10	53%
L2	High	Low	10	83%
L5	High	Low	12	86%

6.5.2 Effect of Carbon Availability

Feed concentration of carbon had a significant effect on overall denitrification, as mentioned above. The concentration of carbon at nodes within the foam block of the bench-scale biofilter also affected denitrification. By comparing the amount of Nit-N accumulation with the Ac^- concentration at a particular node (Figure 6.5.1), it can be seen that Nit-N was not denitrified where Ac^- concentrations were low.

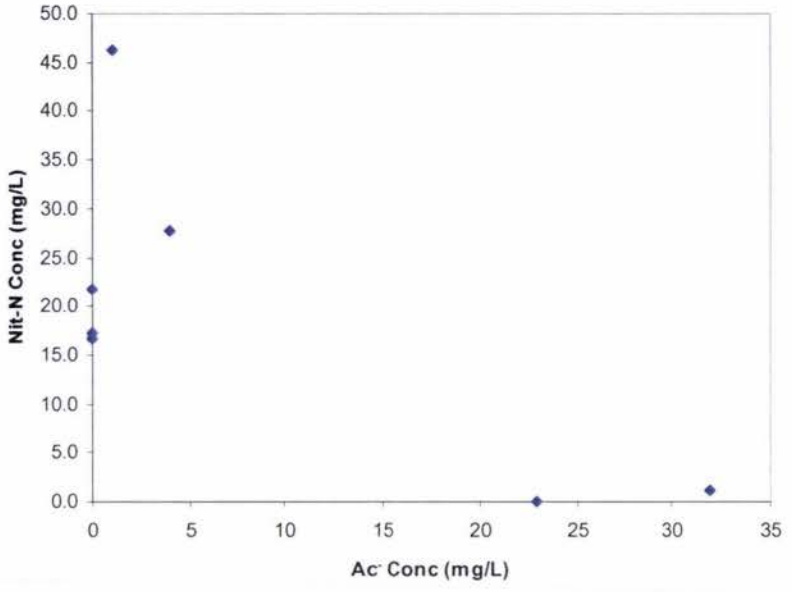

Figure 6.5.1: Effect of carbon availability on Nit-N accumulation at nodes (study L1).

This shows that as well as feed concentration of carbon, the concentration of carbon at nodes within the foam media will determine the extent of denitrification occurring.

6.5.3 Effect of DO Concentration at Nodes

Denitrification was calculated at nodes within the foam block for studies L2 and L3.

DO concentration at nodes within the foam block for study L2 was a maximum of 1.20 mg/L. No relationship between DO concentration and denitrification was observed in this case, and the average extent of denitrification at the nodes was 25.4 mg/L (95 %).

The average extent of denitrification in study L3 was 18.4 mg-N/L (93 %). Denitrification was not limited at nodes with high DO concentrations. 100 % denitrification was observed at DO concentrations up to 2.70 mg/L within the foam block (denitrification up to 18.7 mg-N/L).

Overall denitrification decreased with increasing DO concentration (Section 6.5.1). However, denitrification at nodes within the foam block was substantial even at high DO concentrations.

7 Conclusion

Foam media biofilters were studied in on-site wastewater treatment systems in the field, and in the laboratory using a bench-scale biofilter. Field studies also involved the assessment of three different septic tank and biofilter configurations.

Increasing septic tank volume from configuration F1 (4000 L) to F2 and F3 (6000 L) increased hydraulic residence time and gave lower effluent concentrations of TSS, COD and TN. 1 mm disc filters were installed on septic tanks in all configurations; removing the 100 μm disc filter for configurations F2 and F3 had no adverse effects. Septic tank effluent from configurations F2 and F3 had lower TSS concentrations than those reported in the literature (20 mg/L from F2, 30 mg/L from F3, 73 mg/L in the literature). COD concentrations were low compared with those calculated from BOD values in the literature. TN concentrations were similar to values from the literature.

Foam media biofilters in the field provided additional removal of TSS and COD, with configurations F2 and F3 performing better than F1. In configuration F1, a random-packed arrangement of foam led to short-circuiting. Configurations F2 and F3 used different arrangements of foam, giving average effluent TSS concentrations of 9 mg/L. COD concentrations in effluent from configurations F2 and F3 were 36 and 116 mg/L respectively.

Nitrogen removal in biofilters in the field varied depending on configuration. Average effluent TN concentrations from configurations F1, F2 and F3 were 49.2, 40.6 and 53.0 mg/L respectively. Configuration F1 achieved 59 % removal of Amm-N (32.0 g-N/d Amm-N removal) compared with 22 % for configuration F2 (7.8 g-N/d Amm-N removal) and only 2 % for configuration F3 (0.8 g-N/d Amm-N removal). Biofilters did not remove Org-N. Effluent Nit-N concentration from configuration F1 was only 1.5 mg/L, despite the level of Amm-N removal achieved. This suggested that nitrification was followed by denitrification in the single-stage foam media biofilter.

Low Amm-N removal in configuration F3 may have been due to high areal loading rate and short biofilter depth. The highest Amm-N removal occurred in configuration F1, which had the lowest ratio of areal loading to biofilter depth. Amm-N removal was also highest where sCOD concentration in feed to the biofilter was highest. This indicated that nitrogen removal by assimilation may have been important as a nitrogen removal mechanism, and should be investigated in any future study. Configuration F3 used smaller foam blocks, which held a higher proportion of water and allowed a greater proportion of biomass growth. However, this did not lead to increased nitrogen removal. Distributors used in configurations F1 and F3 increased wastewater DO concentration by up to 4.80 mg/L. This was expected to increase nitrification, which did not happen in configuration F3. The alkalinity of domestic wastewaters was not measured; this could have given some indication of their suitability for nitrification.

Grab samples were taken from each treatment stage during each site visit. However, this may not have given representative samples of wastewater at each stage. There was no sampling point available for domestic wastewater influent to the system. The composition of wastewater (even soluble components) varied with depth in the septic tank. Samples taken from the distribution pump chamber would have been partially diluted by recirculated effluent. In some cases, systems were not operating under normal conditions, or excessive amounts of potable water or greywater had been flushed through the system. In these cases, samples were not representative; this also indicates that assessing compliance with legislative requirements on the basis of a single grab sample may not be accurate. Compositing samples taken at regular intervals from a system would give a more reliable assessment of performance.

TN removal up to 10.7 mg/L occurred in a single foam block in the bench-scale biofilter. This is significant, since the biofilter depth was only 0.06 m. The excellent performance of the bench-scale biofilter may have been due to lower dosing rates, less variable feed composition, the absence of organic matter or suspended solids, the absence of peaks in loading, or higher wastewater temperature. Ac^- removal up to 101 mg/L also occurred in the bench-scale biofilter.

Nitrification and denitrification both occurred in a single foam block in the bench-scale biofilter. Nitrogen removal by assimilation was also an important removal mechanism, showing that this mechanism must be considered whenever a biological nitrogen removal system is studied.

Nitrification increased at high feed concentrations of carbon, which was not expected. This may indicate the presence of heterotrophic nitrifiers. Alternatively, oxidation of carbon to CO_2 may have provided substrate for increased autotrophic nitrification. Nitrification was greatest at nodes in the foam block with longer hydraulic residence time. Nitrification was highest after an overnight rest period than at any other time during the day. Nitrification in the bench-scale biofilter did not decrease at average DO concentrations as low as 0.88 mg/L.

Denitrification was greatest when the feed composition was high in carbon and low in DO, which was expected. Denitrification did not decrease at DO concentrations as high as 2.70 mg/L at nodes within the foam block.

Methods developed were useful for the determination of DO concentration at nodes within a foam block. DO concentration varied considerably between nodes, and was often much lower than bulk concentrations, even at nodes exposed to the atmosphere. The Diamond General 733 miniature membrane electrode used agreed with a commonly used electrode to within an average of ± 0.20 mg/L. The empirical equation derived to calculate DO concentration was accurate to within ± 2.9 %. Some positive interferences were introduced by the sampling and sample storage methods, most noticeably for samples with low DO concentrations.

When sampling from nodes within the foam block, up to 4.5 mL of liquid was extracted. This means that samples would have been drawn from a considerable area surrounding the node of interest. Now that the existence of aerobic and anoxic microenvironments in foam media has been proven, a more detailed investigation of these biofilms should be conducted in the future. This could involve the use of microelectrodes, fluorescence in-situ hybridisation, and measurement of the oxidation-reduction potential. Accurate determination of DO, Amm-N and Nit-N

profiles could lead to the development of a mathematical model for biological nitrogen removal in foam media biofilters.

Hydraulic loading rate and hydraulic residence time were identified as important factors affecting biological nitrogen removal in foam media biofilters. Pilot-scale trials are recommended as the next stage of research into foam media biofilters for on-site wastewater treatment. Biofilters of various depths and cross-sectional areas could be constructed and run under laboratory conditions, with small foam blocks as media. This would allow the effects of varying areal loading rate, biofilter depth, recirculation ratio and flooding to be determined, and could lead to optimisation of the design for biofilters in the field. This would also allow investigation of residence time distributions, and changes in DO, Amm-N or Nit-N concentrations with depth in the biofilter. If it is found that DO concentration becomes limiting at greater depths of biofilters in the field, the ability of foam media to be reaerated should be assessed. Foam with greater density could also be trialled to increase hydraulic residence time, provided the effects on DO concentration were negligible.

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