CRANFIELD UNIVERSITY

AMINA ABOOBAKAR

QUANTIFICATION OF GREENHOUSE GAS EMISSIONS IN BIOLOGICAL WASTEWATER TREATMENT

Cranfield Water Science Institute
School of Applied Sciences

PhD Thesis

Academic Year: 2012–2014

Supervisors:

Dr Gabriela Dotro

Prof. Elise Cartmell

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ABSTRACT

There is an increasing need to reduce greenhouse gas (GHG) emissions and to identify influencing factors from wastewater treatment plants (WWTPs), particularly process emissions consisting of nitrous oxide (N_2O), and methane (CH_4) GHG, with global warming potentials about 310 and 21 times higher than carbon dioxide (CO_2) respectively (IPCC, 2006). However, the challenges offered by full-scale environments, have to date, restricted a real-time, comprehensive approach of monitoring emissions and influencing factors. This study aimed at addressing this knowledge gap, by reporting the findings of a long-term, online, continuous monitoring of GHG emissions and operational variables. Lanes were monitored in nitrifying activated sludge plants (ASP) controlled under ammonia (NH_4^+) and dissolved oxygen (DO) set-points (DO set-points monitored: 1.5 and 2.0 mg/L), as well as in a biological nutrient removal plant (BNR) under NH_4^+ control.

The findings showed that CH_4, although potentially formed in non-aerated compartments, was emitted in aerobic zones, at an average emission factor (EF) of 0.07 % of influent and removed chemical oxygen demand (COD). Nitrous oxide EFs on the other hand, depended on relative nitrogen fractions, with influent-based EFs showing a best-case scenario, at 0.05–0.72 % of both influent total nitrogen (TN) and NH_4^+, compared to the higher EFs based on removed nitrogen at 0.13–3.9 % of TN and NH_4^+ removed. The processes operated under the same control settings (DO set-point 1.5 mg/L), had similar, or identical, EF, suggesting that settings could help predict the range of EF. Nitrous oxide was always produced in the presence of NH_4^+, even at low concentrations (=<0.5 mg/L), therefore linking N_2O production with NH_4^+ oxidation, particularly with nitrifier nitrification. Incomplete denitrification under low carbon to nitrogen (C/N) ratios also triggered N_2O production (EFs of 2.4 and 4.1 % of reduced TN at C/N ratios of 2.8 and 2.4 respectively), particularly with intermittent aeration. Therefore, nitrifier denitrification and incomplete denitrification simultaneously occurred and triggered N_2O production in the final stages of nitrification. The BNR lane was the most operationally stable process, therefore offering the best balance between efficiency (60–99 % less aeration and energy per kg of treated NH_4^+), low carbon footprint and reduced EFs (0.08–0.1 % of all nitrogen fractions). The second best option was the DO set-point control of 1.5 mg/L, with low EFs (0.05–0.2 %), stable operational conditions and reduction in aeration requirements (up to 340 % less than DO set-point 2.0 mg/L). Operating ASP under NH_4^+ control however, led to 7–96 % more efficiency than under DO set-points, although it required better control in the back end of the process.

Only an online, long-term methodology such as adopted in this study, could provide insights into emission variability and the effect of operational variables on promoting or reducing emissions. Based on this, strategies to mitigate emissions at full-scale were recommended.

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ABBREVIATIONS

Abbreviations are introduced within the text and re-introduced for each individual chapter

ANOVA	Analysis of variance
ASP	Activated sludge plant
BNR	Biological nutrient removal plant
BOD	Biochemical oxygen demand
COD	Chemical oxygen demand
CRC	Carbon Reduction Commitment
DO	Dissolved oxygen
EF	Emission factor
GHG	Greenhouse gases
GWP	Global warming potential
HRT	Hydraulic retention time
MLSS	Mixed liquor suspended solids
ORP	Oxidation reduction potential
ppmv	volumetric parts-per-million
RAS	Return activated sludge
SCADA	Supervisory control and data acquisition
SRT	Solids retention time
TIS	Tanks-in-series
TKN	total Kjeldahl nitrogen
TN	Total nitrogen
TSS	Total suspended solids
VSS	Volatile suspended solids
WFD	Water Framework Directive
WWTP	Wastewater treatment plant

NOTATIONS

$MgSO_4*7H_2O$	Magnesium sulphate heptahydrate
NaCl	Sodium chloride
%	Percentage
µm	Micrometre (10^{-6})
µM	Micromolar (micromol/litre)
µmol	Micromol
^0C	Degree celsius (unit of temperature)
A_n	Surface area per n TIS zone
AQ	Airflow rate
A_T	Total surface area
Atm	Standard unit of pressure (101,325 Pa)
C	Concentration
$C_6H_{12}O_6$	Dextrose anhydrous
$CaCl_2*2H_2O$	Calcium chloride dehydrate
CH_3COOH	Acetic acid
CH_4	Methane
CO_2	Carbon dioxide
CO_2e	Carbon dioxide equivalents
F	Emission fluxes
$FeCl_3*6H_2O$	Iron (III) chloride hexahydrate
g	Grams
h	Hours
K	Kelvin (unit of temperature)
K_H	Henry’s Law solubility constant
KCl	Potassium chloride
Kg	Kilograms
$KgCO_2e$	Kilograms of carbon dioxide equivalents
KNO_3	Potassium nitrate
kWh	Kilowatt hour
L	Litre
LQ	Liquid flow rate
m^3	Cubic metre
mg	Milligrams
Mm	Millimetre
mol	Mole
$MtCO_2e$	Million tonnes per carbon dioxide equivalents
N	Nitrogen
N_2O	Nitrous oxide
$Na_2HPO_4*12H_2O$	Disodium hydrogen orthophosphate dodecahydrate

$NaHCO_3$	Sodium bicarbonate
NH_2OH	Hydroxylamine
NH_4^+/NH_4-N	Ammonia/Ammonia-nitrogen
NH_4Cl	Ammonium chloride
nirK	Gene that encodes for nitrite reductase enzyme
NO	Nitric oxide
NO_2^-/NO_2-N	Nitrite/Nitrite-nitrogen
NO_3^-/NO_3-N	Nitrate/Nitrate-nitrogen
nor	Gene that encodes for nitric oxide reductase enzyme
P	Phosphorus
Q	Flow rate
r^2	Correlation coefficient

CHAPTER 1

INTRODUCTION

1. INTRODUCTION

1.1. Background

The need to reduce greenhouse gas (GHG) emissions and carbon footprint, as well as improving treatment efficiency, is pressing. The water industry therefore, needs to find a balance between reducing their carbon footprint, whilst minimising process emissions and costs, without compromising effluent quality. As wastewater treatment plants (WWTPs) move towards low-carbon electricity sources, direct GHG emissions from the treatment process will become more relevant to the total carbon footprint of a WWTP. In this scenario, quantifying process emissions from the most commonly used biological treatment process, i.e., nitrifying activated sludge plants (ASP), provides critical information about carbon impact, thereby allowing WWTPs to respond to emerging regulations. This is particularly important for nitrous oxide (N_2O), and methane (CH_4), GHG with global warming potentials (GWP) 310 and 21 times (IPCC, 2006) respectively more harmful than carbon dioxide (CO_2), and therefore, even at low emission levels, can impact greatly on the overall carbon footprint.

Nitrous oxide emissions can be released by WWTPs mostly during nitrification and denitrification processes (Fig. 1.1) in ASPs (Dotro et al., 2011; Kimochi et al., 1998). It is now accepted that it can be generated during both anaerobic/anoxic periods as well as under aerobic conditions, due to different transformation processes (Colliver and Stephenson, 2000; Foley et al., 2010a; Kampschreur et a al., 2009a; Tallec et al., 2008; Wrage et al., 2001; Wunderlin et al., 2012). Additionally, even when produced during anoxic periods, it is subsequently emitted during aerobic phases because of air-stripping. Triggers for its generation are believed to be related to the operating conditions of a particular sewage works, with dissolved oxygen (DO) (Tallec et al., 2006), nitrite (Kampschreur et al., 2009b) and plant configuration (Ahn et al., 2010a) being the main influencing factors. However, although evidence has shown that formation and emission of N_2O do occur during biological nitrogen removal processes, the detailed mechanisms of, and quantification of emissions remain unclear. Additionally, methodologies applied for measuring emissions tend to vary considerably, thereby adding to the discrepancy and variability of reported results. Recent studies however, have shown the benefits of applying *in-situ,* real-time monitoring methodologies to providing a better understanding of emission profiles in WWTPs (Ahn et al., 2010a; Foley et al., 2010a).

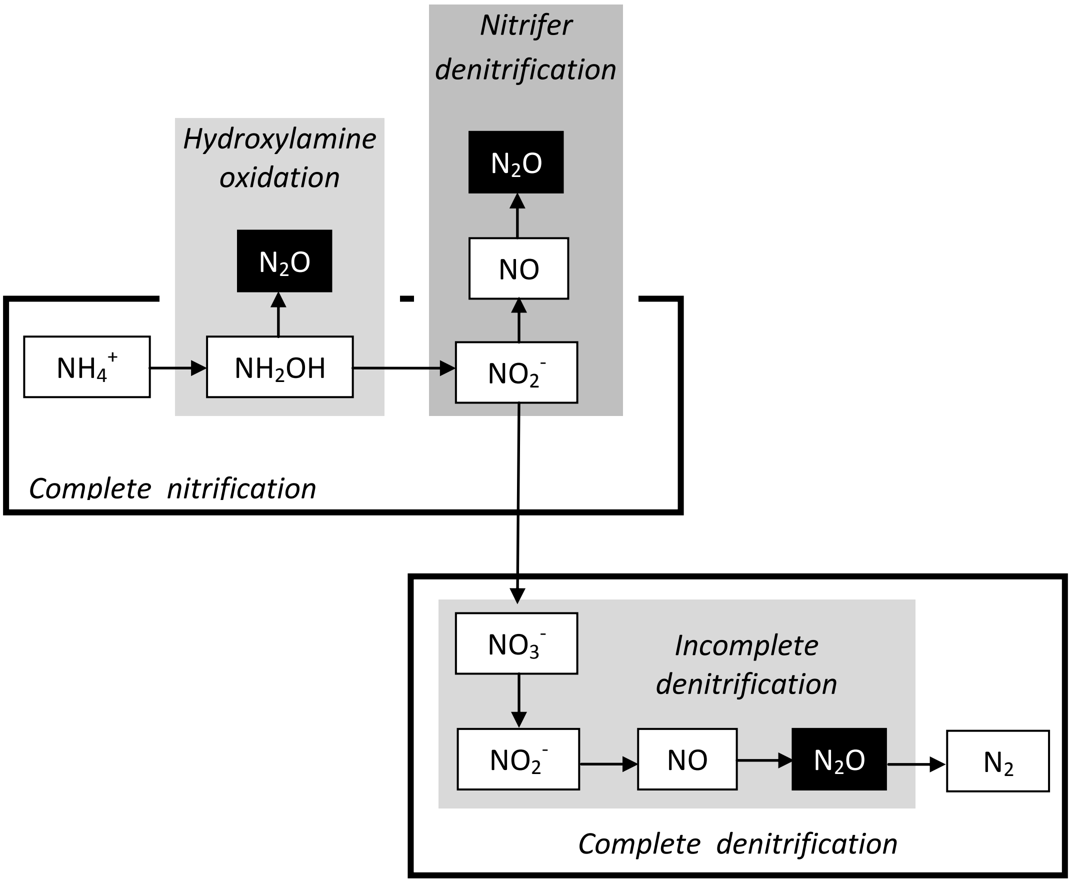

Figure 1.1: Diagram of nitrification and denitrification processes (blank boxes) showing N_2O (black boxes) as an intermediate during denitrification and an end product during incomplete denitrification (shaded box), as well as during nitrification through hydroxylamine (NH_2OH) oxidation and nitrifier denitrification pathways (shaded boxes). During complete nitrification, NH_4^+ oxidising bacteria (AOB) oxidise NH_4^+ to NH_2OH and nitrite (NO_2^-) oxidising bacteria (NOB) oxidise NO_2^- to nitrate (NO_3^-). AOB are also believed to be mainly responsible for nitrifier denitrification and NH_2OH oxidation pathways. Denitrification is carried out by heterotrohpic denitrifying microorganisms.

Methane on the other hand, is considered as the most significant GHG emitted from wastewater management (El-Fadel and Massoud, 2001). It is biologically produced during the chemical reduction of the organic fraction of wastewater, COD (chemical oxygen demand) or BOD (biochemical oxygen demand). Methane is solely synthesised by methanogenic *Archaea*; however, anaerobic bacteria, of which some are facultative rather than obligatory anaerobes, are also involved in anaerobic digestion, whereby they hydrolyse and liquefy organic matter. Therefore, CH_4 production is mostly expected from places such as rising sewers (Guisasola et al., 2009) and parts of a WWTP where anaerobic conditions prevail (Daelman et al., 2012). Due to the oxygen availability in ASPs, particularly in aerated tanks, negligible production of CH_4 is expected to occur and therefore limited information is available (Daelman et al., 2012).

Nevertheless, some studies have reported on CH_4 emitted across WWTPs, even from aeration tanks (Daelman et al., 2012; Ren et al., 2013; Wang et al., 2011a). This highlights the differences between generated and emitted CH_4: although produced in anaerobic environments, it can nevertheless be emitted from places where aerobic conditions prevail, such as in activated sludge plants (Daelman et al., 2012). Because of the liquid-to-gas mass transfer, CH_4 is easily air-stripped to the atmosphere once in contact with air. Indeed, emissions from aerated zones were found to be higher than that from non-aerated zones, where instead, levels of dissolved CH_4 dominated (Ren et al., 2013). Therefore, findings from full-scale studies suggest that methane emissions from aerated zones, in addition to being significantly variable and process-specific, are by no means negligible. However, the limited availability of quantifiable data, both from sources and conditions that promote CH_4 formation and emission at full-scale, may restrict a detailed assessment of carbon mitigation options from WWTPs (Listowski et al., 2011; Wang et al., 2011a).

Therefore, there is a need to quantify GHG process emissions and to examine what operational strategies can be applied to reduce those emissions. This project consisted of a series of intensive full-scale campaigns, monitoring GHG emissions in suspended growth biological treatment processes. The monitoring was carried out under a range of varying operational regimes: nitrifying ASPs, operated under DO set-point and ammonia (NH_4^+) algorithm process controls, as well as a biological nutrient removal plant for enhanced phosphorous removal (BNR), also operated under NH_4^+ control. Bench-scale studies were undertaken to investigate the triggers and factors, under nitrification and denitrification, that promote N_2O production and emissions, under different conditions, typically found in biological wastewater treatment processes. Finally, the operational conditions to deliver the appropriate balance between minimising energy use, whilst improving effluent quality and reducing GHG emissions are recommended.

1.2. Aims and objectives

The aim of this project is to quantify GHG emissions and to establish the operational strategies that reduce GHG process emissions from aerated, suspended growth biological processes. As such, the project aims at answering the following research questions:

1. Do N_2O emissions increase at low DO set-points and decrease at higher DO set-points?

2. Do frequently low DO periods result in higher emissions due to required time for recovery from stress?

3. Can advanced operational control strategies (such as NH_4^+ control) reduce GHG emissions and improve carbon footprint?

4. Is there a specific low NH_4^+ threshold by which N_2O production stops?

5. Is there potential for N_2O emissions through incomplete denitrification in the final stages of nitrifying ASP?

In order to answer these questions, the following objectives have been identified as scientific contribution of the work to be delivered as four research papers:

- Profile of N_2O emissions and DO at a full-scale nitrifying ASP.
- Determine CH_4 emissions in a full-ASP.
- Quantify N_2O emissions from a nitrifying ASP: at target DO set-points and over frequent (transient) and occasional (abrupt) low DO periods; and identify NH_4^+ conditions and C/N ratios that may trigger N_2O production in the final stages of a nitrifying process.
- Examine N_2O emissions under varying operational conditions at full-scale, nitrifying and enhanced biological phosphorus removal treatment processes, with both NH_4^+ and DO set-point controls, in order to identify approaches for minimising GHG process emissions.

The proposed research hypothesis is therefore stated as:
"Nitrous oxide production can be directly linked to oxygen availability in biological treatment processes and therefore, minimised by influencing oxygen presence in the bioreactors".

1.3. Thesis structure

This thesis is presented as a series of chapters formatted in the style of journal papers. The papers were written by the first author, Amina Aboobakar, and edited by Dr Gabriela Dotro, Professor Elise Cartmell, Professor Tom Stephenson, Peter Vale, as well as by other authors who have contributed to the individual papers. All laboratory work was carried out by Amina Aboobakar. The link between the different chapters of the thesis is presented in Figure 1.2.

The thesis starts with a literature review of recent developments in the direct quantification and reporting of GHG emissions from full-scale biological WWTPs, particularly focusing on the operational triggers that promote and minimise N_2O formation and emissions, and gaps in current knowledge. (Chapter 2: *A review of greenhouse gas emissions from biological wastewater treatment plants*).

In Chapter 3 the link between DO and N_2O emissions is investigated, since although believed to be a critical one, is only partially understood. This study aimed at addressing this knowledge gap, and the findings from an online, continuous monitoring of dissolved and off-gas N_2O, were reported, to establish the relationship with DO in a full-scale, plug-flow nitrifying activated sludge treatment plant. (Chapter 3: *Aboobakar A., Cartmell E., Stephenson T., Jones M., Vale P., Dotro G. Nitrous oxide emissions and dissolved oxygen profiling in a full-scale nitrifying activated sludge treatment plant.* Published in Water Research, 2013, 47 (2), pp. 524–534).

Chapter 4 looks at CH_4, which although formed under anaerobic conditions, may be emitted from aerated zones of ASPs. However, very little is still known about CH_4 from these processes. This study reported on the variability in CH_4 emissions, as well as carbon impact, from the same process investigated in Chapter 3. (Chapter 4: *Aboobakar A., Cartmell E., Jones M., Vale P., Dotro G. Methane emissions from aerated zones in a full-scale nitrifying activated sludge treatment plant.* Submitted to Water, Air and Soil Pollution. Published online December 2013, 225:1814).

Chapter 5 follows from the findings in Paper 1 (Chapter 3 of this thesis), whereby DO was shown to significantly influence N_2O production and emissions. A comparison was carried out of N_2O profiles in the same full-scale nitrifying ASP, under the DO set-point controls of 1.5 and 2.0 mg/L, to understand how different set-points impact on emissions. The conditions that trigger N_2O production in the final stages of nitrification were also identified in a bench-scale study. (Chapter 5: *Aboobakar A., Cartmell E., Jones M., Stephenson T., Vale P., Dotro G. Nitrous oxide emissions under different DO set-point controls in a full-scale nitrifying activated sludge plant.* The paper is in finalised draft and a potential journal for publication is under discussion).

Chapter 6 assesses the impact of different control settings and configurations, on operational variables and on N_2O (following on from, and inclusive of, the process investigated on Chapters 3 to 5 of this thesis). The study determined the best balance in terms of process efficiency and low operational carbon impact from electric energy and GHG process emissions. (Chapter 6: *Aboobakar A., Ballinger D., Brookes, A., Cartmell E., Peacock, S., Stephenson T., Taliana A., Vale P., Wilkinson A., Winter P., Dotro G. Minimising nitrous oxide emissions from full-scale wastewater treatment plants.* The paper is in preparation as a final draft. Potential journal for publication is under discussion).

Chapter 7 discusses the overall outcomes of the research and Chapter 8 is the main conclusions of the research.

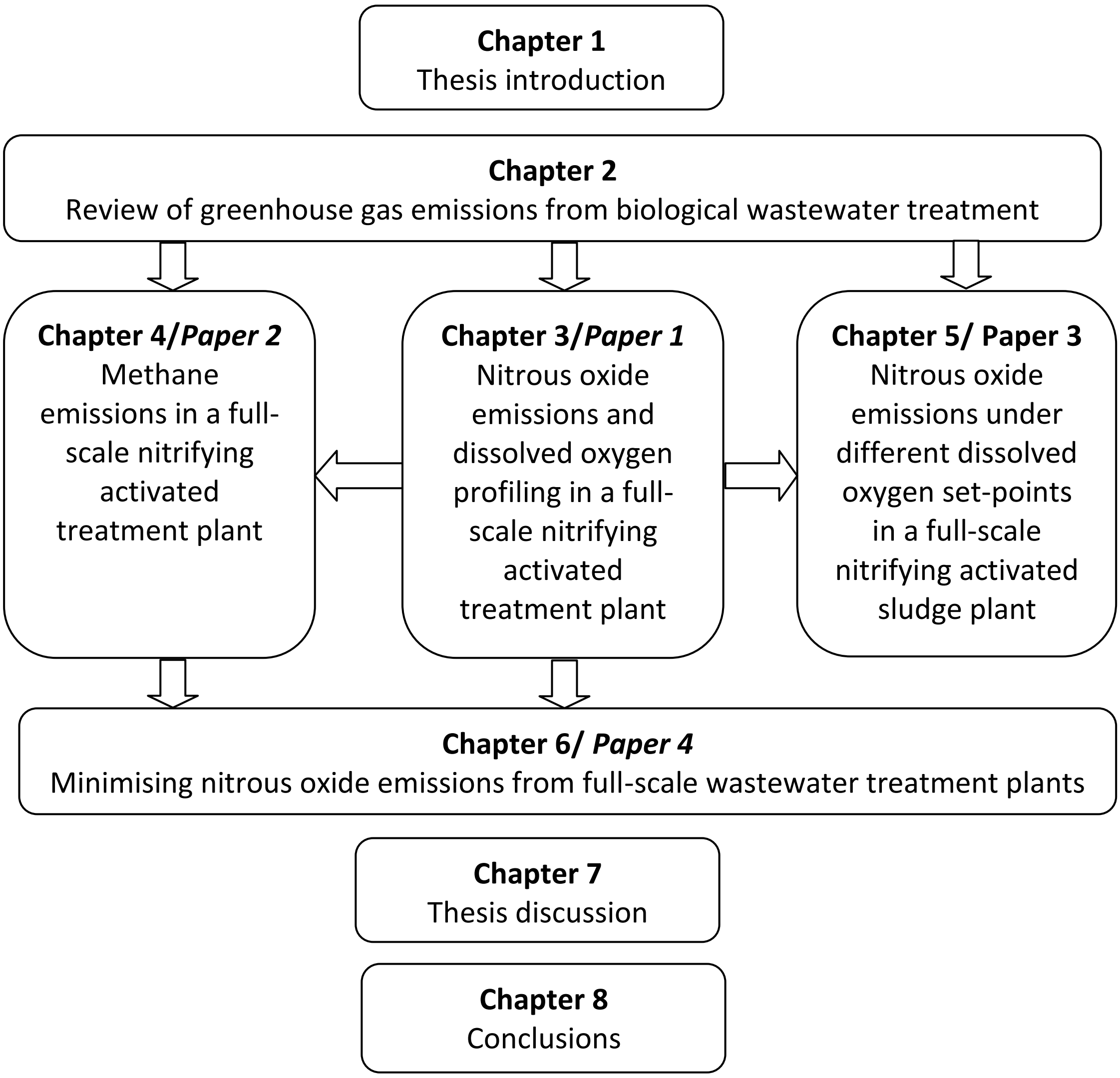

Figure 1.2: Structure of thesis as a flow diagram with titles of each chapter

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1. Introduction

The Water Framework Directive (WFD) is an overarching legislation focusing more on outcomes to achieve “good ecological status” in inland and coastal waters, than on consents (Ainger et al., 2009; DEFRA, 2011). The WFD is therefore pushing for improved, high quality effluent and greater biological nitrogen removal from wastewater treatment plants (WWTPs). This implicitly leads to more energy-intensive processes in wastewater treatment, particularly with aeration systems in activated sludge plants (ASP), which account for most of the energy consumption (55 %) in WWTPs (Cafoor, 2008; George et al., 2009; Reffold et al., 2008;). Currently, around 56 % of the greenhouse gas (GHG) emissions from the water industry derive from wastewater (Reffold et al., 2008), and this is likely to increase under the requirements of the WFD. On that basis, carbon dioxide equivalent (CO_2e) emissions by WWTP are expected to increase by 110,000 tonnes per year (George et al., 2009). On the other hand, the Climate Change Act imposes a legal target of significantly reducing UK GHG emissions by 80 %, from the 1990 levels, by 2050 (Tribe, 2010). The UK Government’s commitment to achieving this target is visible through the Stern Report, Energy White Paper and Climate Change Bill (Reffold et al., 2008), all of which provide the scientific and legislative drive to reduce the overall impact of GHGs (Reffold et al., 2008).

In order to respond to these stringent regulations and reduce carbon footprint in a cost-effective way (Tribe, 2010), the focus is shifting towards more sustainable and more advanced control technologies that can off-set the ever-increasing energy demand in wastewater treatment, particularly as populations grow and consent regulation tightens (Ainger et al., 2009; Rothausen and Conway, 2011). An example of such approaches is the introduction of more variable discharge consents. However, as the industry becomes more driven by improved water quality standards and reduction of carbon footprint, there is the risk is that these measures may come at the expense of higher GHG emissions into the atmosphere (Tallec et al., 2006). At the same time, as sustainable energy sources become more readily available, added to a potential decarbonisation of the power grid (Ainger et al., 2009; Listowski et al., 2011), an increase in GHG emissions will have a negative effect on the carbon footprint of a WWTP. This will become more relevant if changes in legislation lead to an enforcement of process emissions reporting. Therefore, WWTPs are faced with the challenge of balancing between increasing wastewater treatment efficiency and effluent quality as well as reducing carbon and GHG emissions. This emphasises the need for further investigation towards directly quantifying emissions from wastewater treatment, in order to link them to data on operational activities (Foley et al., 2010a). However, readily available inventories for WWTPs, particularly for methane (CH_4) and nitrous oxide (N_2O) emissions, are largely based on either lab-based studies or estimations from model applications, at times with high uncertainty levels (GWRC, 2011; UKWIR, 2009). This review addresses recent developments in the direct quantification and reporting of CH_4 and N_2O process emissions from full-scale WWTPs, with particular focus on aerated biological wastewater treatment processes and operational triggers contributing to formation and emission of N_2O. Finally, gaps in current knowledge are identified.

2.2. Greenhouse gas emissions from full-scale biological wastewater treatment

The growth in anthropogenic activities such as higher production of fossil fuels and waste, and intensive industrial and agricultural activity (Cakir and Stenstrom 2005), has led to a steady rise in the levels of GHG in the Earth's atmosphere, with specific emphasis on: CO_2, CH_4 and N_2O, which have increased by 30, 145 and 15 % respectively (El-Fadel and Massoud, 2001). It is believed that these increases are contributing to the global warming potential (GWP) (Søvik and Kløve 2007). Wastewater treatment can contribute to this effect through CO_2 emissions associated with the energy requirements of a WWTP but also via direct GHG emissions produced by the biological processes used to remove pollutants from wastewater. The most prominent process emissions are those from CH_4 and N_2O, with GWP 21 and 310 times stronger than CO_2 (IPCC, 2006), respectively. Therefore, they can have a significant impact on the carbon footprint of a WWTP.

2.2.1. Methane emissions

Human activities alone were estimated to contribute to a total of 6,875 million tonnes of CO_2e equivalents (MtCO_2e) to CH_4 emissions in 2010 (Fig. 2.1), with 9 % of that coming from wastewater treatment (GMI, 2010; USEPA, 2006; Yusuf et al., 2012). Indeed, CH_4 is considered the most significant GHG emitted from wastewater management (El-Fadel and Massoud, 2001). Since the 1990s, when it stood at 446 MtCO_2e, CH_4 emissions from wastewater treatment have increased by 17 % in 2000 and 33 % by 2010 (Yusuf et al., 2012). This therefore means that wastewater contribution to global CH_4 emissions is expanding, with a forecasted rise of 12 % by 2020 (GMI, 2010; USEPA, 2006) and 18 % by 2030 (USEPA, 2012). However, these values are estimated projections, with a high degree of uncertainty (USEPA, 2012), whereby quantifiable data is largely missing due to time and available methodology restrictions (USEPA, 2012).

Methane is biologically produced during the chemical reduction of the organic fraction of wastewater, COD (chemical oxygen demand) or BOD (biochemical oxygen demand), by methanogenic *Archaea*, under anaerobic conditions. Therefore, CH_4 production is mostly expected from places such as rising sewers (Guisasola et al., 2009) and parts of a WWTP where anaerobic conditions prevail (Daelman et al., 2012). Due to the oxygen availability in ASPs, particularly in aerated tanks, negligible CH_4 production is expected to occur therein and therefore limited information is available (Daelman et al., 2012). Nevertheless, a few studies have reported on emissions across primary to secondary treatments (Table 2.1), with significant variation in numbers. In one study for example (Ren et al., 2013), three different biological nutrient removal processes (BNR) were investigated, with emissions varying from 63 to 928 gCH_4/person/year (Table 2.1). This highlights the differences between CH_4 formation versus emission, i.e., although produced in oxygen-absent environments, it can nevertheless be emitted from a number of sources within a WWTP. This is particularly the case with units where aerated conditions prevail, such as in ASPs (Daelman et al., 2012) and oxic tanks in general (Ren et al., 2013; Wang et al., 2011a), where dissolved CH_4 can be released into the atmosphere through air-stripping. Indeed, the release from aerated zones has been found to be higher than that from non-aerated areas, where instead, the dissolved CH_4 levels were higher (Ren et al., 2013). Therefore, CH_4 trends from full-scale studies show a high degree of variability, with emissions reported to be site and process-specific.

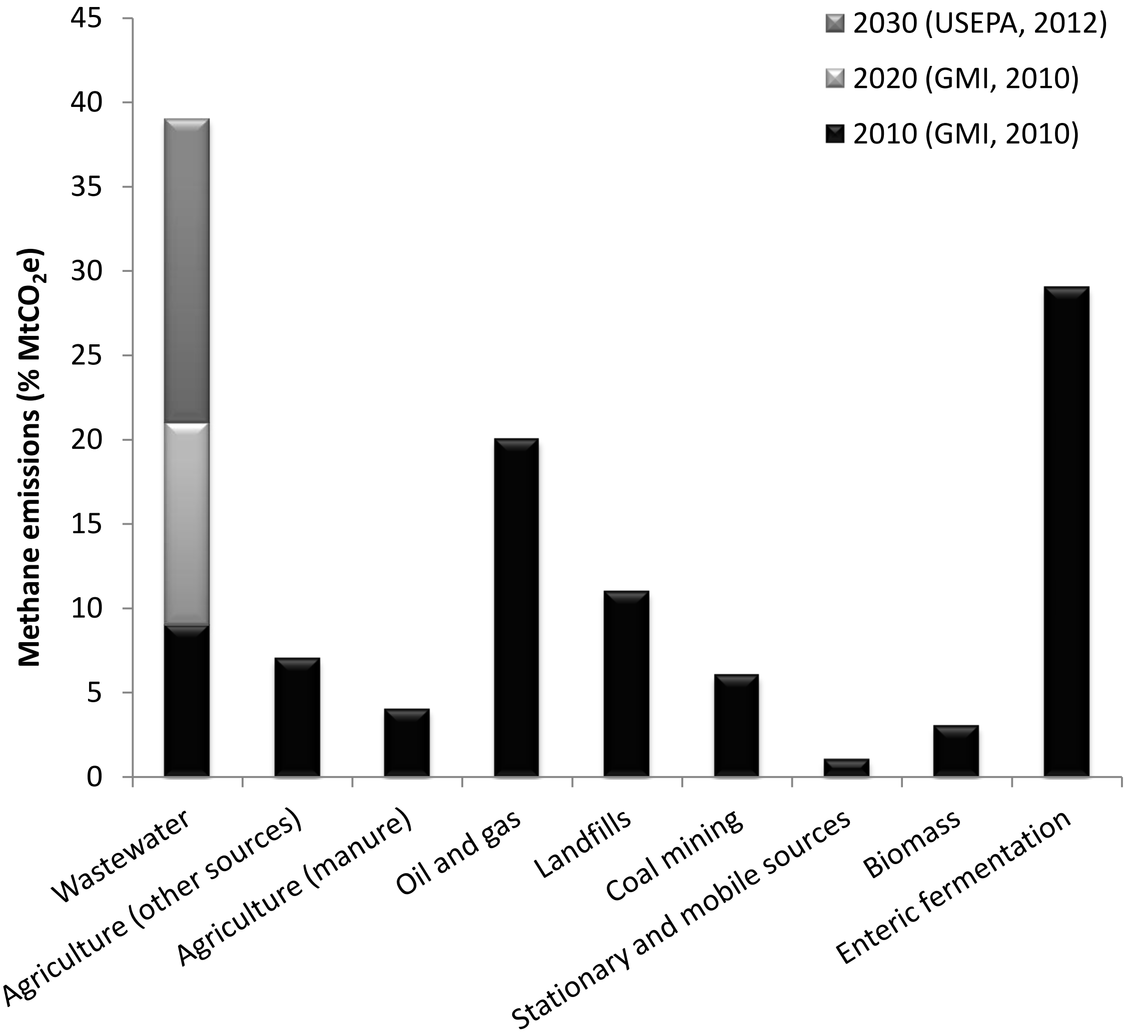

Figure 2.1: Estimated global anthropogenic contribution to CH_4 emissions (in CO_2e) by sources for 2010 and 2020 and 2030 projections for wastewater treatment (adapted from: GMI, 2010; USEPA, 2012)

Table 2.1: Normalised CH_4 emission factors for this and other full-scale studies

Author	gCH_4/person/ year	Emission factor $KgCH_4$ /kg influent COD (%)	Comments
Czepiel et al. (1993)	39	0.34 [a]	Durham WWTP, New Hampshire, United States. Grab samples method. Used by the Environment Agency (UK) to estimate emissions from ASPs (George et al., 2009).
Daelman et al. (2012)	306	1.13 [b]	Kralingseveer WWTP, Netherlands. Online measurements of CH_4 off-gas. Dissolved CH_4 measured.
Ren et al. (2013)	63–149 82–207 292–928	0.14 [c] 0.71 [c] 1.26 [c]	WWTPs in Jinan and Qingdao, China. Grab samples method. Dissolved CH_4 measured.
Wang et al. (2011a)	11	0.08	Jinan WWTP, China. Grab samples method. Dissolved CH_4 measured.

[a] *Originally expressed as 0.16 % as $kgCH_4/kgBOD_5$. Conversion factor from Grady et al. (1999) where: COD ≈ (2.1) (BOD_5) used to convert to $kgCH_4/kgCOD$*
[b] *Includes an anaerobic digestion facility*
[c] *Expressed as $kgCH_4/kgTOC$ (total organic carbon) removed*

2.2.2. Nitrous oxide emissions

In terms of global warming impact, N_2O emissions contribute much more than CH_4 because of its strong GWP (Åkerman et al., 2011). The assessment of N_2O emissions from WWTP by full-scale measurements (Table 2.2) has shown variability in N_2O emissions between sites and processes, with 0.001 to 25 % of the nitrogen load emitted as N_2O (Table 2.2). Indeed, this variability is not only seen at full-scale but also at lab-scale, under controlled conditions, where emissions varied from zero to 44 % (Table 2.2). Variability in N_2O exhibits a diurnal trend, which correlates well with diurnal variability in nitrogen loading (Ahn et al., 2010a; b). The sequence of anoxic and aerobic zones in ASPs, the different configurations and operational conditions, are expected to drive overall N_2O emissions at full-scale (Ahn et al., 2010a; Law et al., 2012). Furthermore, WWTPS designed and operated for low effluent total nitrogen, as for example below 10 mgN/L, were shown to have less variability in produced N_2O than plants which only achieved partial denitrification (Foley et al., 2010a). Differences in monitoring and quantification methods, ranging from short-term grab sampling to long-term online monitoring (Table 2.2) have also been suggested as contributing towards observed variations (Law et al., 2012). Most full-scale studies report on N_2O emitted mainly from aerated tanks (Ahn et al., 2010a; b; Ren et al., 2013), although significant accumulation can occur in anoxic zones (Ren et al., 2013), which once in contact with more aerated environments, is air-stripped. Equally, N_2O generated during aerobic phases is quickly stripped due to aeration, thereby making nitrifying tanks an important source of off-gas N_2O emissions from WWTPs (Ahn et al., 2010a; Law et al., 2012).

Nitrous oxide production seems to mainly occur during nitrification pathways (Tallec et al., 2006; Wunderlin et al., 2012), particularly during ammonia (NH_4^+) oxidation (Kim et al., 2010), controlled mostly by changes in operational parameters (Kampschreur et al., 2008a), specifically in dissolved oxygen (DO) and nitrite (NO_2^-) concentrations, but also by nitrogen loadings, solids retention times (SRT), pH and temperature. Production of N_2O during denitrification is expected, as an intermediate pathway in the reduction of nitrate (NO_3^-) to dinitrogen gas (N_2), although certain conditions can also trigger accumulation of N_2O, such as transient low DO and limited organic carbon source, therefore leading to incomplete denitrification. As such, complete nitrification followed by complete denitrification can limit N_2O production and subsequent release (Ahn et al., 2011). Based on the findings reported in Table 2.2, the main factors contributing to N_2O production are discussed in the next section.

Table 2.2: Overview of nitrous oxide emissions at full and at laboratory scales

Reference	Emitted N_2O (% N load)[a]	Type of process	Wastewater type/location	Sampling frequency	Remarks
Full-scale					
Ahn et al., 2010a	0.003–2.59	BNR and non-BNR – ASP primary influent (12 plants)	Municipal/ USA	Online monitoring, 2 years	Aerated zones significantly contributed to N_2O emissions compared to non-aerated zones.
Beckinser et al., 1996	0.001–0.04	Anoxic-aerobic ASP	Municipal/ Germany	Grab samples	N_2O emissions largely dependent on COD/N ratio – negative correlation.
Czepiel et al., 1995	0.035–0.05	ASP	Municipal/ USA	Grab samples taken once a week for 15 weeks	N_2O emitted mostly from aerated zones. Very little from non-aerated zones.
Desloover et al., 2011	5.1–6.6	Floc-based sequential partial nitritation and anammox	Industrial/ Belgium	Online (snapshot cycles), over 7 weeks	Average of 27 Kg-N/day from partial nitritation, (DO was lower at =<1 mg/L so ideal for N_2O emissions). No N_2O from nitrification, DN or annamox.
Foley et al., 2010a	0.6–25	BNR (7 plants)	Municipal/ Australia	Intensive grab sampling, 2–4 hours duration, over 2 days for 5 months	Correlation between N_2O emissions and NO_2^-.
GWRC, 2011	0–0.3	Four WWTP: completely mixed, plug-flow, membrane reactor)	Municipal/ France	Online. Protocol for dissolved N_2O developed	NH_4^- and DO most influencing parameters on N_2O emissions. Aeration also important due to air-stripping, since N_2O was always emitted during aerated steps.
Joss et al., 2009	0.4–0.6	Partial nitritation-anammox sequencing batch		Online measurements	Observed N_2O emissions slightly higher than in conventional nitrogen removal systems.

		reactor (SBR), 3 plants, 5 tanks)			
Kampschreur et al., 2008b	2.3	Nitritation-annamox	Reject water/ Netherlands	Online measurements over 3 days	Low DO in aerated phase and high NO_2^- concentrations in anoxic phase increased N_2O emissions.
Kampschreur et al., 2009b	1.2	Nitritation-annamox, potato processing plant	Industrial/ Netherlands	Online measurements over 92 hours	Emissions responded to operational variations. Over-aeration could dramatically increase N_2O emissions.
Ren et al., 2013	0.006–0.14 (% removed TN)	Anaerobic/anoxic/oxic (A/A/O) BNR plants	Municipal/ China	Grab sampling	NO_2^- concentration and oxidation-reduction potential (ORP) significantly influenced N_2O emissions. Oxic tanks were dominant source of emissions.
Kimochi et al., 1998	0.01–0.08	Intermittent aeration ASP	Municipal/ Japan	Grab sampling over 2-hour period covering 4 aeration cycles	Shorter aeration periods led to lower N_2O emissions. Most N_2O emitted during aerobic periods of intermittent aeration.
Sümer et al., 1995	0.001	ASP	Municipal/ Germany	Grab samples every other week over 1 year	N_2O emitted more during nitrification than denitrification. Production of N_2O related to NO_2^- and NO_3^- concentrations and pH.
Sun et al., 2013	1.95–6.52	SBR and A/A/O plants	Municipal/ China	Grab samples collected every 10 minutes for 30 minutes	N_2O emissions from SBR 3.4 times higher than in A/A/O. Highest N_2O emissions from oxic tank in A/A/O plus feeding and aeration periods in SBR largest respectively.

Wang et al., 2011b	0.09–0.12	Tertiary WWTP with A/A/O BNR	Municipal/ China	Grab sampling over 8 hours, 3 times a week for 3 months	DO and NO_2^- concentrations in oxic tanks most significant factors influencing N_2O emissions.
Laboratory scale					
Ahn et al., 2011	0.13–2 (% NH_4^+ load)	Full and partial nitrification processes	High strength nitrogen wastewater/ USA	Grab sampling 2 hours (per minute), every other week, 104 days	Transient N_2O emissions higher in partial nitrification than in steady-state full nitrification.
Burgess et al., 2002a	0.08–1.17 (% NH_4^+ load)	ASP	Synthetic/ UK	Online monitoring in a pilot plant.	At shock loads <1.6 mg ammonia (NH_3-N/gTSS), N_2O rate of increase related to size of load. At >1.6 mgNH_3-N/gTSS, and during aeration failure, N_2O dependent on NO_2^- peaks.
Hu et al., 2010	26.1	Anoxic-aerobic SBR	Synthetic/ China	Grab sampling with headspace method, 3 months	Emissions highly dependent on aeration and DO.
Hu et al., 2011a	0.4–27.5	Anoxic-aerobic SBR	Synthetic/ China	Grab sampling	N_2O emitted mostly during the aerobic phase, lowest during full nitrification. Emissions increased with drop in temperature.
Hu et al., 2011b	0.83–1.72	Anoxic-aerobic SBR	Synthetic/ China	Grab sampling over 3 months.	N_2O accumulation increased with NH_4^+ oxidation and low aeration. Emissions stripped mostly during aerobic phases.
Kampschreur et al., 2008a	2.8 (%NH_4^+ load)	Plug-flow nitrifying ASP	Synthetic/ Netherlands	Continuous online monitoring, 9 months	N_2O emissions strongly influenced by DO, NO_2^- and NH_4^+, particularly under dynamic conditions.

Kim et al., 2010	2.94 (% oxidised NH_4^+)	Nitrifying ASP	Piggery effluent/ China	Isotopic and gas analysis	N_2O emissions dependent on NH_4^+ oxidation by AOB. N_2O produced through nitrifier denitrification pathway.
Law et al., 2011	1 (% oxidised NH_4^+)	Partial nitritation SBR	Municipal/ Australia	Online monitoring	pH significantly impacted on N_2O production, which was highest at pH 8.
Lo et al., 2010	0.5–21.2	Hybrid simultaneous nitrification, denitrification and phosphorus removal	Synthetic/ Canada	Online monitoring over 620 days.	Whilst N_2 was the main end product for biofilm system, for suspended sludge and hybrid systems it was N_2O.
Lotito et al., 2012	0.12–0.56	Nitrifying/denitrifying ASP	Municipal/ Switzerland	Online measurements from pilot-scale plant over several months	DO set-point in NH_4^+ oxidation significantly impacted on emissions. Low sludge age and high nitrogen loads also important.
Rassamee et al., 2011	0–0.39	Anoxic-aerobic SBR	Municipal/ USA	Online measurement of dissolved N_2O over 6 months	N_2O emitted during incomplete nitrification and denitrification. N_2O produced mostly due to changes in DO, NH_4^+ and NO_2^- concentrations and process disturbances.
Shi et al., 2011	5.3	Partial nitrification-denitrification aerobic granulation SBR	Synthetic/ China	Grab sampling over 60 days	Higher emission rates during nitrification stage.
Tallec et al. 2006	0.1–0.4 (% oxidised NH_4^+)	Nitrifying ASP	Municipal/ France	Online measurements	N_2O emissions higher during low oxygenation (around 1 mg/L), mostly due to nitrifier denitrification.

Tallec et al., 2008	0.4 (% reduced NO_3^-)	Denitrifying ASP	Municipal/ France	Online measurements	Under DO conditions 0.4 to 1.1 mg/L, denitrification contributed 40 % and nitrification 60 % to N_2O production.
Wunderlin et al., 2012	0.2–15 (% nitrogen conversion)	Nitrifying-denitrifying ASP	Municipal/ Switzerland	Online measurements	N_2O produced mainly by AOB under aerobic and low COD conditions, dominated by nitrifier denitrification. Under anoxic conditions heterotrophic N_2O production triggered by low DO and high NO_2^-.
Xiuhong et al., 2008	4–44 (% removed TN)	BNR SBR	Municipal/ China	Grab sampling	N_2O produced mainly during initial stage of aeration. N_2O produced at end of nitrification was further reduced to N_2 during denitrification.
Yu et al., 2010	Below detection limit (40 ppb) at steady state	Nitrifying culture	Pure culture/ USA	Online monitoring	N_2O production by AOB increased in response to a recovery from transient anoxia, due to a shift in metabolism from low to high specific activity.
Zheng et al., 1994	2.3–16	Continuous nitrifying ASP	Synthetic/ Japan	Grab sampling	N_2O emission increased with decreases in DO and in SRT.

[a] *Refers to influent total nitrogen load, unless otherwise indicated*

2.3. Nitrous oxide production during wastewater treatment

Both field and lab-scale studies show that N_2O in WWTPs is mainly generated during nitrogen removal processes (Ahn et al., 2010a; b; Kampschreur et al., 2008a; Tallec et. al., 2006). Excessive nitrogen in wastewater effluent can lead to eutrophication of receiving waters (high content of nutrients that stimulate excessive plant growth in the water), with depletion of oxygen in the water (hypoxia, due to higher oxygen demand) and ammonia (NH_3) toxicity, having a negative impact on fish populations and other aquatic organisms. Additionally, NO_3^- in drinking water can cause methemoglobinemia or "blue baby syndrome" in infants (Fewtrell, 2004). This therefore justifies the stringent regulations on wastewater treatment with regards to nitrogen effluent discharge consents (particularly with ammonia-nitrogen, NH_4-N). Nitrogen is removed from wastewater during a complex biological process (Gernaey et al., 1997) consisting of two steps (Fig. 2.2): nitrification and denitrification – both largely associated with N_2O emissions (Kampschreur et al., 2009a; Tallec et al., 2006). Traditional wastewater treatment processes utilize a two-stage activated sludge plant for nitrogen removal, an aeration tank where nitrification takes place adjoined to an anoxic zone for denitrification. These processes, and the possible routes by which N_2O is produced, are further explained in the next sub-sections, and relevant N_2O production pathways are shown in Fig. 2.2.

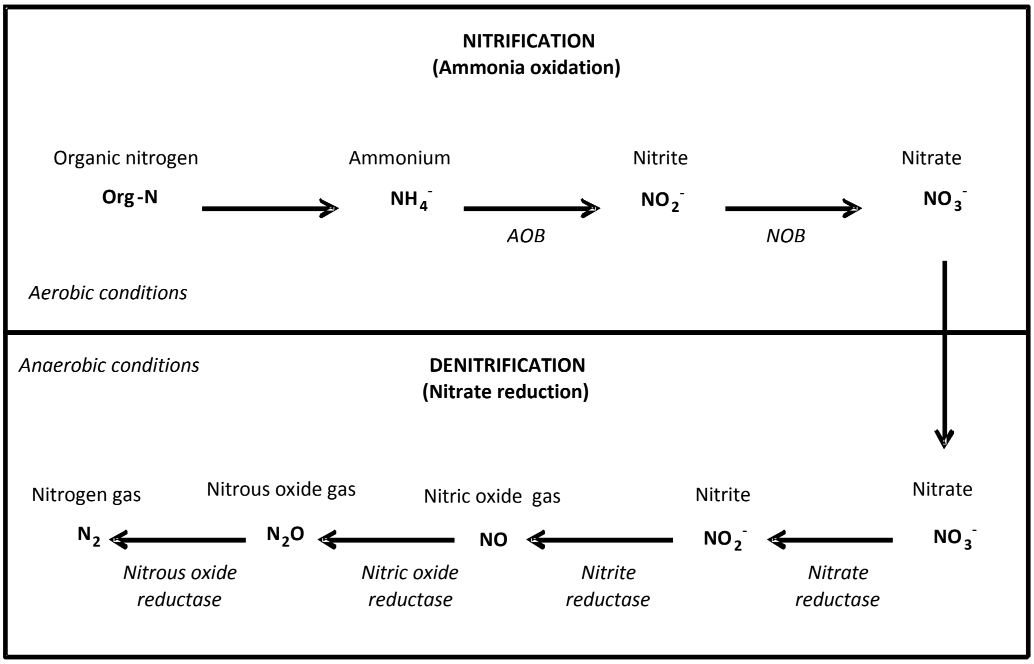

Figure 2.2: Biological nitrogen conversions during wastewater treatment (nitrification and denitrification steps)

2.3.1. Nitrous oxide production during nitrification

Nitrification is concerned with the oxidation of NH_4^+ to NO_2^- and then to NO_3^-, under aerobic conditions, by two groups of autotrophic nitrifying bacteria: ammonia-oxidising bacteria (AOB) that convert NH_4^+ to NO_2^- and NO_2^- oxidising bacteria (NOB) that convert NO_2^- to NO_3^- (Fig. 2.2). Metcalf and Eddy (2003) suggest a minimum DO concentration of 2.0 mg/L in order to ensure maximum nitrification rates. Heterotrophic ammonia-oxidising bacteria and, to a lesser degree ammonium-oxidising archaea, will also occur during nitrification, particularly at low DO levels, long SRT and high organic loading rates (Park et al., 2000; Kampschreur et al., 2009a). During microbial nitrification, N_2O can be produced via two pathways, both related to the oxidation of NH_4^+ (Kampschreur et al., 2009a): through the reduction of NO_2^-, in a pathway called nitrifier denitrification and through hydroxylamine (NH_2OH) oxidation, one of the intermediates in NH_4^+ oxidation.

Nitrifier denitrification

Under limited DO conditions, nitrifying AOB will contribute significantly to emissions (Colliver and Stephenson, 2000; Yu et al., 2010), particularly with high NO_2^- accumulation, through a nitrifier denitrification pathway (Hu et al., 2011a; Kampschreur et al., 2009b; Tallec et al., 2006). Because AOB have a greater affinity for oxygen than NOB (Grady et al., 1999), under anoxic or sub-oxic conditions, the oxidation of NO_2^- to NO_3^- in the final step of nitrification is therefore limited, with resulting accumulation of NO_2^- (Colliver and Stephenson, 2000; Wrage et al., 2001). In these situations, AOB will reduce the accumulating NO_2^- to nitric oxide (NO) and then to N_2O, using NH_4^+, NH_2OH, molecular hydrogen or pyruvate as electron donors (Wrage et al., 2001; Wunderlin et al., 2012). Furthermore, literature has shown that AOB have an active NO_2^- reductase enzyme system (Bock et al., 1991, Wrage et al., 2001), allowing it to use NH_2OH as an electron donor for example, and NO_2^- as an electron acceptor, with the latter being further reduced to N_2O (Shiskowski et al., 2004). Indeed, only the genes that encode for the reductase enzymes that reduce NO_2^- and NO, *nirK* and *nor* genes respectively, are found in the genome of AOB, but there is no gene in the bacteria that encodes for the enzyme N_2O reductase, which further reduces N_2O to N_2. This suggests that N_2O is the final product of nitrifier denitrification (Beaumont et al., 2004; 2005; Casciotti and Ward, 2001; Law et al., 2012; Shaw et al., 2006). Low DO conditions seem to be the necessary trigger to induce NO_2^- reductase activity (Bock et al., 1991; Goreau et al., 1980).

Furthermore, AOB have been shown to simultaneously use NO_2^- (nitrifier denitrification) and oxygen (complete nitrification) as electron acceptors (Bock et al., 1990). The ratio of oxygen to NO_2^- used as electron acceptor is dependent on available DO concentrations in the nitrifying culture, and this ratio lowers as DO increases, therefore, oxygen becomes the preferred electron acceptor and complete nitrification takes place (Wrage et al., 2001). This mechanism can have huge implications at full-scale in terms of N_2O production by AOB, particularly under sub-optimal DO conditions or in partial nitrification processes, where NO_2^- accumulates in very high levels. Indeed, it has been reported that under very low DO conditions, nitrifier denitrification can contribute up to 83 % of the N_2O emissions (Law et al., 2012; Tallec et al., 2006) and this pathway was found to be the main contributor of N_2O in a nitrifying activated sludge (Kim et al., 2010), particularly under aerobic conditions and low COD loads (Wunderlin et al., 2012).

Hydroxylamine oxidation

An alternate route linked to the production of N_2O during nitrification is that of NH_2OH oxidation (Kampschreur et al., 2009a; Kim et al., 2010; Wrage et al., 2001; Wunderlin et al., 2012), either by biological oxidation or by chemodenitrification (Ritchie and Nicholas, 1972; Wunderlin et al., 2012). It has been suggested that N_2O production can occur through the intermediates of biological NH_2OH oxidation, potentially due to an imbalance in metabolisms of AOB (Wunderlin et al., 2012; Yu et al., 2010) or chemically formed as part of incomplete oxidation of NH_2OH with NO_2^- as an electron acceptor (Ni et al., 2013); however, the biological versus chemical oxidation of NH_2OH is a poorly understood mechanism. Finally, the production of N_2O via this route is likely to be minimal during biological wastewater treatment, as the concentrations of NH_2OH in full-scale are much lower than those found under experimental conditions (Kampschreur et al., 2009a; Wunderlin et al., 2012) and nitrifier denitrification by comparison, has been reported as a more significant N_2O production pathway in nitrifying activated sludge (Kim et al., 2010; Yang et al., 2009).

2.3.2. Nitrous oxide production during heterotrophic denitrification

Denitrification is a respiratory process carried out under anoxic conditions by metabolically different microbial groups (Kampschreur et al., 2009a; Tallec et al., 2008), during which organic matter is oxidised through the reduction of NO_3^-, NO_2^-, NO and N_2O (Fig. 2.2), with ultimate conversion to N_2 (Wicht, 1996). With N_2O generally acting as an intermediate during denitrification (Hu et al., 2011a; Tallec et al., 2008; Zheng et al., 1994), this process had been previously identified as the predominant source of N_2O production (Czepiel et al., 1995; Hanaki et al., 1992; Itokawa et al., 2001), mostly as an end product instead of N_2, under low DO conditions (Hu et al., 2011a; Tallec et al., 2008; Zheng et al., 1994). A pathway in which heterotrophic microorganisms carry out denitrification to N_2O as the final product is referred to as incomplete denitrification. A number of operational factors can lead to accumulation of N_2O in ASPs thus triggering incomplete denitrification: NO_2^- accumulation, low DO, short SRT, low pH, and low carbon to nitrogen (C/N) ratio (Hanaki et al., 1992; Itokawa et al., 2001; Schulthess et al., 1994, 1995).

2.4. Factors influencing N_2O emissions at full-scale

Operational parameters such as DO, organic load, SRT, temperature, pH and NO_2^- concentrations have been linked as influencing N_2O production during biological wastewater treatment (Kampschreur et al., 2009a; Law et al., 2012). As more effort is put into evaluating N_2O production during full-scale wastewater treatment, the more it seems that it is about a number of factors creating conditions favourable to emissions, rather than individual parameters; more so under sub-optimal conditions (Kampschreur et al., 2008b). Overall, research suggests that the key operational conditions influencing and/or controlling emissions include: low DO conditions with high NO_2^- accumulation, during both nitrification and denitrification, and low COD/N ratio during denitrification also with NO_2^- accumulation (Colliver and Stephenson, 2000; Kampschreur et al., 2009a; Tallec et al., 2006). Finally, fluctuating, or dynamic operating conditions, can also contribute to N_2O emissions at full-scale (Kampschreur et al., 2008a; b, 2009; Yu et al., 2010). These factors are summarised in Fig. 2.3 and reviewed in the following sub-sections.

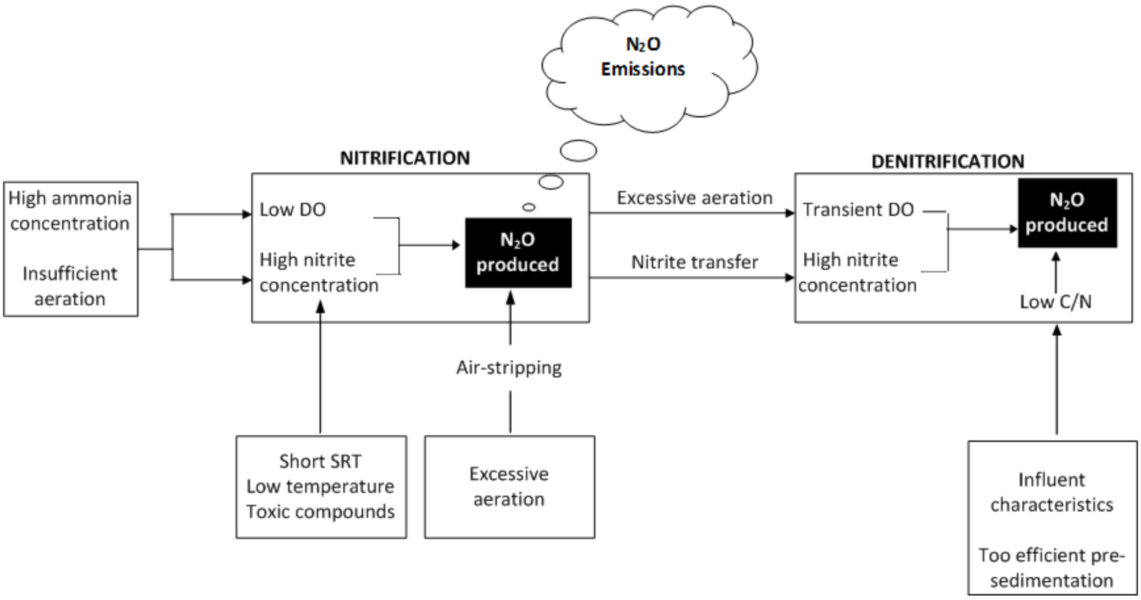

Figure 2.3: Main operational variables leading to N_2O production and emissions (adapted from GWRC, 2011; Kampschreur et al., 2009a)

2.4.1. Dissolved oxygen and aeration

Dissolved oxygen levels have a direct impact on N_2O emissions during both nitrification and denitrification (Colliver and Stephenson, 2000, Kampschreur et al., 2008a; 2009; Tallec et al., 2006; Zheng et al., 1994). Indeed, low oxygen leads to aerobic denitrification (Colliver and Stephenson, 2000), increasing the release of N_2O as a by-product during nitrification (Zheng et al., 1994; Kampschreur et al., 2008a; 2009; Tallec et al., 2006). Latest research indicates that most N_2O is generated during nitrification by autotrophic AOB (Ahn et al., 2010b; Tallec et al., 2006), with accumulation of NO_2^-. Furthermore, NO_2^- is reported to significantly influence N_2O emissions at DO concentrations around 1.0 mg/L, with that influence decreasing above and below that concentration (Tallec et al., 2006). Heterotrophic nitrifiers may also carry out nitrifier denitrification under low DO conditions, provided there is sufficient availability of an organic carbon source.

Additionally, highly aerated processes can dramatically increase oxygen levels in the wastewater, with the risk of some escaping to anoxic compartments (Kampschreur et al., 2009a). When DO is present in low amounts during anoxic or anaerobic phases, it can lead to incomplete denitrification, thereby resulting in N_2O accumulation (Tallec et al., 2008; Law et al., 2012). Indeed, without active air-stripping caused by mechanical turbulence (through aeration and/or mixing), N_2O can significantly accumulate in the bulk liquid (Law et al., 2012; Ren et al., 2013). Off-gas emissions on the other hand, are highly dependent on aeration rates (Hu et al., 2010; 2011a). Therefore, N_2O produced in non-aerated compartments such as anoxic zones, can nevertheless be emitted in aerated tanks where nitrification takes place, because of the effect of air-stripping (Law et al., 2012). The oxygen demand of nitrifying bacteria however, is particularly high, and hence the costs associated with aeration for oxygen supply represent a large section of the overall energy requirements of a WWTP. These costs are not solely related to the high oxygen demand exerted by the biomass, but also to the fact that oxygen is relatively insoluble in water, with low transfer efficiency. Therefore, DO is an important influencing factor, not only for N_2O production and emissions, but also for process efficiency and good settling characteristics (Rassamee et al., 2011; Sivret et al., 2008). Indeed, because of the effect of low DO on NH_4^+ oxidation, which triggers a biological stress response leading to N_2O production (Sivret et al., 2008), the application of N_2O monitoring has been suggested as a tool to detect early warning failure of nitrification (Burgess et al., 2002a; b; Butler et al., 2005; 2009). Real-time monitoring of N_2O emissions has also been investigated as a potential parameter to be integrated with real-time aeration control systems (Shiskowski et al., 2004; Sivret et al., 2008).

2.4.3. Low C/N ratio

During denitrification, other than transient low DO, N_2O production is strongly dependent on low C/N ratio, caused by limited availability in biodegradable organic carbon, thus leading to incomplete denitrification (Kishida et al., 2004). Under a COD/N ratio below 3.5, 20–30 % of influent nitrogen was emitted as N_2O during denitrification in anoxic phase (Itokawa et al., 2001), whereas in a pure culture study of *Alcaligenes faecalis (A. faecalis)*, up to 64 % was emitted as N_2O when organic carbon became limiting (Schalk-Otte et al., 2000). At a low C/N ratio of 2.6, N_2O production was 270 times higher when compared to optimal ratio of 4.5 (Kishida et al., 2004). Itokawa et al. (2001) found that denitrifiers have a larger N_2O than NO_3^- or NO_2^- reduction capacity; and that under low COD/N, high N_2O emission rates were mainly a result of endogenous denitrification with NO_2^- accumulation. This accumulation in turn, only observable during denitrification at low C/N conditions (Hanaki et al., 1992; Itokawa et al., 2001), is due to differences between NO_3^- and NO_2^- reduction capacity (Itokawa et al., 2001). Indeed, the inhibitory effect of NO_2^- on N_2O reduction was shown to be immediate (Alisanfi et al., 2008), with highest emissions reported shortly after accumulation of NO_2^- to 20 mg/L, at a C/N ratio of 3.0.

2.4.4. Dynamic operating conditions

Nitrous oxide concentrations are reported to be clearly dynamic in response to rapidly changing physical and chemical conditions (Ahn et al., 2010a; Burgess et al., 2002a; Desloover et al., 2012; Gejlsbjerg et al., 1997; Kampschreur et al., 2009a; b), specifically in the case of drops in DO levels (Kampschreur et al., 2008a), variable NO_2^- concentrations (Tallec et al., 2006) or NH_4^+ shock loads (Burgess et al., 2002a). Although low DO conditions are implicated as the key factor triggering nitrifier denitrification, studies have found this to happen also under aerobic conditions (Beaumont et al., 2004; Kim et al., 2010; Shaw et al., 2006; Yu et al., 2010). Indeed, fluctuating DO concentrations are more likely to generate N_2O than sustained low or high DO conditions (Ahn et al., 2010a; b; Chandran et al., 2011; Kampschreur et al., 2008a). On the other hand, abrupt or sudden changes in operating conditions trigger N_2O production (Kampschreur et al., 2008a; Rassamee et al., 2011; Yu et al., 2010). This is because high variability in NH_4^+, NO_2^- and NO_3^- concentrations, wastewater temperature and pH, submit the biomass to alternated aerobic and anaerobic environments, which in turn, result in N_2O production as a biological stress response (Hu et al. 2010; 2011a,b; Kampschreur et al., 2008b). Nevertheless, it has been reported that microbial populations that are subjected to a continuously dynamic environment may reduce their N_2O production, as they adapt over time to the changing conditions (Kampschreur et al., 2009a; Schalk-Otte et al., 2000).

However, most of the information available on the increase in N_2O emissions as a biological response to environmental changes has been mainly provided by lab-scale studies (Kampschreur et al., 2009a), where the controlled, steady-state conditions could be inadequate to predict the complexity of full-scale microbial and operational conditions, particularly under dynamic settings (Kampschreur et al., 2008b, 2009a). Caution is therefore advised when extrapolating such data to represent what happens in full-scale WWTPs (Kampschreur et al., 2008b).

2.5. Nitrous oxide emissions from WWTP: assessing current gaps in knowledge

With the current trends in legislation moving towards more stringent discharge consents and reduced carbon footprint, WWTPs are faced with two problems: firstly with minimising nitrogen discharge and secondly with reducing energy consumption (Chachuat et al., 2005). In order to achieve the latter, aeration reduction strategies may offer an appealing prospect. However, lower aeration rates lead to low DO conditions, which in turn not only compromises effluent quality but also triggers N_2O production. On the other hand, variable aeration control could potentially provide operational efficiency and cost-effective benefits. This implies the need for a more dynamic aeration control system, since traditionally, DO controls have been managed under fixed set-points, mostly based on theoretical values or operational experiences (Sivret et al., 2008). A number of process control methods are being investigated that can reduce aeration and therefore energy requirements and carbon footprint. Improved methods, such as adjusting DO set-points according to changes in loading rates (Sahlmann et al., 2004) or controlling the aeration on feedback or feed-forward depending on influent NH_4^+ count (Ingildsen et al., 2002), have indeed resulted in better aeration control and a 5–15 % cost reduction from therein (Sivret et al., 2008). Intermittent aeration can also provide prospective economic savings (Dotro et al., 2011), although there is the risk of a rapid DO depletion having a negative influence on the process as a whole, particularly on nitrification rates, and potentially increasing N_2O emissions.

Furthermore, studies suggest that it is in fact the abrupt “recovery” from low DO levels that may lead to higher N_2O generation rather than the “imposition” of low and sustained oxygenation (Ahn et al., 2010a; Yu et al., 2010). Indeed, if enough NH_4^+ is available, a sudden increase in DO during nitrification may result in NO_2^- accumulation, thus generating N_2O under high airflow rates (Ahn et al., 2010a; Kampschreur et al., 2008b; Yu et al., 2010) due to a nitrification denitrification pathway (Colliver and Stephenson, 2000). Therefore, further investigation is required in order to understand how these aeration control methods may, or may not, affect N_2O emissions. Furthermore, it is important that any changes are integrated into the long-term behaviour of the whole WWTPs as well as ensuring that they are safe and reliable (Chachuat et al., 2005). This is prompting researchers to look deeper into the impact of dynamic process conditions on N_2O emissions, firstly by attempting to quantify N_2O in WWTP as well as simultaneously look for ways to minimise emissions by integrating emission monitoring as part of operational control strategies (Chandran et al., 2011; Flores-Alsina et al., 2011). Indeed, the monitoring of N_2O emissions as an indicator for nitrification failure (Burgess et al., 2002a; b; Butler et al., 2005; 2009) and aeration control systems (Shiskowski et al., 2004; Sivret et al., 2008), has been investigated. However, in order to integrate N_2O monitoring into process control strategies, a robust monitoring framework, which both captures N_2O emissions and interactions with operational variables, must firstly be developed. Such robust methodology, will in turn, provide better knowledge of the relationship between aeration, DO and N_2O emissions during wastewater treatment, so that an optimal balance between reduced emissions and lower carbon footprint as well as improved final effluent, can be achieved.

However, consensus on the mechanisms of N_2O production, as well as conclusive quantifiable data from full-scale studies, is still lacking within the scientific community (Corominas et al., 2012). This limitation comes mainly from the absence of regulatory enforcement to report on process emissions. As such, there is a lack of compliance standards, which means that quantification of full-scale emissions is usually reliant on various methodologies (Listowski, 2011), which not surprisingly, leads to considerable variation in reported values (Table 2.2). Additionally, without legislative backing or financial benefits, it will be challenging for WWTPs to promote GHG mitigating measures which will undoubtedly impact on operational expenditures (Pijuan et al., 2014). Ultimately, this will rely on the balance between doing the right thing for the environment versus cost implications. However, as the water industry moves towards a “carbon neutral” future, driven by legislation such as the UK’s Climate Change Act, if made compulsory, reporting of GHG process emissions will become increasingly relevant to the total carbon footprint of a WWTP (Listowski et al., 2011), particularly under the prospect of carbon taxing (Pijuan et al., 2014). This scenario will indeed encourage accurate methodologies to account for, as well as to mitigate process emissions.

Nevertheless, the challenges offered by the very nature of full-scale research, have somewhat limited development of robust methods. However, the variability on reported emissions (Table 2.2) implies that, reliance on estimated data may oversimplify what is really emitted at full-scale, since it fails to take into account influencing factors such as changes in operational conditions, which are inherent to a complex wastewater treatment environment (Ahn et al., 2010a; b; Foley et al., 2010a). A lack of quantitative data may hinder further evaluation of carbon mitigation strategies (Wang et al. 2011c), such as in recognising sources and conditions (both from physical and biological processes) that promote emissions (Listowski et al. 2011). Therefore, over and under-estimation of data can be best avoided by employing a real-time, online monitoring methodology (Kampschreur et al., 2009a), to provide an accurate picture of emissions at full-scale, with impact on the associated operational carbon footprint. Although a N_2O emission monitoring method has been developed and adopted by the Environmental Protection Agency (EPA) in the United States (Chandran et al., 2009), key differences still prevail in measuring techniques employed worldwide (Table 2.2). Without a consistent approach, it may be difficult to assess the real contribution from WWTPs to N_2O emissions, since different methods clearly lead to diverse findings.

Indeed, where available, findings show a fluctuating emission profile, dependent on dynamic operational behaviour (Ahn et al., 2010a; b; Foley et al., 2010a), although online measurements to confirm these observations at full-scale remain limited (Kampschreur et al., 2009a). Therefore, the repercussions of rapidly changing operating conditions on N_2O emissions at full-scale, remain somewhat inconclusive. Nevertheless, it has been postulated that a sub-optimal environment may be responsible for inducing N_2O production and subsequent emissions in ASPs (Gejlsbjerg et al., 1997; Hu et al., 2011a,b; Kampschreur et al., 2008b, 2009a; Law et al., 2011; Zheng et al., 1994). Zheng et al., (1994) reported that although N_2O production to some extent, could not be completely removed from nitrification, it could nevertheless be minimised (and even prevented during denitrification), if optimised conditions were kept in order to prevent incomplete nitrification. Additional to DO and airflow rate, however, other parameters must be kept optimal in order for efficient nitrogen removal and low emissions to prevail. This therefore suggests that promoting complete nitrification and denitrification may lead to a reduction in N_2O emissions, since N_2O production in nitrification would eventually be consumed during denitrification instead of emitted. Indeed, in two lab-scale studies, partial nitrification was reported to trigger significantly higher N_2O emissions than complete nitrification processes (Ahn et al., 2011; Hwang et al., 2006). However, outside of these two studies, and particularly at full-scale, robust comparative data categorising different nitrogen removal processes according to N_2O emissions are very limited (Desloover et al., 2012).

Nevertheless, the changes to which activated sludge systems are subjected, with constant switches between anoxic and oxic conditions, are quite common for engineered-based nitrogen removal wastewater treatment processes (Chandran et al., 2011), even when full nitrification and denitrification are promoted. Therefore, the exact mechanisms that trigger N_2O production during nitrogen removal are not fully understood. Through previous research, two different biological pathways of N_2O production by AOB have been proposed: nitrifier denitrification and oxidation of NH_4^+ to NH_2OH, both explained in previous sections of this review. However, there are still issues to unravel: firstly, the triggers for N_2O production via the NH_2OH route, particularly on the impact of this pathway at full-scale; and secondly, a clear distinction between nitrifier denitrification and NH_2OH oxidation, which due to the complex interactions between the two pathways makes it difficult to differentiate between respective contributing factors. Indeed, although several links between N_2O production and various conditions have been established for different types of processes (Table 2.2), a universal consensus is still lacking. Recently, considerable steps have been made towards reconstructing the metabolic pathways responsible for N_2O production by AOB under conditions which are relevant for BNR systems (Chandran et al., 2011). However, additional research remains paramount in order to build a genomic inventory around microbial populations and metabolic pathways involved in N_2O production. This inventory must include information on the quantitative relationship with influencing operating parameters, particularly DO, without which a comprehensive picture of how emissions evolve at full-scale cannot be completed. These therefore, continue to be the most important challenges to be tackled.

2.6. Conclusions

This review addressed recent developments in the quantification and reporting of GHG emissions in full-scale, from WWTPs. It also evaluated main operational and mechanistic triggers for N_2O production and gaps in current knowledge. The main findings include:

- Methane is emitted from full-scale biological wastewater treatment with considerable variability in emission trends, from 0.08–1.13 % of influent COD.

- Although not produced therein due to various inhibitory factors such as aerobic conditions and limited organic carbon, CH_4 is nevertheless emitted from aerobic compartments.

- Nitrous oxide emissions were also shown to vary considerably, both at full-scale (0.001–25 % of influent TN) and lab-scale (from zero to 44 % of various nitrogen fractions).

- The most significant biochemical pathways of N_2O production are suggested to occur during NH_4^+ oxidation by AOB, namely through nitrifier denitrification and NH_2OH oxidation. Accumulation of N_2O also occurs during heterotrophic incomplete denitrification.

- Therefore, the main operational conditions to influence N_2O production and emissions include: low aeration and high NH_4^+ concentrations leading to low DO (<1.0 mg/L) and accumulation of NO_2^- during nitrification; low C/N ratio, DO presence and high NO_2^- concentrations during denitrification.

- Dynamic or rapidly changing operational conditions, such as fluctuating DO, NH_4^+ shock loads and changes in aeration are also suggested to promote N_2O production and emission.

- The main gaps in current knowledge about N_2O emissions from WWTP include:
    - Scientific consensus on the relationship between N_2O emissions and influencing operational factors
    - A clear distinction between nitrifier denitrification and NH_2OH oxidation contributions to N_2O production
    - Knowledge of microbial species and consortia involved in nitrous oxide generation (genomic inventory)
    - A quantifiable N_2O emission inventory obtained from various full-scale nitrogen removal reactor configurations
    - A robust monitoring framework which captures both N_2O emissions and interactions with operational variables
    - Legislative backing and economical incentives to drive standard compliance and benchmarking in GHG emission reporting and mitigating strategies
    - Qualitative and quantitative requirements to achieve a balance between reduced GHG process emissions, lower carbon footprint and improved final effluent.

CHAPTER 3

PAPER 1: NITROUS OXIDE EMISSIONS AND DISSOLVED OXYGEN PROFILING IN A FULL-SCALE NITRIFYING ACTIVATED SLUDGE TREATMENT PLANT

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3. NITROUS OXIDE EMISSIONS AND DISSOLVED OXYGEN PROFILING IN A FULL-SCALE NITRIFYING ACTIVATED SLUDGE TREATMENT PLANT

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Abstract

This paper reports findings from online, continuous monitoring of dissolved and off-gas nitrous oxide (N_2O), combined with dissolved oxygen (DO) and ammonia (NH_4^+) loading, in a full-scale nitrifying activated sludge plant (ASP). The study was conducted over eight weeks, at a 210,000 population equivalent sewage treatment works in the UK. Results showed diurnal variability in the off-gas and dissolved N_2O emissions, with hourly averages ranging from 0–0.00009 kgN_2O-N/h for dissolved and 0.00077–0.0027 kgN_2O-N/h for off-gas N_2O emissions respectively, per NH_4^+ loading, depending on the time of day. Similarly, the spatial variability was high, with the highest emissions recorded immediately after the anoxic zone and in the final third pass of the aeration lane, where NH_4^+ concentrations were typically below 0.5 mg/L. The relationship between emissions and oxygenation showed that the highest figures were, on average, recorded during lower DO periods. Dissolved oxygen was shown to fluctuate between 0.5 to 2.5 mg/L, at the control set-point of 1.5 mg/L. This can thereby create dynamic (rapidly changing) DO conditions, which are known to favour N_2O production, both by autotrophic and heterotrophic processes in mixed cultures. Average mass emissions from the lane were greater in the off-gas (0.036 % of the influent total nitrogen) than in the dissolved (0.01 % of the influent total nitrogen) phase, and followed the same diurnal and spatial patterns. Nitrous oxide emissions corresponded to over 34,000 kg of carbon dioxide equivalents/year (kgCO_2e/year), adding 13 % to the carbon footprint associated with the energy requirements of the monitored lane. A clearer understanding of emissions obtained from real-time data can help towards finding the right balance between improving operational efficiency and saving energy, without increasing N_2O emissions.

Keywords: nitrous oxide, dissolved oxygen, nitrification, denitrification, wastewater, carbon footprint.

3.1. Introduction

Nitrous oxide (N_2O) is a greenhouse gas (GH) with a global warming potential (GWP) approximately 310 times higher than carbon dioxide (CO_2) (IPCC, 2006), and therefore unwanted even at small levels. Additionally, N_2O reacts with atomic oxygen to form nitric oxide (NO), which leads to the destruction of the stratospheric ozone layer (Tallec et al., 2008). Research shows that N_2O emissions can be released during wastewater treatment, particularly during nitrification and denitrification (Colliver and Stephenson, 2000; Dotro et al., 2011; Kimochi et al., 1998). Denitrification is the multi-stepped, anoxic reduction of nitrate (NO_3^-) to dinitrogen gas (N_2) by heterotrophic microorganisms. Nitrification consists of the aerobic oxidation of ammonia (NH_4^+) to NO_3^- via nitrite (NO_2^-), carried out in a two-stepped reaction by ammonia-oxidising (AOB) bacteria that oxidise NH_4^+ to NO_2^-, and by nitrite-oxidising bacteria (NOB) that oxidise NO_2^- to NO_3^-.

It is generally agreed that the mechanisms of N_2O emission during wastewater treatment are process-specific and therefore, related to operating conditions (Ahn et al., 2010b; Rassamee et al., 2011). An operating parameter believed to play a critical role in influencing emissions is dissolved oxygen (DO) (Tallec et al., 2008). An insufficient supply of oxygen in a nitrifying process can lead to incomplete nitrification, whereby autotrophic AOB reduce NO_2^- to N_2O, instead of oxidation to NO_3^- (Colliver and Stephenson, 2000), in a pathway known as nitrifier denitrification. Another route also linked to the production of nitrous oxide by AOB during nitrification is that of hydroxylamine (NH_2OH) oxidation (Kampschreur et al., 2009a; Wrage et al., 2001; Wunderlin et al., 2012), either by biological oxidation or by chemodenitrification (Wunderlin et al., 2012). Hydroxylamine is an intermediate formed during the first step of the oxidation of NH_4^+ to NO_2^-, and, under favourable experimental conditions (high NH_4^+ and low NO_2^- concentrations with a high oxidation rate), the presence of this compound has been shown to produce more N_2O than NH_4^+ oxidation (Wunderlin et al., 2012). However, the production of N_2O via this route is likely to be minimal during biological wastewater treatment, as the concentrations of NH_2OH in full-scale are in much lower magnitude than those found under experimental conditions (Wunderlin et al., 2012).

On the other hand, heterotrophic denitrification relies on the absence of oxygen, and the availability of nitrate and organic carbon. The presence of oxygen however, can inhibit denitrification enzymes, particularly N_2O reductase, which converts N_2O to N_2. This results in incomplete denitrification, whereby N_2O is generated as the end product instead of N_2. Therefore, DO may be key in determining the metabolic mechanisms that trigger N_2O production, from either nitrifying or denitrifying microorganisms, depending on whether conditions are aerobic and/or anoxic (Rassamee et al., 2011). This is more relevant in situations where transient DO levels are frequent (Kampschreur et al., 2008a), thereby creating a favourable environment for anoxic and aerobic conditions to co-exist. Dissolved oxygen, however, is the target of most efficiency-driven interventions on an activated sludge process (ASP).

The aeration demands required to keep adequate DO conditions in a nitrifying ASP account for 55 % of the total energy consumption of a sewage treatment works (George et al., 2009). Thus, it has a clear impact on the running costs of any given ASP. The reduction of energy use by lowering the DO set-point at an ASP also has a positive effect on operational carbon emissions, as there is a direct link between energy use and carbon equivalents in currently available carbon accounting tools (UKWIR, 2008). On the other hand, the introduction of legislation such as the European Water Framework Directive (WFD), demanding increased nitrogen removal to improve the quality in the receiving water bodies, has the side effect of requiring more energy to carry out required levels of removal, thus increasing the overall carbon footprint of the treatment works. Strategies to mitigate carbon footprint or improve nitrogen removal must thus consider the impact on process emissions.

The challenging, difficult to control full-scale environment however restricts a real-time, comprehensive approach of monitoring emissions and influencing factors. And although measurements may consider off-gas or dissolved N_2O emissions, these often rely on off-line analysis (Foley et al., 2010a; Kampschreur et al., 2008b) or spot readings (Ahn et al., 2010b; Desloover et al., 2011). As a result, the link between DO and N_2O emissions, although believed to be a critical one, is only partially understood. This paper aims to address this knowledge gap, by reporting the findings from online, continuous monitoring of dissolved and off-gas N_2O, and establishing if there is a direct relationship between to DO and emissions (normalised to influent NH_4^+ loads), in real-time, in a full-scale nitrifying ASP. The associated carbon impact of the process emissions is calculated and reported in relationship to current carbon accounting practices.

3.2. Materials and methods

3.2.1. Monitoring site

The study was carried out in a plug-flow, three-pass, full-scale sewage treatment works in the Midlands, UK, with a capacity to treat 210,000 population equivalents. The chosen ASP unit is one of three at the works designed to nitrify, and it consists of two identical aeration lanes, each preceded by a small anoxic zone. This is the most common configuration in Severn Trent Water’s 57 ASPs. The ASP is run on DO control set-point of 1.5 mg/L, employing blowers in duty/assist/standby modes. Each lane treats on average 10 % of the daily incoming flow and was designed to provide eight hours of hydraulic retention time (HRT) and 10 days of solid retention time (SRT) at its average flow rate. The monitoring campaign during this study was carried out in one of the lanes only. The experimental plan consisted of combined online monitoring of N_2O emissions and environmental conditions in the nitrifying lane, with discrete diurnal sampling campaigns for mass balance purposes.

3.2.2. Monitoring and sampling campaigns

For the online analysis, a gas collection floating hood with a surface area of 0.34 m^2 (Water Innovate, UK) was suspended over the mixed liquor on the nitrifying lane and connected to a PTFE tubing sampling line, where the off-gases were pumped through to an infra-red gas analyser, with an integrated sample pump, moisture trap, auto-calibration system and data-logging unit, recording readings every minute (N-TOX®, Water Innovate, UK). The gas analyser had a measurement range of 0–1000 ppmv, with a detection limit of 2.0 ppmv at an accuracy of ± 1 % of the scale, with readings ranging between 1.0–220 ppmv during the monitored period. The monitor was serviced and calibrated on-site, according to manufacturer's instructions, using compressed air (zero gas) and 500 ppmv gas standard (Specialty Gases Ltd., UK). Corrections for CO_2 concentrations were performed as per manufacturer's instructions, by monitoring CO_2 emissions with a gas analyser monitor (LMSr, Gas Data, UK).

Dissolved N_2O was detected using a modified Clark electrode probe (N_2O-R mini-sensor, Unisense A/S, Denmark) with a measurement range of 0.1–500 µM (typical concentrations ranging between 0–50 µM), placed next to the floating hood, where readings were taken every minute, whilst connected to a picoammeter and data-logging laptop left on-site. The instrument was polarised before and after every sampling run, as well as calibrated using a calibration chamber (CAL300, Unisense A/S, Denmark), zero gas and 500 ppmv gas standard (Specialty Gases Ltd., UK), as per manufacturer's instructions and as described elsewhere (Foley et al., 2010a; Chandran, 2009).

Dissolved oxygen was monitored every 15 minutes with a rugged probe (LDO probe with Sc100 monitor, Hach Lange, Germany) placed next to the floating hood. The equipment was deployed in the lane in eight equally-distributed sampling points for the three aeration passes, which were determined theoretically by dividing the aerated lane in "zones" according to the tanks-in-series (TIS) model for plug-flow (Fig. 3.1, Appendix 1). The airflow rate into the lane was monitored continuously with the use of an insertion-type airflow meter (VPFlowScope, Omni Instruments, UK), with readings recorded every 15 minutes.

The anoxic zone was not directly monitored due to limitations in the methodology; namely, the off-gas emissions monitoring require process air to transport the gas into the hood before being pumped out for analysis and numerous issues with the dissolved N_2O probe meant it was too fragile for safe submersion into the anoxic zone. Indirect measurements of N_2O production in the anoxic zone were made by measuring the dissolved phase N_2O in the return activated sludge and immediately following the anoxic zone (i.e., zone 1).

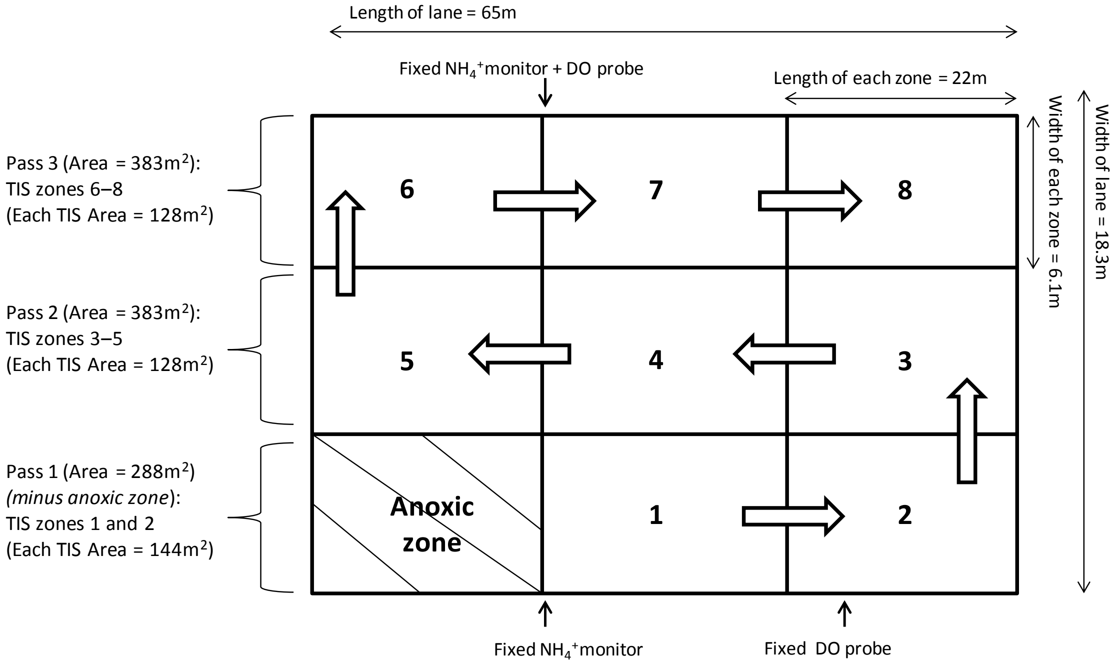

Figure 3.1: Configuration of the plug-flow nitrifying lane showing dimensions of the lane and of the theoretical tanks-in-series zones (numbered boxes) within the passes. The arrows indicate the direction of flow. The fixed DO probes seen on the diagram (zones 2 and 6) are linked to the blowers, which are controlled by the supervisory control and data acquisition (SCADA) system. The fixed NH_4^+ monitor (zone 6) is also linked to SCADA, and is set to trigger an alarm when the NH_4^+ levels go above the consented discharge value of 5.0 mgNH_4-N/L (in the final aeration pass).

Other key monitoring equipment included two fixed DO probes (which also recorded wastewater temperature; LDO probe with Sc100 monitor, Hach Lange, Germany) and two NH_4^+ monitors (STIP PBS1, Envitech, UK).

The accuracy of the monitor recording off-gas emissions (N-TOX®) was tested by collecting samples with a gas bag and running these in a gas chromatograph. Additionally, off-gas emissions were recorded and a sampling campaign (to analyse for NH_4^+, NO_2^-, NO_3^-, chemical oxygen demand (COD) and solids), as well as microbiology analysis, carried out.

Data were continuously logged for eight weeks (one week per each TIS zone), with the exception of the dissolved N_2O, which was recorded for 24-hour periods (one day per each TIS zone). The monitoring campaign took place during August to October 2011.
In order to assess the suitability of the site and methodology employed for this study, a pre-assessment campaign consisting of collecting historic information on the sewage treatment works and the chosen lane and in-lane spot sampling for nitrogen species and COD was carried out in May 2011. Triplicate grab samples were collected from the

middle of the monitoring zones and analysed for all the parameters as described for the intensive monitoring. Also, four years of historical site information on influent flow, DO, ammonia concentrations (influent and final effluent) were taken. The pre-assessment showed that the site's operating conditions were consistent year-on-year (based on the four years of data), thereby making it appropriate for this study and the methodology robust for the proposed experimental plan.

In parallel with the online monitoring, a sampling campaign was carried out every two weeks, with a total of four sampling events during the eight weeks of monitoring. Discrete auto-samplers were used to collect 24 discrete hourly samples from settled sewage and final effluent sampling points, in addition to four grab samples from the returned activated sludge (RAS) at peak and low load times. Every other sample in the diurnal cycle was preserved with sulphuric acid (USEPA, 2001) and filtered using 0.45 µm filters on collection at the end of the 24-hour period. These samples were analysed for NH_4^+, NO_2^-, NO_3^-, total nitrogen (TN) and COD using commercial colorimetric Hach-Lange test kits. The remaining half of the samples (without acid) were used to determine total and volatile suspended solids (TSS and VSS, respectively) following Standard Methods (APHA, 2005). The combined data were used to perform a nitrogen mass balance of the aerated lane and to determine the percentage of influent NH_4^+ and total nitrogen being emitted as N_2O in the nitrifying ASP lane (i.e., the emission factor).

3.2.3. Dissolved and off-gas N_2O fluxes

The net mass flux of N_2O emissions was calculated based on the air and liquid flow rates applied to the lane, taking into account the surface areas for each sampling point where the hood was placed and the total aerated zone and the N_2O concentration from the sampled air and liquid. The gas flux was calculated by:

$$F = C \times Q \times (A_n/A_T) \qquad \text{(Eq. 1)}$$

where F is the mass of N_2O fluxes over a 24-hour period per TIS zone (g/h), C is the sampled N_2O concentration converted from parts-per-million v/v and µmol/L to g/m^3 for off-gas and dissolved N_2O respectively, Q is the airflow rate (m^3/h) (for off-gas N_2O fluxes) and liquid flow rate (m^3/h) (for dissolved N_2O fluxes) and A_n/A_T is the ratio of surface area (m^2) of *n* TIS sampling zone (A_n) per surface area (m^2) of total aerated pass (A_T). Nitrous oxide emissions were then normalised to average ammonia loading into the nitrifying lane for diurnal (kgN_2O-N/h per kgNH_4-N/h) and spatial (kgN_2O-N/day per kgNH_4-N/day) profiling.

3.2.4. Statistical analysis

Hourly averages of DO concentrations, the mass of dissolved and off-gas N_2O, and the NH_4^+ loading rate were calculated per day, per zone. To validate the monitoring approach, a one-way ANOVA was conducted on the hourly emissions normalised per influent NH_4^+ load on each day per zone to determine the effect the day of monitoring had on data collected. To determine the significance of each parameter on N_2O emissions, a step-wise multiple regression test was conducted on each zone. To evaluate the differences in mass emissions between zones, the lane was analysed based on its three aeration passes (i.e., zones 1 and 2 belong to the first aeration pass; zones 3–5 to the second pass; and zones 6–8 to the third pass) with a one-way, repeated measures ANOVA. All data were checked for normality before running the analysis and the distribution of the residuals checked after the tests. All statistical analysis was conducted with STATISTICA v10 (StatSoft Inc, Oklahoma, USA).

3.3. Results

The treatment works achieves over 95 % removal rates, with average effluent concentrations of 0.25 mgNH_4-N/L for NH_4^+, 25 mg/L for COD and 12 mg/L for TSS. This is within the expected performance of the works and notably, well below the 5.0 mgNH_4-N/L consent for effluent NH_4^+. Average NH_4^+ concentrations entering the lane were 15 mg/L, with most of the nitrification taking place by zone 6 (Fig. 3.2). In-lane measurements during the pre-assessment period showed the majority of the oxidised nitrogen was in NO_3^- form (average 12 mgN/L), with limited to no detection of NO_2^- in lane (average 0.3 mgN/L). This is consistent with what is expected in a full-scale nitrifying ASP (Coskuner and Curtis 2002).

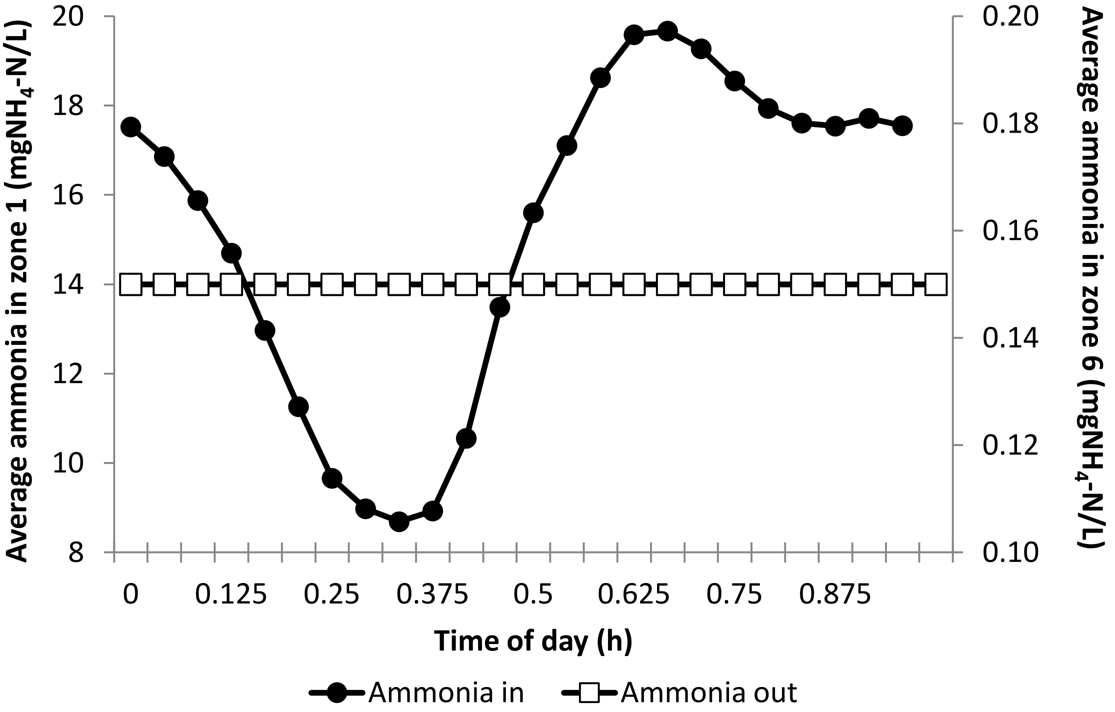

Figure 3.2: Average NH_4^+ diurnal profile in zone 1 during eight weeks of the study (influent to aeration zones) and for zone 6 on the corresponding week for N_2O emissions monitoring. Data was recorded online in 30-minute intervals and is expressed in mgNH_4-N/L.

The operational conditions were measured during the study and used to assess the relationship between emissions and the environmental conditions (Table 3.1).

Table 3.1: Measured wastewater characteristics and operating conditions

Operational conditions with units	**Range of Values**	**Average (± standard deviation)**
Settled sewage [a]		
Chemical oxygen demand, COD (mg/L)	300 - 500	450 ± 50
Total nitrogen, TN (mg/L)	40 - 60	45 ± 6
Ammonium, NH_4^+ (mgN/L)	20 - 50	38 ± 5
Nitrate, NO_3^- (mgN/L)	0.19 - 1.06	0.55 ± 0.2
Nitrite, NO_2^- (mgN/L)	0.01 - 0.023	0.01 ± 0
Total suspended solids, TSS (mg/L)	75 - 260	125± 31
Volatile suspended solids, VSS (mg/L)	50 - 150	90± 31
Nitrifying ASP lane		
Mixed liquor suspended solids, MLSS (mg/L) [b]	1730 - 2760	2200 ± 200
Stirred specific volume index, SSVI (mL/g) [b]	45 - 65	58 ± 6
Liquid flow rate, LQ (m^3/h) [c]	50 - 600	185 ± 75
Airflow rate, AQ (m^3/h) [c]	11 - 320	85 ± 45
Wastewater temperature (^{0}C) [c]	15 - 19	17.8 ± 0.8
pH [c]	6.5- 7.4	6.9 ± 0.2

[a] *Values based on four 24-hour sampling campaigns, with a total of 96 samples*
[b] *Data obtained from site operators (records from operational control)*
[c] *Online data readings*

3.3.1. Nitrous oxide emissions

The data show high diurnal variability in both dissolved and off-gas N_2O emissions, with dissolved reflected by a more irregular trend (Fig. 3.3).

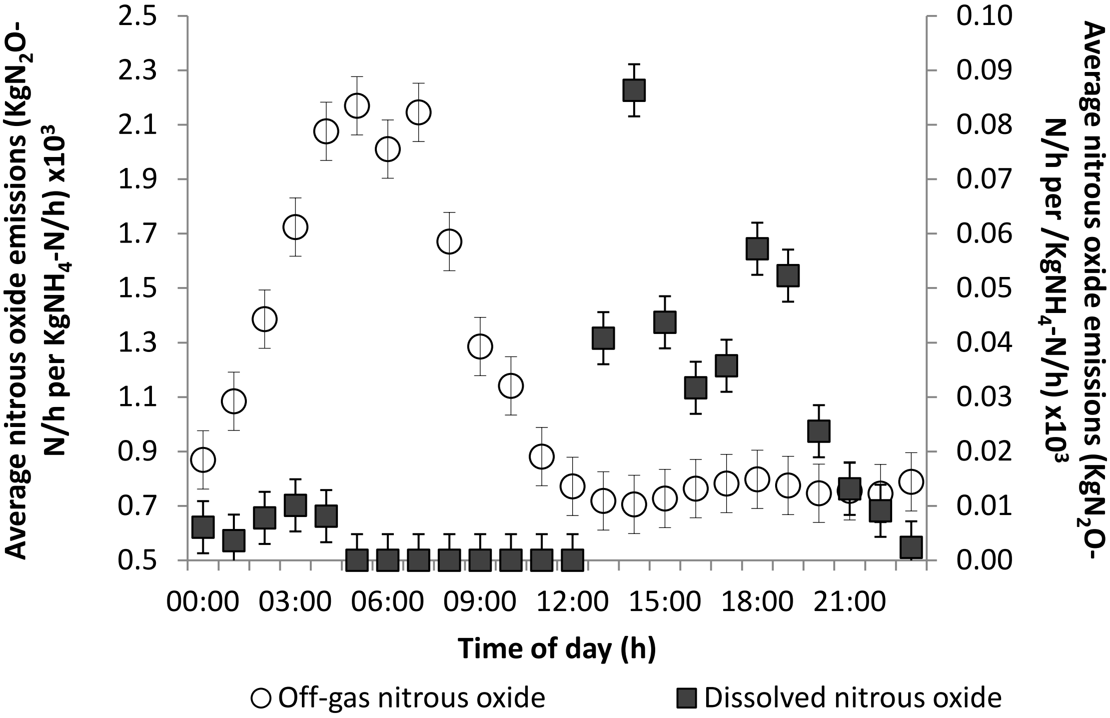

Figure 3.3: Diurnal profile of normalised average emissions (kgN_2O-N/h) obtained over the eight-week trial per NH_4^+ load (kgNH_4-N/h). The graph shows diurnal variation across the nitrifying lane, for both off-gas and dissolved N_2O (multiplied by a 10^3 factor for easier reading), with standard error bars. The off-gas emissions include average values from each theoretical zone, whereas dissolved emissions include values from zone 8 only, as these represent the N_2O emissions leaving the process in the bulk liquid. The readings correspond to: n= 80,700 for off-gas 1 and 1,438 (zone 8 only) for dissolved N_2O respectively.

The dissolved N_2O emissions considered for the diurnal and spatial trends consist of the values computed from zone 8 only, as these are the only emissions exiting the process in the bulk liquid. The dissolved fluxes ranged between 0–0.00009 kgN_2O-N/h of the NH_4^+ loading (kgNH_4-N/h). The data show a small peak around the early hours of the morning, between 02:30 and 05:00, subsequently dropping to zero values until about 12:30 in the afternoon, just before increasing sharply and peaking between 14:00 to 19:00, a period of time which coincides with peak nitrogen loadings into the nitrifying lane.

Off-gas emissions on the other hand, ranged between 0.00077–0.00217 kgN_2O-N/h of the ammonia loading (kgNH_4-N/h), peaking between midnight and 08:00 in the morning. The emissions drop after that time, and continue lower for the rest of the day, showing only a small increase between 16:00 to 18:00 in the evening.
Similarly, the spatial analysis is dominated by great emission variability (Fig. 3.4), with N2O being emitted from TIS zone 1 (closer to the anoxic zone) up to the end of the lane at TIS zone 8. The data in zone 8 show off-gas and dissolved emissions leaving the

nitrifying lane, whereas the other zones consist of off-gas emissions only and N_2O in the bulk liquid (Fig. 3.4).

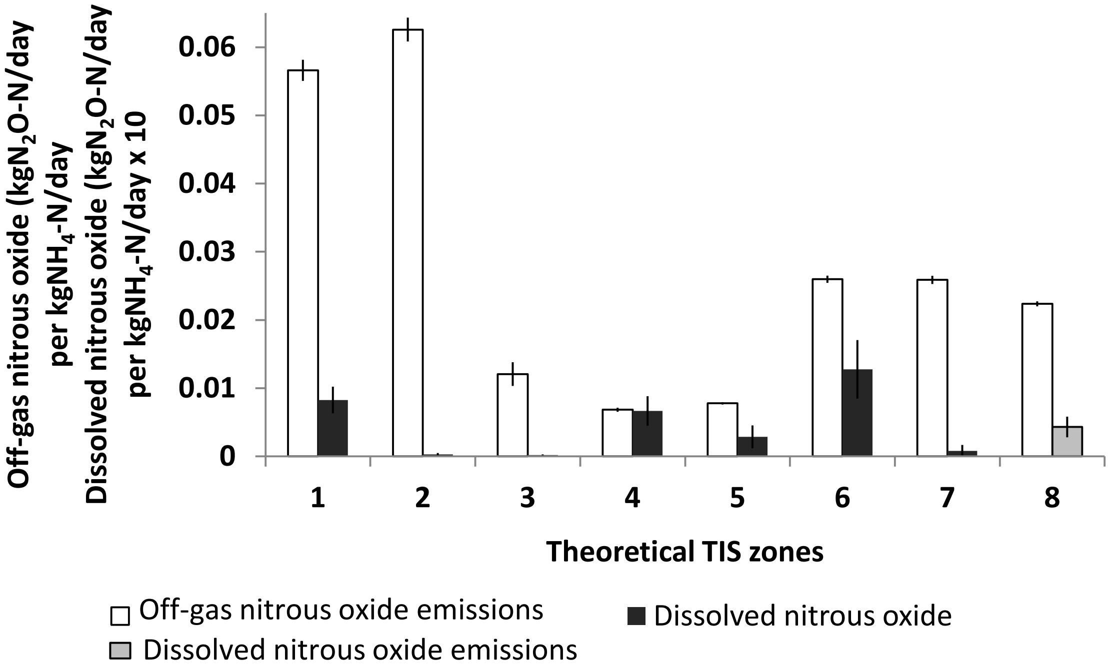

Figure 3.4: Spatial profile of normalised average N_2O (kg-N_2O-N/day) per average NH_4^+ load (kgNH_4-N/day) obtained over the eight-week trial. Gaseous phase bars represent average mass of off-gas N_2O emissions each tanks-in-series zone (1 to 8). Dissolved phase bars (multiplied by a factor of 10 for easier reading) represent average mass of N_2O in the bulk liquid for zones 1 to 7 and average dissolved N_2O emissions in zone 8. Dissolved N_2O emissions include values from zone 8 only, as these represent the emissions leaving the process in the bulk liquid. The error bars represent standard deviations (±).The readings correspond to: n= 80,700 for off-gas and 11,500 for dissolved N_2O respectively.

The statistical analysis of the emissions in the zones within the same aeration passes revealed that these differed in each pass, whereby mass emissions decreased in the following order: zones 1–2, first pass > zone 6–8, middle pass > zones 3–5, last pass ($p < 0.05$ when comparing all three passes).

It seems therefore, that location of the monitoring and sample collection can have a significant impact on the quantification of emissions. Furthermore, the statistical analysis looking at the interaction between day and zones within same passes (supplementary data) revealed that each day of the week within the same zone is the same as the next, i.e., not statistically different. Therefore, the seven days of the week per each TIS zone can be considered to be representative of that particular zone.

3.3.2. Dissolved oxygen profile

Similarly to N_2O emissions, the DO measurements show high temporal and spatial variability (Fig. 3.5), with the recorded DO values in the nitrifying lane fluctuating considerably from the control set-point of 1.5 mg/L (broken horizontal line in Fig. 3.5). Indeed, values ranged from very low (<0.5 mg/L) to adequately aerated (>2.5 mg/L) concentrations. The fluctuations occurred on a daily basis, revealing not only a distinct spatial profile in each zone but also in different days within the same monitoring zone (Fig. 3.5).

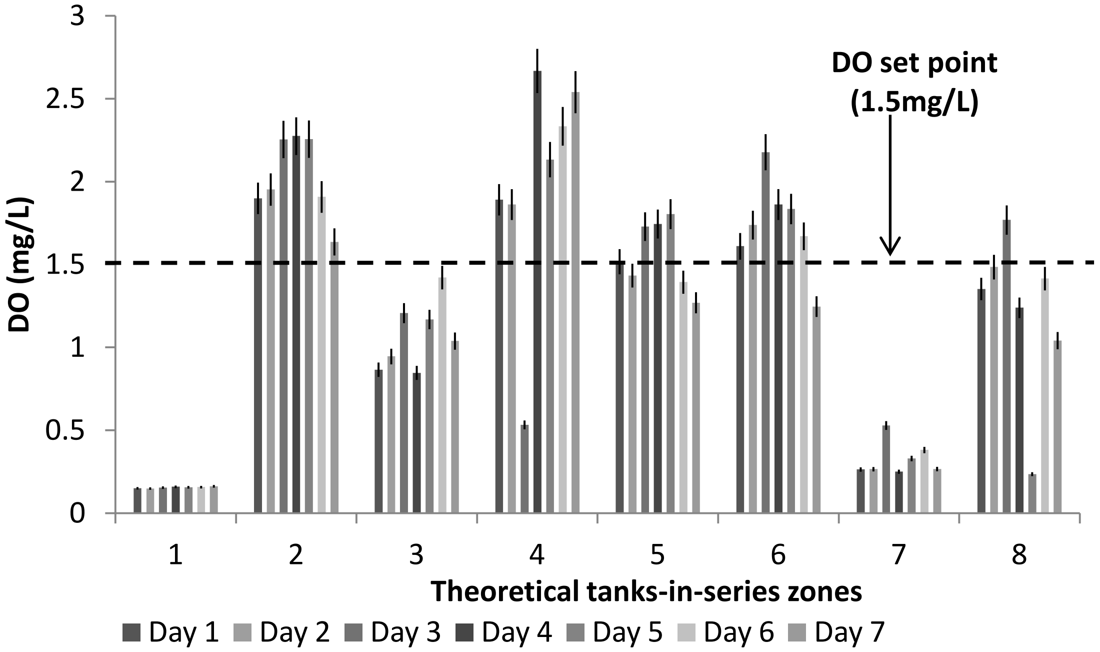

Figure 3.5: Average DO profile in the nitrifying ASP over the eight-week trial: the graph shows the DO spatial distribution for each TIS zone (1–8) and the diurnal variation in the zones, where each individual bar represents one day of the week (total of seven days per zone), from Wednesday (first bar in each zone) to Tuesday (last bar in each zone). The horizontal broken line marks the DO control set-point of 1.5 mg/L. Readings: n= 16,000 readings.

3.3.3. Nitrous oxide emissions and oxygenation

Multiple regression analysis shows that the relationship between the monitored parameters and resulting N_2O emissions changed depending on the studied zone, with the strongest DO links to off-gas N_2O emissions in zones 1, 6 and 8, and weakest to no links in zones 3, 5, and 7 (Table 3.2). This coincides with consistently low residual DO concentrations in these zones (Fig. 3.5). It should be noted that, whilst the equations on Table 3.2 cannot be used for predictions, they nevertheless illustrate the importance other parameters can have on N_2O emissions.

Table 3.2: Multiple regression relationship between measured parameters and N_2O emissions

Zone	Equation	P value	Significant
1	$N_2O = 4 + (0.006*load) – (11.95*DO)$	<0.05	Yes
2	$N_2O = -1.67 + (0.12*temperature) + (0.04*DO)$	<0.05	Yes
3	$N_2O = 1.51 + (0.00002*load) + (0.08*temperature)$	<0.05	Yes
4	$N_2O = 7.12 + (0.0002*load) - (0.38*temperature) - (0.026*DO)$	<0.05	Yes
5	$N_2O = 1.19 - (0.09*DO) - (0.03*temperature)$	<0.05	Yes
6	$N_2O = 1.88 + (0.007*load) - (0.47*DO)$	<0.05	Yes
7	$N_2O = 3.62 + (0.2*temperature) + (0.0001*load)$	<0.05	Yes
8	$N_2O = 7.03 - (0.28*DO) + (0.0001*load) - (0.3*temperature)$	<0.05	Yes

On average, the highest N_2O emissions were seen during lower DO ranges (Fig. 3.6): DO concentrations below 1 mg/L corresponded to combined emissions closer to 0.0035 kgN_2O-N/h, and, at DO ranges above 2.0 mg/L, emissions dropped below 0.001 kgN_2O-N/h.

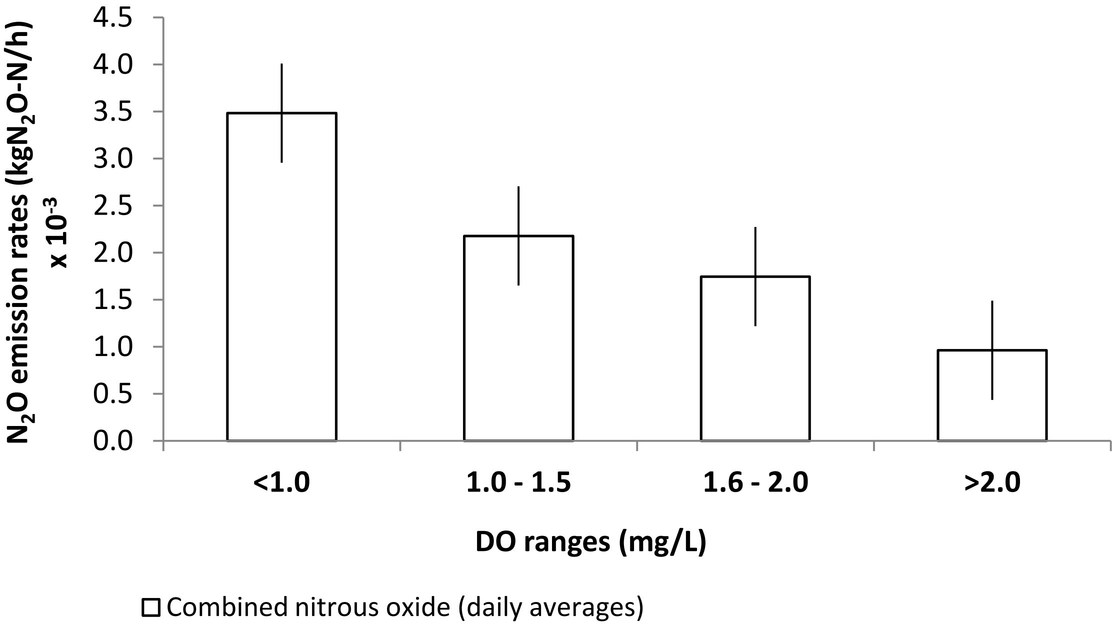

Figure 3.6: Histogram showing combined dissolved and off-gas N_2O emissions (in kgN_2O-N/h multiplied to a factor of 10^{-3} for easier reading) at different DO ranges. Data relate to average mass of emissions from daily variability.

Low DO periods coincide with peak NH_4^+ loadings into the nitrifying lane, which is consistent with the periods of higher oxygen demand and lower residual DO levels in the wastewater. This can be confirmed by the strong correlation (r^2 = 0.77) between the average diurnal variability of DO and load (Fig. 3.7).

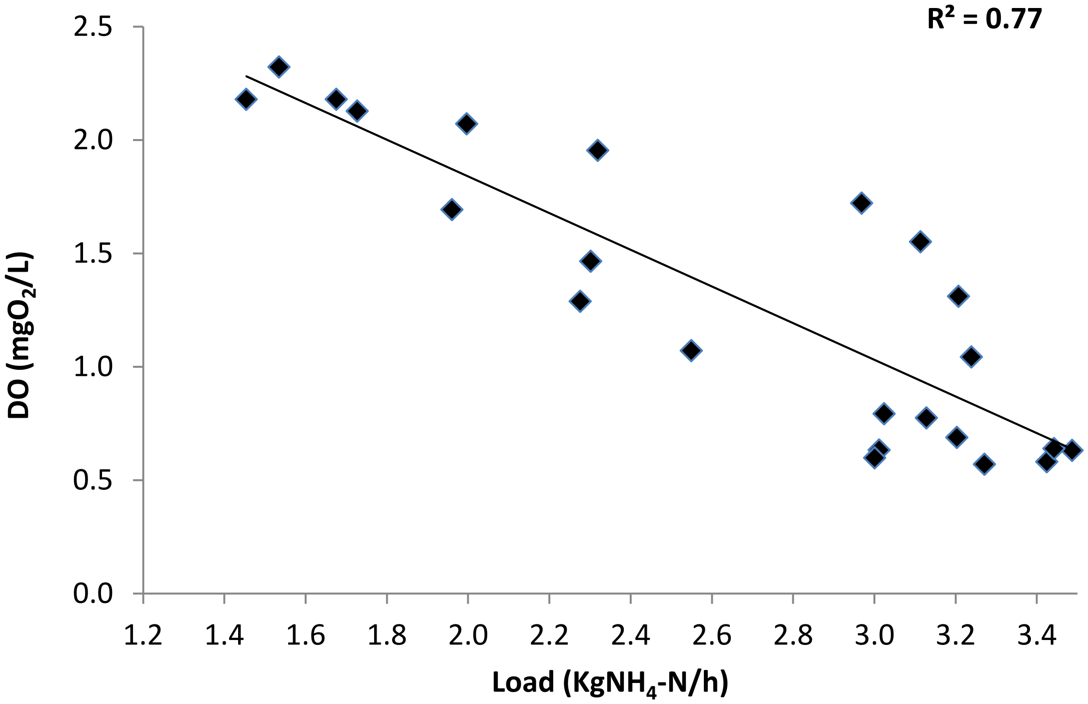

Figure 3.7: Correlation line showing DO versus load, with the square of the correlation coefficient (r^2). Values are based on average diurnal variability in DO across the nitrifying lane and in NH_4^+ load over the 8-week monitoring.

Overall, the spatial relationship between emissions and DO is dominated by fluctuations, shown in the individual zones within each aeration pass: in zone 1, the average DO is very low (<0.5 mg/L), whereas emissions in the off-gas are higher. At zone 2 (still within the first aeration pass), the average DO is above the control set-point (2.0 mg/L), although the off-gas emissions shown in this zone are the highest seen in the lane, with averages of approximately 0.06 kgN_2O-N/day per daily NH_4^+ loading (Fig. 3.4). In the second pass (zones 3 to 5), DO continues to fluctuate between below (zone 3) and above (zone 4) control set-point, although zone 5 shows average DO values closer to the control set-point (1.5 mg/L). Off-gas N_2O fluxes in this pass drop considerably, ranging between 0.007–0.01 kgN_2O-N/day per NH_4^+ loading, in comparison to the first two zones (first pass). The DO and emissions profiles in the last aeration pass also show a variable trend, where zone 6 displays higher emissions than in the previous pass and average DO is about 1.8 mg/L, just above control set-point. Dissolved oxygen drops again in the final two zones and N_2O continues to be emitted.

3.3.4. Nitrous oxide emissions and carbon impact

The mass balance for dissolved and off-gas N_2O emissions were calculated based on influent TN and influent NH_4^+ (Fig. 3.8) and found to be: for dissolved N_2O emissions (leaving the nitrifying lane in zone 8), 0.0001 kgN_2O-N per both influent NH_4^+ and TN (emission factor of 0.01 %); for the off-gas emissions, 0.0004 kgN_2O-N per influent NH_4^+ (emission factor of 0.04 %) and 0.00036 kgN_2O-N per influent TN (emission factor of 0.036 %).

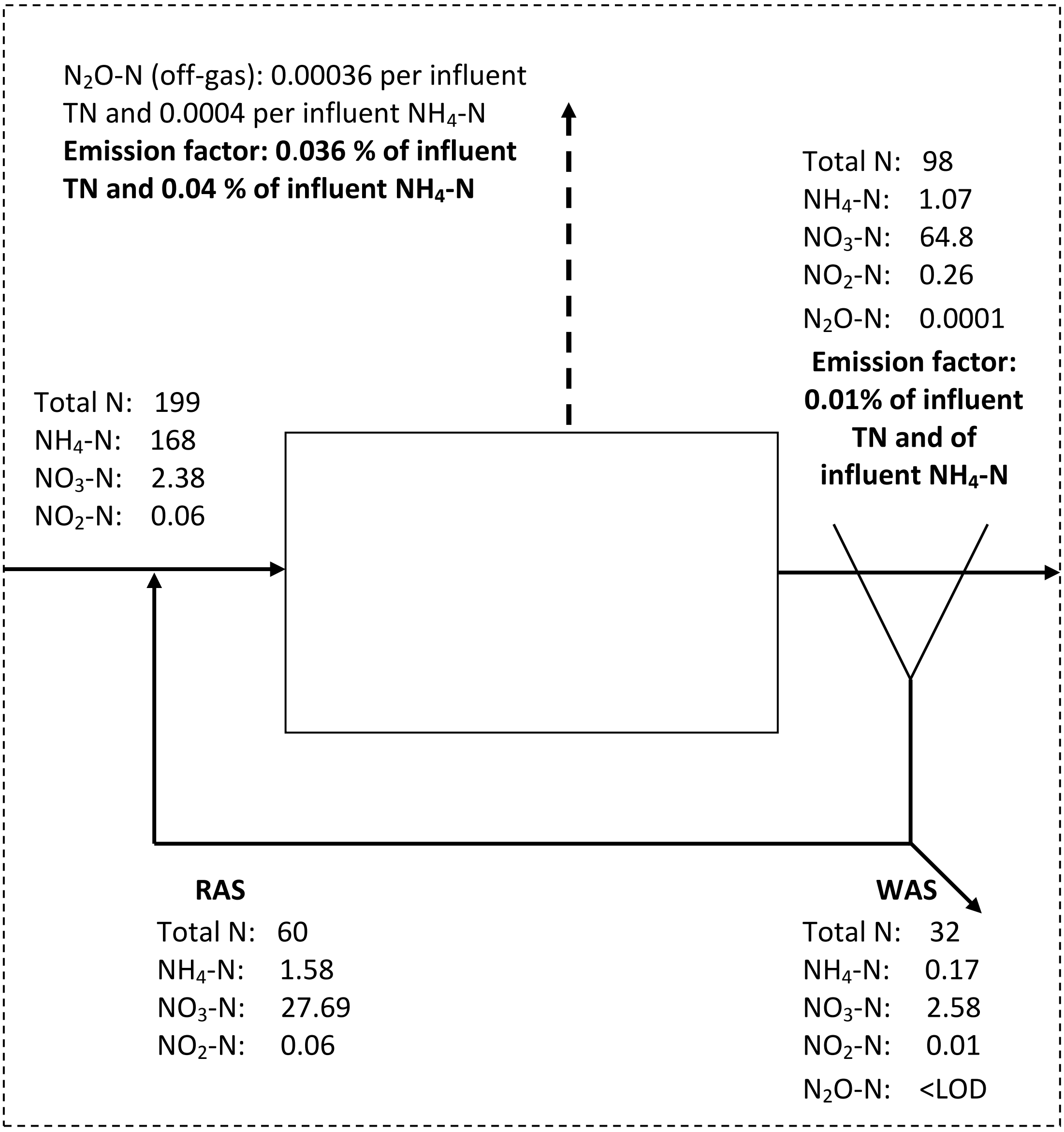

Figure 3.8: Mass balance envelope showing average loadings for nitrogen species of: influent into the lane, effluent out of the lane and returned activated sludge (RAS). The N_2O emissions are shown in the lane both in the dissolved phase and off-gas (dashed arrow). For dissolved N_2O only the emissions in the tanks-in-series zone 8 have been considered, as these are the only N_2O emissions exiting the process in the bulk liquid. For off-gas emissions all zones have been considered for the calculations.

The dissolved N2O in the WAS (wasted activated sludge) was below the limit of detection (<LOD). All figures numbers are represented in kgN/day, and for N_2O, these have also been considered in kgNH_4-N/day. The N_2O emission yield factors are represented as percentages relative to influent TN and NH_4^+ into the lane.

Using the average influent TN load into the lane, this translates into over 34,000 carbon equivalents per year. The process emissions from this particular nitrifying lane represent a 13 % increase of the carbon footprint associated with electricity used to run the aeration lane (Table 3.3).

Table 3.3: Carbon impact of off-gas N_2O emissions to carbon footprint of the nitrifying process

Data	Values	Units
Annual N_2O mass emitted	110	kg/year
N_2O global warming potential	310[a]	
Annual process emissions	34,143	kgCO_2e/year
Annual energy requirements for aeration	430,560	kWh/year
Conversion factor from grid electricity to carbon equivalents	0.544[b]	kgCO_2e/kWh
Annual operational carbon footprint	234,225	kgCO_2e/year
Total annual operational carbon emissions	268,368	kgCO_2e/year
Carbon impact of N_2O emissions	**13 %**	

[a] *1.0 kg of N_2O = 310 CO_2 equivalents (IPCC, 2006)*

[b] *1.0 kWh = 0.544 kgCO_2 equivalents (UKWIR, 2008)*

3.4. Discussion

Nitrous oxide can be emitted from ASPs under aerobic and anoxic conditions due to stressed nitrification and incomplete denitrification, and the resulting emissions can have a significant impact on the carbon footprint associated with the normal operation of an activated sludge plant. Although links have been established between N_2O emissions and oxygenation levels at lab-scale level (Tallec et al., 2008; Rassamee et al., 2011; Wunderlin et al., 2012), evidence of these links at full-scale remains somewhat inconclusive. In this paper, a comprehensive, online approach was adopted to quantify emissions temporally and spatially, in order to provide a detailed profile of how these evolve during a full-scale biological wastewater treatment process, and more importantly, how they relate to DO conditions.

3.4.1. Quantification of emissions

The average dissolved N_2O emissions were found to be low when compared against off-gas emissions, at 0.0001 kgN_2O-N/day (0.01 %) per influent NH_4^+ as well as per influent TN (Fig. 8). Although studies that have considered both dissolved and off-gas emissions are limited, the emission factors found here are low compared to other full-scale processes (Table 3.4). The differences in reported emissions may be “true” differences associated with the variability of the biological processes studied and the inherent variability of full-scale testing, but could also be due to discrepancies in employed methodologies (i.e., online monitoring versus spot measurements). Findings from the present study indicate that there is significant variability of dissolved N_2O concentrations within the treatment lane (i.e., spatially) and at different times of the day (i.e., temporally). Thus, a comparison of a detailed profile against spot readings should be used with care.

Although values are low, it is nevertheless noteworthy that dissolved N_2O was indeed measured. Even with a solubility not as low as that of methane or oxygen (Table 3.5) nitrous oxide has nevertheless relatively low solubility in water (Table 3.5, K_H for N_2O = 0.024 mol/kg*atm; Wilhelm et al., 1977), which means that it will leave the liquid phase with some ease, and saturated dissolved N_2O concentrations at 20 ^{0}C correspond to 1.27 gN_2O/L (Table 3.5). For this reason, sometimes the dissolved phase is ignored in research studies. However, the N_2O emissions leaving the process in the bulk liquid will eventually be released to the atmosphere due to mixing or air-stripping. In terms of mass, whilst the concentrations are low, the large volume of wastewater treated means that the contribution of liquid phase N_2O emissions to carbon footprint can be significant, as evidenced in this study. Moreover, when measured concomitantly with off-gas emissions, it provides a better understanding of how emissions may be formed and released from the process.

Off-gas nitrous oxide lost to the atmosphere was found to be an average of 0.036 % of the total nitrogen and of TKN (total Kjeldahl nitrogen) loadings (differences between TN and TKN were negligible), and 0.04 % of the influent NH_4^+. This value is lower than those reported in recent full-scale studies (Table 3.4). Generally, N_2O emissions measured in full-scale seem to be on the lower range when compared to lab-scale findings, where values can fall within wider ranges, from low, at 0.83–1.72 % (Hu et al., 2011), to the much higher at 44 % of total nitrogen removed (Xiuhong, et al., 2008). However, as with the dissolved N_2O, the differences in methodologies may somewhat contribute to the variability in observed emission values.

Table 3.4: Emission factors reported in the literature and in this study

Reference	Process type[a]	Scale	Nitrous oxide emissions	
			Factor	***Method***
Ahn et al., 2010a; b	Bardenpho BNR[b] Plug flow non-BNR Step-feed non-BNR	Sewage Works	0.16 % of TKN 0.4–0.62 % of TKN 0.18 % of TKN	Continuous, online monitoring of off-gas N_2O and 4-5 spot readings of aqueous N_2O
Foley et al., 2010a	BNR	Sewage Works	0.006–0.253 kgN_2O–N per kgN denitrified	Spot readings over 2-4 hours of aqueous N_2O
Law et al., 2011	Partial nitritation	Laboratory	1 % of converted NH_4^+	Off-gas and dissolved N_2O measured continuously online
Lotito et al., 2012	Nitrifying/denitrifying ASP	Pilot	Daily averages ranged between 0.12–0.356 % of influent TN, depending on experimental configurations	Off-gas N_2O measured continuously online
Rassamee et al., 2011	Anoxic/aerobic BNR	Laboratory	Ranged between 0–0.39 % of TN, depending on DO conditions	Online monitoring of dissolved N_2O and estimation of off-gas emissions using an equation derived from aqueous N_2O and volumetric mass transfer coefficient (kLa)
Tallec et al. 2006	Nitrifying ASP	Laboratory	0.1–0.4 % of oxidised NH_4^+	Online off-gas N_2O measured continuously
Tallec et al. 2008	Denitrifying ASP	Laboratory	Average of 0.4 % of reduced NO_3^-	Online off-gas N_2O measured continuously

Reference	Process type[a]	Scale	Nitrous oxide emissions	
			Factor	***Method***
Wunderlin et al. 2012	Nitrifying/denitrifying ASP	Laboratory	Ranged between 0.2–18.95 % of nitrogen conversion rate, depending on experimental conditions	Online off-gas N_2O measured continuously
Xiuhong et al. 2008	BNR	Laboratory	4 % of TN removed, which corresponded to 44 % of TN removed during nitrification	Off-line analysis (gas chromatography) of off-gas and aqueous N_2O. Samples collected at intervals between 0.5 and 1 hour (gas bags for off-gas and headspace method for aqueous N_2O respectively)

[a] Processes using real wastewater, from municipal sewage only

[b] BNR stands for biological nutrient removal

Table 3.5: Comparison table of gas solubilities

Substance	K_H (mol/kg*atm)[a]	Saturation in water (g/L)[b]
Nitrous oxide (N_2O)	0.024	1.27
Methane (CH_4)	0.0014	0.028
Oxygen (O_2)	0.0013	0.009

[a] *Henry's law constant for solubility in water at 298.15 K (Wilhelm et al., 1977)*
[b] *At atmospheric pressure and 20 ^{0}C temperature*

3.4.2. Spatial and temporal N_2O variability

The findings from this study are particularly relevant when observing the diurnal and spatial patterns (Figs. 3.3 and 3.4). The variability agrees well with the findings of other full-scale studies, using either online (Ahn et al., 2010 a; b) or off-line measurements (Foley et al., 2010a). The temporal changes can be associated with the diurnal pattern of wastewater generation. There was a strong, positive correlation with NH_4^+ loading into the nitrifying lane ($r^2 = 0.82$), thus supporting the theory that N_2O emissions are more likely to occur during higher nitrification rates (Kampschreur et al., 2008b; Kim et al., 2010), when the biomass can be most stressed due to competition for available oxygen in the water. Whilst temporal variability as a function of NH_4^+ loadings at full-scale has been suggested by other researchers (Ahn et al., 2010b), this is the first study to include statistically robust data to capture day-to-day variability in plant operating conditions and link the diurnal pattern to DO concentrations in the lane.

In terms of spatial variability, the high emissions in zones 1 and 2 could be explained by assuming N_2O generation in the immediately preceding anoxic phase, where incomplete denitrification could be taking place (Butler et al. 2009). For this to occur, it is necessary to have a heterotrophic bacterial population, NO_3^- or NO_2^-, a source of organic carbon, and periods of complete absence of oxygen followed by intermittent oxygenation of the water (Kampschreur et al., 2009a). The anoxic zone therefore fulfils some of the criteria, where the settled sewage is mixed with the returned activated sludge, thus recycling an average of 10–16 mgNO_3-N/L into the lane. The N_2O produced during the anoxic phase would then move to the aeration tank in the bulk liquid and be immediately stripped off once in contact with air from zones 1 and 2.

The high emissions in zones 6–8 were, however, unexpected. Notably, there was an increase in dissolved N_2O from zone 5 (0.0003 kgN_2O-N/KgNH_4-N per day) to zone 6 (0.0013 kgN_2O-N/KgNH_4-N per day), with the levels in this zone even exceeding those found after the anoxic zone (zone 1, at 0.001 kgN_2O-N/KgNH_4-N per day). The online readings from the NH_4^+ monitor in zone 6 confirm nitrification is complete by that stage 95 % of the time (Fig. 3.2) and yet, N_2O generation and emission increases significantly when compared against zone 5 and continues from that zone until the end of the ASP lane (Fig. 3.4). This finding is two-fold. First, it indicates that N_2O is indeed being produced in the aeration lane, as opposed to simply air-stripped from the generation that occurred in previous zones. Second, it indicates that other nitrogen species (e.g., NO_3^-) may be transformed and emitted as N_2O when the NH_4^+ is fully depleted. Further insight into potential mechanisms was found when observing DO values and variability within the lane.

3.4.3. Variability of DO concentrations and N_2O emissions

Residual DO in the lane changed throughout the day and within the lane, to meet the dynamic oxygen demand from settled sewage loading. Remarkably, despite the control set-point of 1.5 mg/L, average DO concentrations ranged from very low at values lower than 0.5 mg/L, to the more aerobic at over 2.5 mg/L (Fig. 3.4). Furthermore, for 75 % of the time, the oxygen demand in the aerated lane meant that the residual DO could not reach the required set-point. The dynamic DO levels create different "micro-sites" within the same process, with oxygen availability changing considerably. This in turn can have a profound effect on the oxygen transfer from the liquid phase into the sludge floc (Ahn et al., 2001; Zeng et al., 2003; Zhen et al., 2011). Under oxygen transfer limitations, an outer aerobic region may be created within the floc, which benefits from an immediate interface with the bulk DO, where therefore nitrification is most likely to take place (Zhen et al., 2011). An inner floc region is also created, where anoxic conditions prevail, allowing heterotrophic microorganisms to denitrify (Ahn et al., 2001; Zeng et al., 2003). Zhen et al. (2011) observed that an aerobic-anoxic interface was then created within the floc, where N_2O was mainly produced. The high variability in oxygenation levels from the obtained data may certainly contribute to this aerobic-anoxic divide, not only in the bulk liquid but also within the sludge floc, particularly so at low DO, when less oxygen is available to be transferred into the floc.

Although this study is not able to quantify the individual contribution of the various mechanisms of N_2O production occurring at a nitrifying works, it can nevertheless offer the evidence that the emissions occur due to a combination of different pathways, and these change depending on the location within the lane. During nitrification, two mechanisms may be responsible as potential pathways: nitrifier denitrification and NH_2OH oxidation (Kampschreur et al., 2009a; Wrage et al., 2001; Wunderlin et al., 2012). Main requirements for these pathways are: the availability of ammonia, presence of active ammonia-oxidising bacteria (i.e., limited competition by heterotrophic bacteria) and insufficient oxygenation generally estimated to be below 2 to 1.5 mg/L.

In this study, the conditions that seem to favour nitrifier denitrification are those most likely occurring in zones 3–5, after the bulk of BOD removal has occurred in the first zones and where DO is below 1.5 mg/L.

In the last aeration pass (zones 6 to 8), the pathways for N_2O generation are likely to be different. By zone 6, most if not all of the NH_4^+ has been depleted (Fig. 3.2), being primarily transformed into NO_3^-, based on effluent NO_3^- concentrations measured throughout the study (Table 3.1 and Fig. 3.8). In a study by Lotito et al. (2012) at a nitrifying pilot-scale ASP under tightly controlled DO conditions, N_2O emissions ceased once NH_4^+ and NO_2^- were depleted. Ahn et al. (2010) found dissolved N_2O concentrations were statistically similar in the two aeration zones monitored in analogous full-scale plants (i.e., nitrifying plug-flow). In this study, emissions not only continued but sharply increased when compared against previous zones. This supports the view that N_2O is being generated within the lane and by mechanisms other than nitrifier denitrification in the last pass of the nitrifying lane. Based on the DO fluctuations, the availability of NO_3^-, and the lack of NH_4^+ and NO_2^- in zones 6 to 8, it indicates incomplete denitrification could be taking place.

3.4.4 Carbon impact and operational strategy

The combined N_2O emissions factors (off-gas plus dissolved), represent a daily average of 0.00046–0.0005 kgN_2O per kg of influent TN or NH_4^+ load respectively, which translates as 0.046 % to 0.05 %. The average value for the United Kingdom, as estimated by the UK Water Industry Research Limited (UKWIR) is that of 0.002 kgN_2O-N per kg TN load, or 0.2 % (for nitrification only), which makes the measured emission factor from this study four times lower than the UKWIR factor. It should be noted however, that the UK value is an estimation to be considered across the country, with high uncertainty levels at 30–300 % (UKWIR, 2009).

The discrepancies between estimated and measured factors highlight the need for an emission inventory based on full-scale measurements, with site-specific operating conditions taken into account, since these are key in shaping emission profiles.

More importantly, with a GWP about 310 times stronger than that of CO_2, (IPCC, 2006), a small N_2O emission factor can nevertheless have an impact on the total carbon footprint of a sewage treatment works. In this particular study, the mass of N_2O emissions measured represent a total of 110 kgN_2O-N/year, which equates to an annual 34,000 kg of CO_2 equivalent ($kgCO_2e$), or 13 % (Table 3.3) added to the carbon footprint for energy requirements associated with the operation of the lane.

In the UK, the Carbon Reduction Commitment (CRC) is a mandatory scheme aimed at improving energy efficiency and cutting emissions in large public and private sector organisations. In 2012, Severn Trent Water made a payment of £5.9m to CRC solely based on the carbon footprint associated with energy consumption, on top of the £53m annual electricity bill (Severn Trent Plc, 2012). Thus, a potential 13 % increase would add to the carbon costs of the water industry, moving it in the opposite direction set out by the Government.

Clearly, as the industry moves towards more sustainable electricity sources in order to reduce their carbon footprint (Ainger et al., 2009; Listowski et al., 2011), process emissions will become more prominent in terms of carbon impact. This, together with a potential decarbonisation of the power grid, can catapult process emissions and their mitigation to the forefront of the carbon and financial efficiencies agenda. An adequate profiling of N_2O emissions is thus critical for future proofing the existing treatment technologies.

Current operational strategies being considered by the water industry involve lowering the DO control set-point, matching aeration levels with influent NH_4^+ loading, and enhanced in-lane DO control (Dotro et al., 2011). Based on the results from this study, lowering of the DO set-point could have a detrimental impact on process emissions, with higher N_2O expected to be produced as average DO levels are reduced. On the other hand, improved in-lane DO control could reduce the wide ranges of residual oxygen observed, and thus reduce the stress levels on both nitrifying and denitrifying organisms. More research on the impacts of lowering the DO set-points at full scale, improving oxygen control mechanisms in the lane, and their associated emissions would help to identify the more balanced approach to carbon management for nitrifying ASPs in wastewater treatment.

3.5 Conclusions

The aim of this study was to profile N_2O emissions and the relationship with operational DO in a full-scale nitrifying ASP. The main findings include:

- The results reveal great variability in emissions and DO conditions in the lane, with greater emissions found at the beginning (zones 1 and 2) and at the end of the lane (zones 6 to 8).

- The comprehensive N_2O emission and DO profiles provided by this study suggest that both anoxic and aerobic conditions co-exist in the nitrifying lane, which may be behind the mechanistic triggers of N_2O formation.

- The reported conditions are indeed favourable for different interactions during autotrophic and heterotrophic production of N_2O due to low or inadequate DO conditions.

- The emission factors are 0.036 % and 0.01 % of influent TN for off-gas (0.04 % of influent NH_4^+) and dissolved (0.01% of influent NH_4^+) N_2O respectively.

- The carbon impact of emissions was determined as adding about 13 % to the carbon footprint of the process associated with electricity consumption, thereby highlighting the importance of considering process emissions before adopting low-energy strategies.

- This study shows a clear link between DO and N_2O production at full-scale, and illustrate the importance of diurnal, continuous profiling of both DO and N_2O, as well as influencing operational conditions, to better understand the emissions from a nitrifying ASP.

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CHAPTER 4

PAPER 2: METHANE EMISSIONS IN A FULL-SCALE NITRIFYING ACTIVATED SLUDGE TREATMENT PLANT

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4. METHANE EMISSIONS IN A FULL-SCALE NITRIFYING ACTIVATED SLUDGE TREATMENT PLANT

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Abstract

Findings from an online, continuous, eight-week monitoring campaign of methane (CH_4) emissions and operational conditions, in a full-scale nitrifying activated sludge plant (ASP), are reported in this study. Methane emissions show an irregular trend and great variability, with the highest average values (20–24 gCH_4/h) seen two-thirds down the lane, and emissions generally lower during peak flows. Emissions can be attributed to air-stripping of dissolved CH_4 from the bulk liquid to the atmosphere due to aeration, although CH_4 production (methanogenesis) is likely to have occurred before the ASP, possibly in the sewers, where strictly anaerobic conditions and available organic carbon, make it a more favourable environment for methanogenesis. However, the highly dynamic residual DO profile suggests that aerobic and anoxic conditions simultaneously exist in the ASP, leading to limited oxygen diffusion from the bulk liquid to the inner regions of the floc, where anoxic/anaerobic layers may allow methanogenic microorganisms to survive. However, low availability of biodegradable carbon and the presence of nitrogen oxides in the ASP, can completely inhibit methanogenesis. Therefore, it seems likely that the CH_4 emissions mainly result from air-stripping rather than in-lane production, although further research is required to confirm this. The average emission factor in the nitrifying ASP was found to be 0.07 % (influent and removed COD), giving a total of 667 kg CH_4/year (14,000 $kgCO_2$ equivalents/year). The operational carbon associated with the energy requirements of the ASP increased by 5 %. With emerging legislation requiring the mandatory reporting of greenhouse gas emissions, the carbon impact therein may be significant, particularly as the industry moves towards a carbon-reducing future. Therefore, an adequate profiling of full-scale emissions is critical for future proofing existing treatment technologies.

Keywords: *methane emissions, methanogenesis, activated sludge plant, carbon footprint*

4.1. Introduction

The last two centuries have seen an increase of 30, 145 and 15 % in atmospheric greenhouse gas (GHG) concentrations of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) respectively (El-Fadel and Massoud 2001), due to anthropogenic activities such as the production of fossil fuels, as well as emissions from waste, agricultural and industrial systems (Cakir and Stenstrom 2005). It is widely accepted that such increases are inevitably contributing to the global warming effect of the earth's surface (Søvik and Kløve 2007). Wastewater treatment plants (WWTP) can add to this effect through direct process emissions and CO_2 produced from the energy required for treatment. Because of the global warming potential (GWP) associated with CH_4 and N_2O, which are 21 and 310 times more powerful than CO_2 respectively (IPCC 2006), process emissions may significantly add to the carbon footprint of a WWTP. It is therefore important to measure direct process GHG emissions in a WWTP, with view to creating mitigating strategies.

Methane is biologically produced during the chemical reduction of the organic fraction of wastewater, COD (chemical oxygen demand) or BOD (biochemical oxygen demand), by methanogenic archaea, under anaerobic conditions. The amount of organic carbon present during methanogenesis is therefore a key factor in CH_4 production (El-Fadel and Massoud 2001). Other important operating parameters are temperature, pH, retention time and the presence of oxygen especially, which can be a limiting factor in the formation of CH_4 in anaerobic systems (El-Fadel and Massoud 2001).

Guisasola et al. (2009) reported that significant amounts of CH_4 were formed in rising sewers (20-100 mg/L as COD); Czepiel et al. (1993), and more recently, Daelman et al. (2012) and Wang et al. (2011a), all observed emissions from a range of primary and secondary treatment processes, ranging from 11 (Wang et al., 2011a) to 306 gCH_4/person/year (Daelman et al., 2012). This shows that CH_4, although expected to be formed in the sewers and in areas of a WWTP where anaerobic conditions prevail (Daelman 2012), may nevertheless be emitted from a diversity of locations within a WWTP, more so through air-stripping from the aerated zones of activated sludge plants (ASPs), such as in plug-flow reactors (Daelman et al. 2011; 2012) and in other oxic tanks (Wang et al. 2011a). However, very little is still known about CH_4 emissions from wastewater treatment processes, particularly from ASPs, although these processes already account for a large proportion of the carbon footprint of a WWTP, associated with the energy required to keep them aerated. Full-scale measurements remain limited mostly due to the lack of regulatory requirements and compliance standards for fugitive emissions, as well as expensive and diverse monitoring methods (Listowski et al. 2011). This in turn means that most methodologies rely on estimations and assumptions, which incur the risk of oversimplifying the importance of emissions released from wastewater treatment (El-Fadel and Massoud 2001), particularly from aerated processes. Hence, the lack of quantitative data from CH_4 measured in WWTP may hinder further evaluation of carbon mitigation strategies (Wang et al. 2011a), such as in recognising sources and conditions (both from physical and biological processes) that promote emissions (Listowski et al. 2011).

A methodology which employs continuous, online monitoring can provide an accurate picture of emissions at full-scale. This paper therefore reports the findings from an online, continuous monitoring study of CH_4 emissions in a full-scale nitrifying ASP. The results are interpreted in terms of spatial and temporal variability of emissions, as well as the emission impact on the associated operational carbon footprint of the overall process.

4.2. Materials and methods

The study was carried out in a plug-flow, three-pass, full-scale wastewater treatment plant in the UK, with a capacity to treat 210,000 population equivalents. The ASP was designed to nitrify to achieve discharge consent of 5.0 mgNH_4-N/L. The aeration lane under study was preceded by a small anoxic zone (about 10 % of the total lane volume) and runs on a dissolved oxygen (DO) control set-point of 1.5 mg/L, employing blowers in duty/assist/standby modes. The lane treated on average 10 % of the daily incoming flow and was designed to provide eight hours of hydraulic retention time (HRT) at an average flow rate. The method consisted of combined online monitoring of off-gas emissions and environmental conditions in the nitrifying lane, with discrete diurnal sampling campaigns of nitrogen species and COD (samples taken every two hours for 24-hour periods, every two weeks) for mass balance purposes. For the online analysis, a square floating hood of 0.34 m^2 (Water Innovate, UK) was employed, which was suspended over the mixed liquor on the lane and connected to a sampling line, where the off-gases were pumped through to an infra-red gas analyser (LMSr, Gas Data, UK) where CH_4 emissions were recorded every 15 minutes. Dissolved oxygen was monitored every 15 minutes with a rugged probe (LDO probe with Sc100 monitor, Hach Lange, Germany) placed next to the floating hood. The airflow rate into the lane was monitored continuously with the use of an insertion-type airflow meter (VPFlowScope, Omni Instruments, UK), with readings recorded every 15 minutes. Other key monitoring equipment included two fixed DO probes (which also recorded wastewater temperature; LDO probe with Sc100 monitor, Hach Lange, Germany) and two ammonia (NH_4^+) probes (STIP PBS1, Envitech, UK).

The equipment was deployed in the lane in eight equally-distributed sampling points, which were determined theoretically by dividing the lane in “zones” according to the tanks-in-series (TIS) model for plug-flow (Fig. 4.1). Data were continuously logged for eight weeks (one week per each TIS zone).

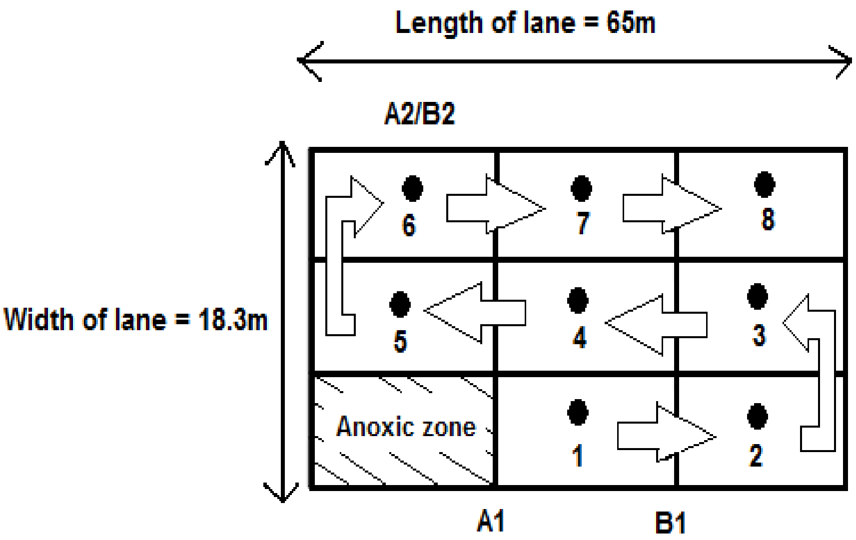


Figure 4.1: Configuration of the plug-flow nitrifying lane showing dimensions of the lane and of the theoretical tanks-in-series zones (numbered boxes) within the passes. The arrows indicate the direction of flow.

Hourly averages of off-gas CH_4, DO, NH_4 loading rate and temperature were calculated per day, per zone, based on the online and discrete data collected. Further details on the methodology of calculations employed can be found in Aboobakar et al. (2013a).

4.3. Results

The average influent concentrations in the settled sewage consisted of around 38 mg NH_4-N/L (ranging between 20–50 mgNH_4-N/L), 450 mg/L for COD (ranging between 300–500 mg/L) and 125 mg/L for total suspended solids (TSS, ranges between 75–260 mg/L). The load had a distinct diurnal pattern, with peaks reaching the aeration lane at around 12:00 to 15:00 and 19:00 to midnight (Fig. 4.2).

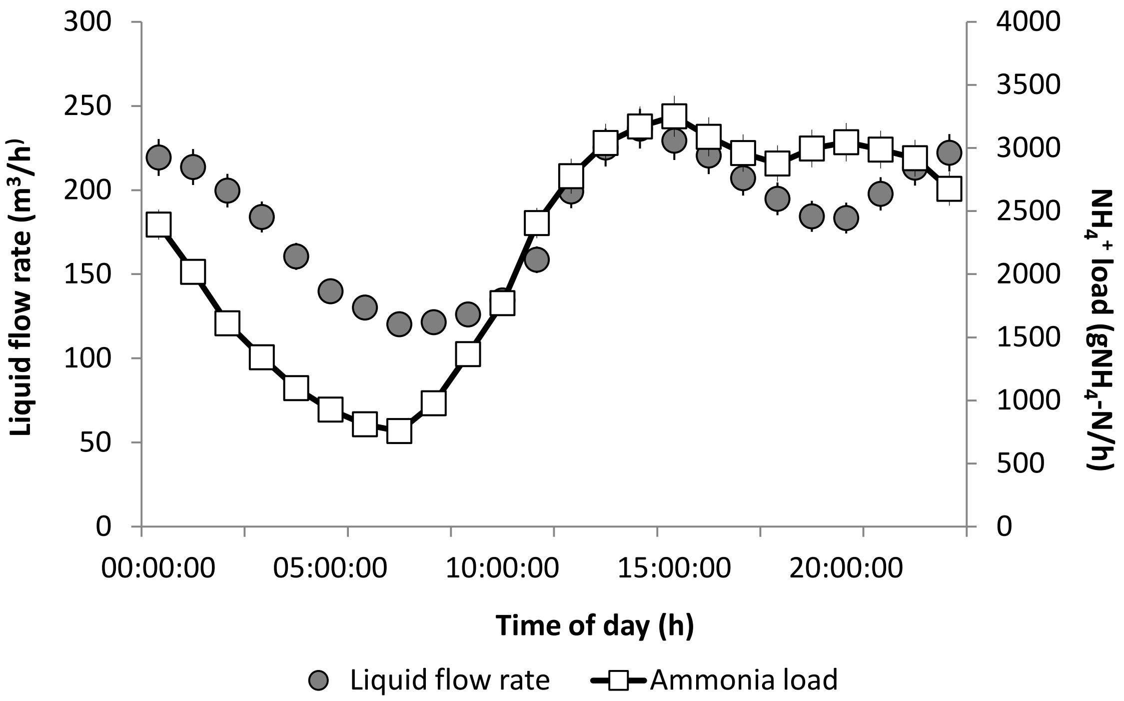


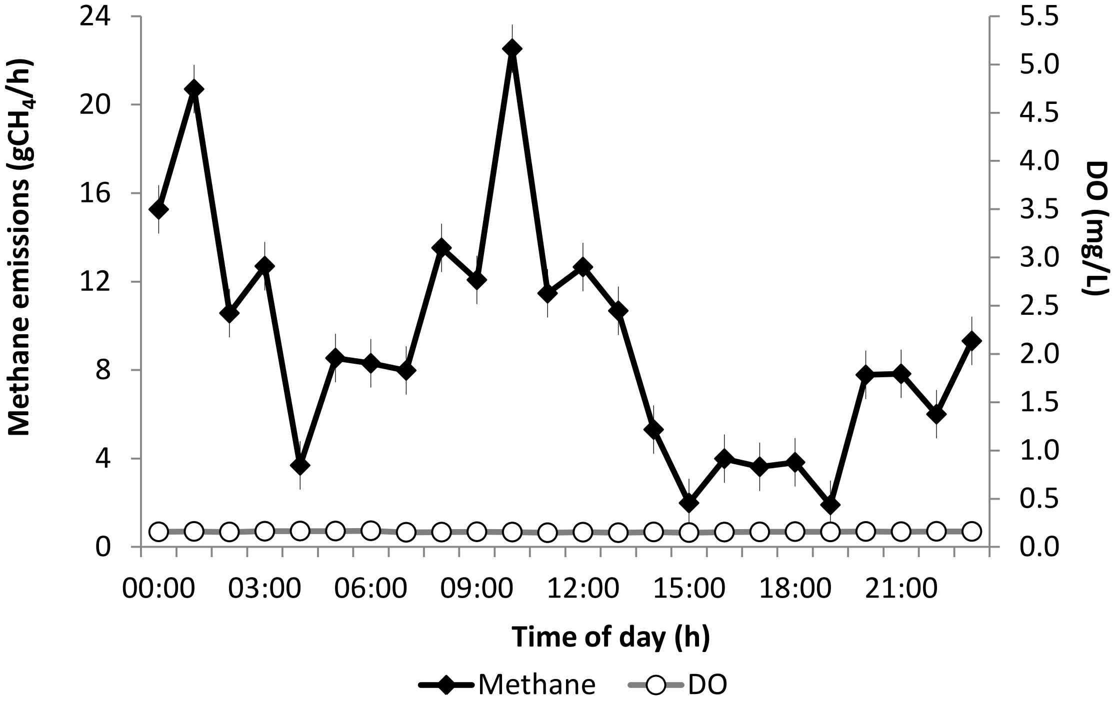
Figure 4.2: Diurnal pattern of flow and load (NH_4^+) pattern into the lane, as measured online 24/7 in zone 1, with error bars.

With effluent concentrations averaging 0.25 mgNH$_4$-N/L (the discharge consent for NH_4^+ was 5.0 mgNH$_4$-N/L), 25 mg/L for COD and 12 mg/L for TSS, the WWTP achieves 95 % removal rates, which is within expected performance levels.

4.3.1. Fugitive gas emissions

Diurnal variability in CH_4 emissions (Fig. 4.3) was observed in all zones, with CH_4 emissions recorded from zone 1 (closer to the anoxic zone) up to the end of the lane at zone 8 (Fig. 4.4). The highest emissions (around 20 gCH$_4$/h) were recorded in zones 6 and 7, two-thirds down the aerated tank.

A



Methane emissions (gCH₄/h)
24
20
16
12
8
4
0
DO (mg/L)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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09:00
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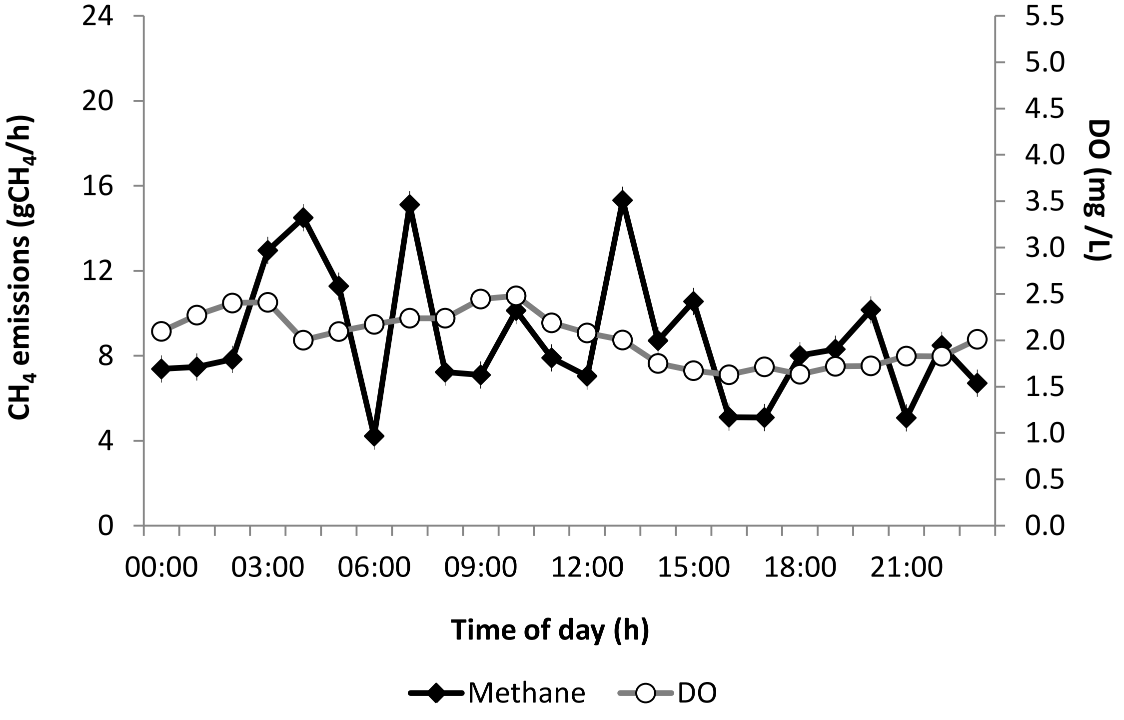
15:00
18:00
21:00
Time of day (h)
Methane
DO

B



CH₄ emissions (gCH₄/h)
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DO (mg /L)
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Time of day (h)
Methane
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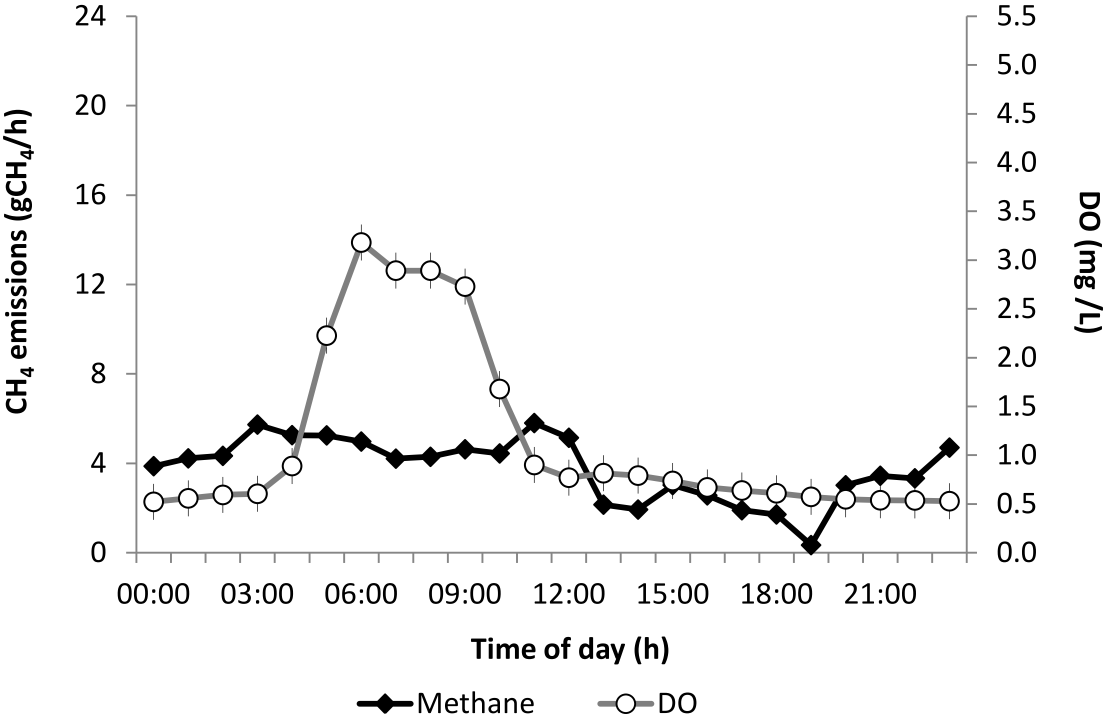
CH$_4$ emissions (gCH$_4$/h)
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DO (mg /L)
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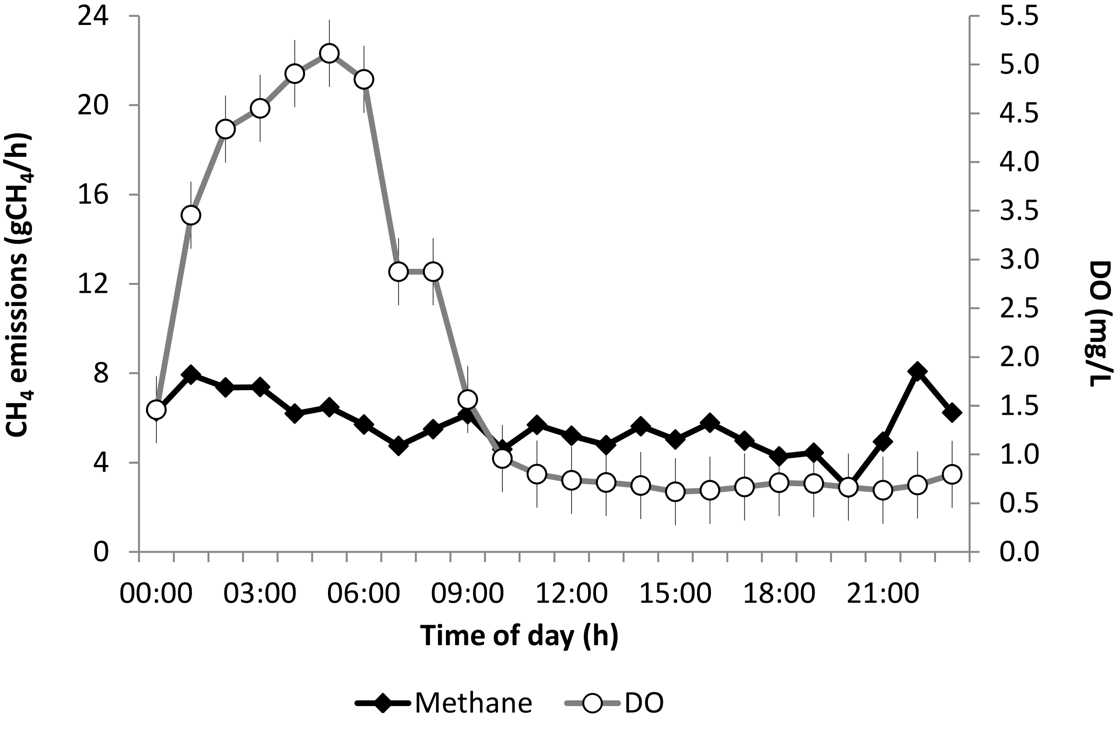
CH$_4$ emissions (gCH$_4$/h)
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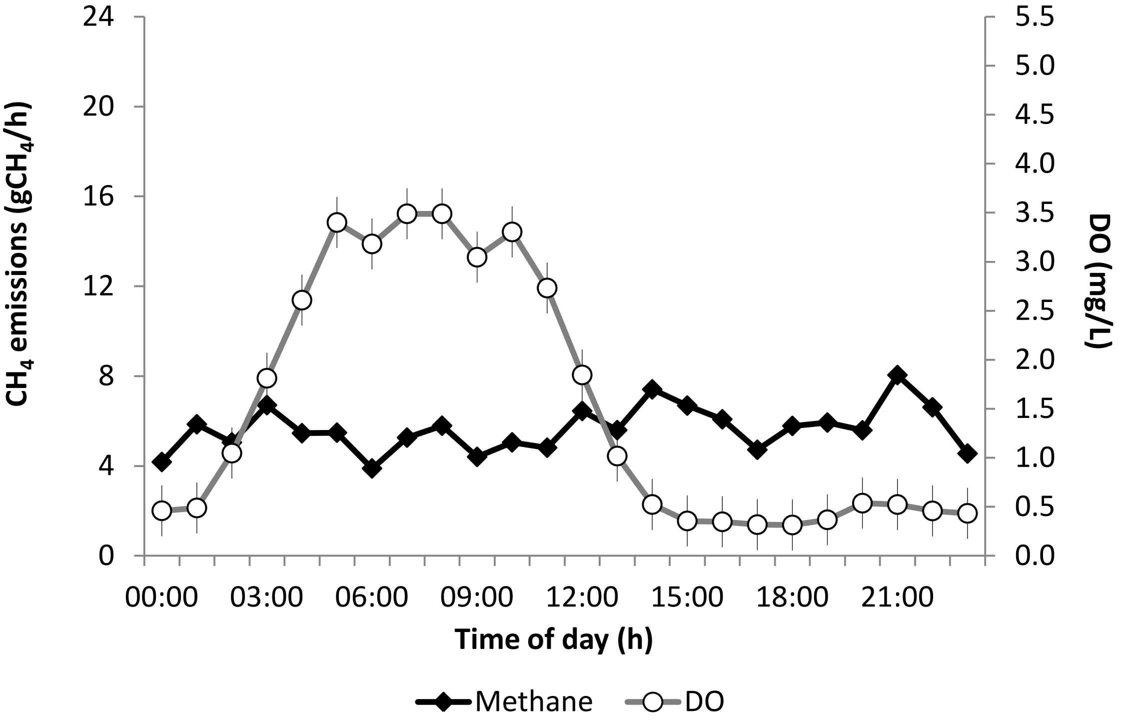
Time of day (h)
Methane
DO

E


CH$_4$ emissions (gCH$_4$/h)
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Time of day (h)
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Methane
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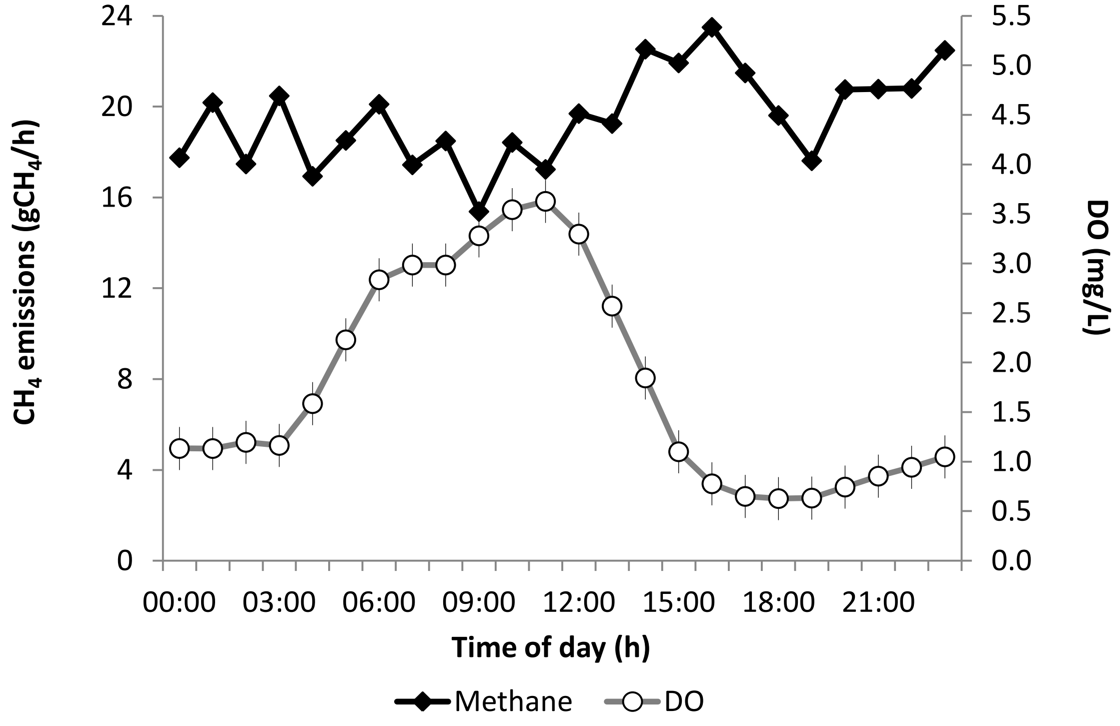
CH$_4$ emissions (gCH$_4$/h)
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21:00
Time of day (h)
DO (mg/L)
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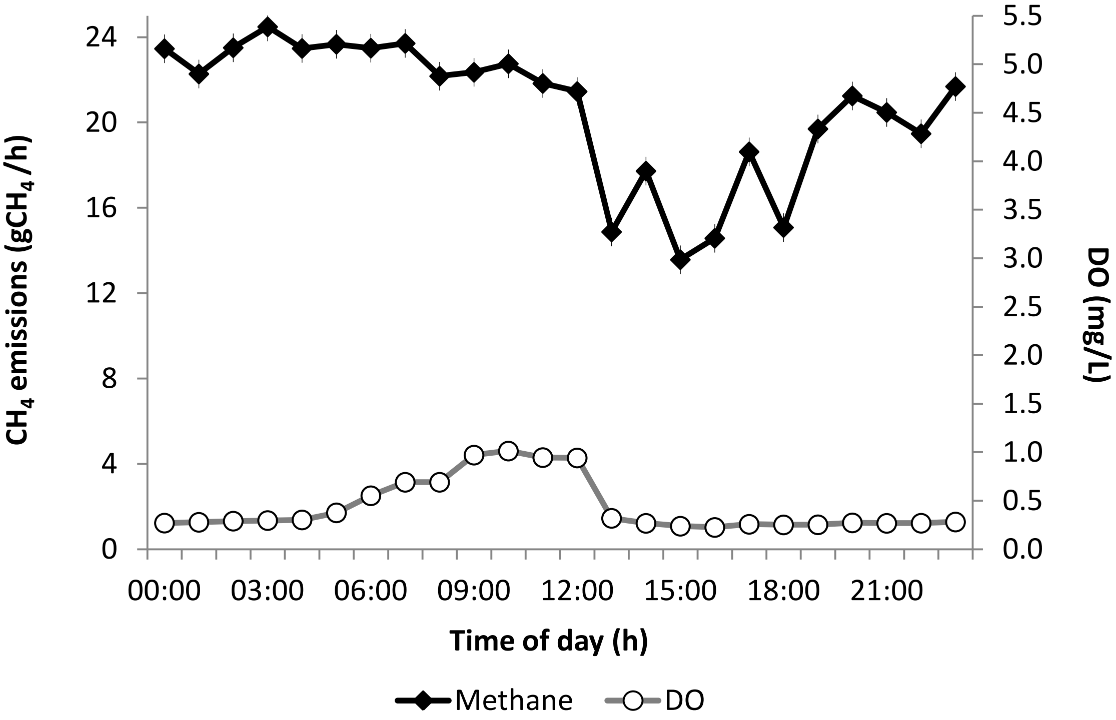
Methane
DO

G



H

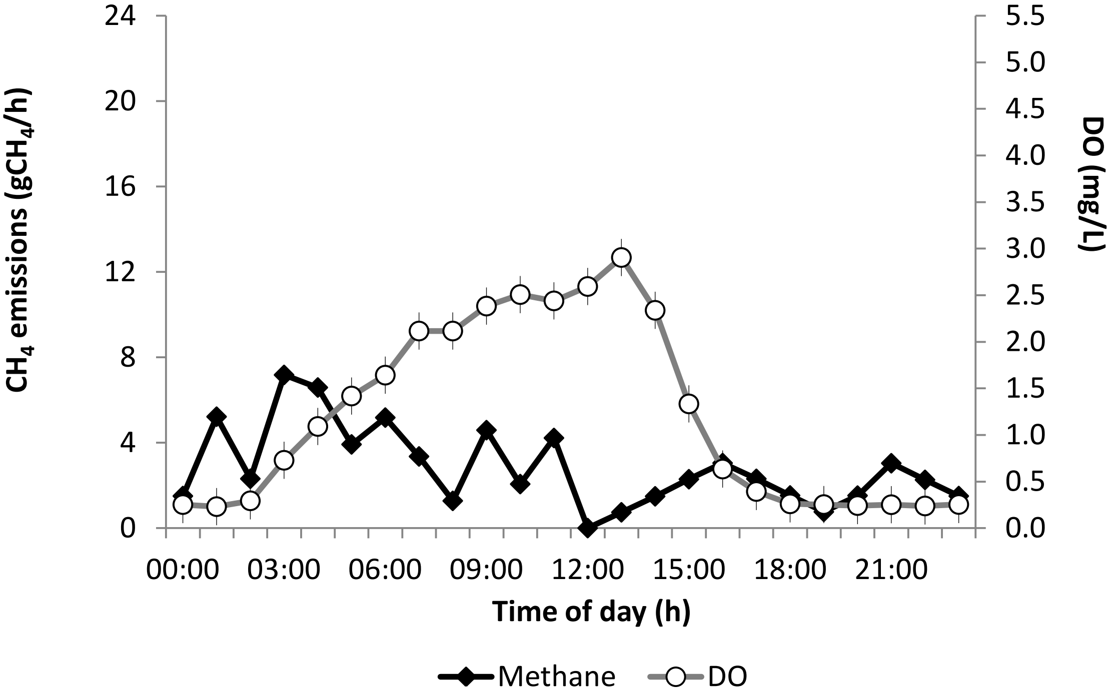


Figure 4.3 (A to H): Comparison between diurnal variability in CH$_4$ emissions and DO with standard error bars. Each graph looks at the relationship between CH$_4$ and DO in each of the eight zones (A to H).

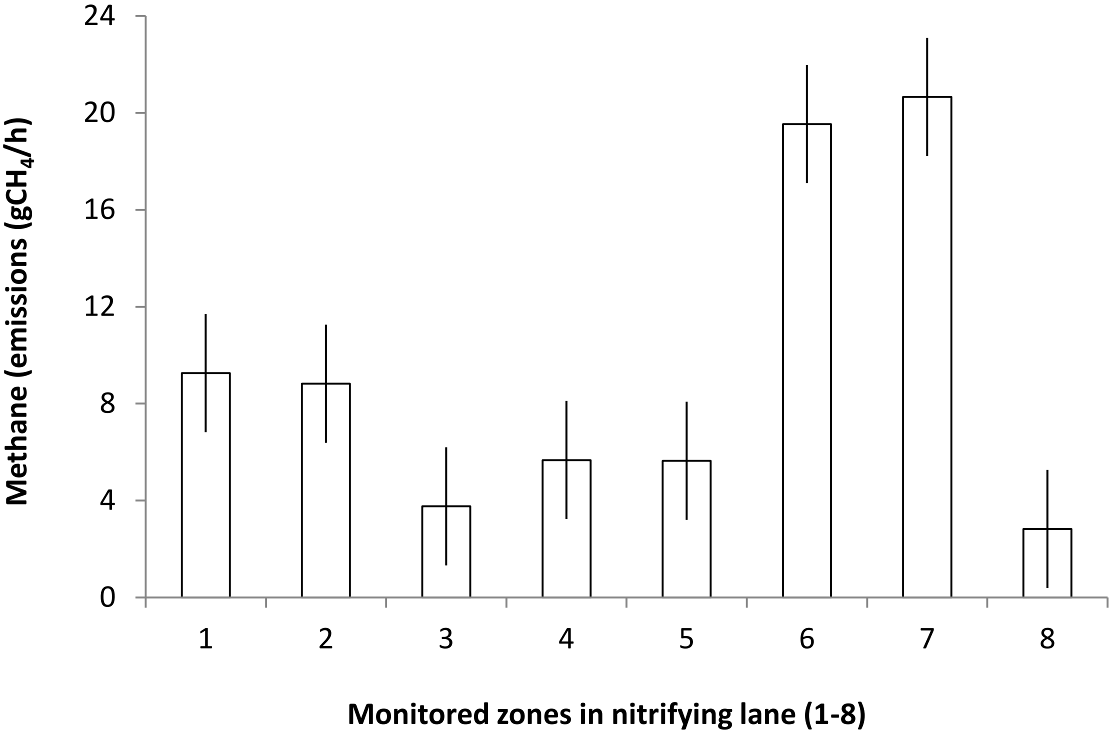


Figure 4.4: Spatial profile of average emissions obtained over the eight-week trial, showing mass fluxes for each monitored zone in the nitrifying lane (1–8), with error bars.

4.3.2. Methane emissions and operating conditions

Emissions showed a weak link ($r^2 = 0.30$) to DO concentrations, with CH_4 being emitted at both high DO concentrations in zones 2, 4, 5 and 6, and very low DO concentrations in zones 1 and 7 (Figs. 4.3 and 4.4). The lowest DO concentrations were found in zones 1, 3, 7 and 8. This is within the expected pattern as higher organic and NH_4^+ load at the inlet of the lane are typically associated with lower bulk oxygen concentrations and, as the oxygen demand diminishes as the flow progresses through the lane lower aeration levels are expected in the last treatment zones.

Comparison with the diurnal trend in influent flow rate (Fig 4.5) shows that generally, CH_4 emissions tend to be lower during peak flows (around 12:00 to 15:00), with the lowest emissions seen around 19:00. The flow rate however, increases towards the late evening, which is accompanied by an increase in emissions. Flow rate drops after midnight, whereas emissions continue to increase on an irregular trend.

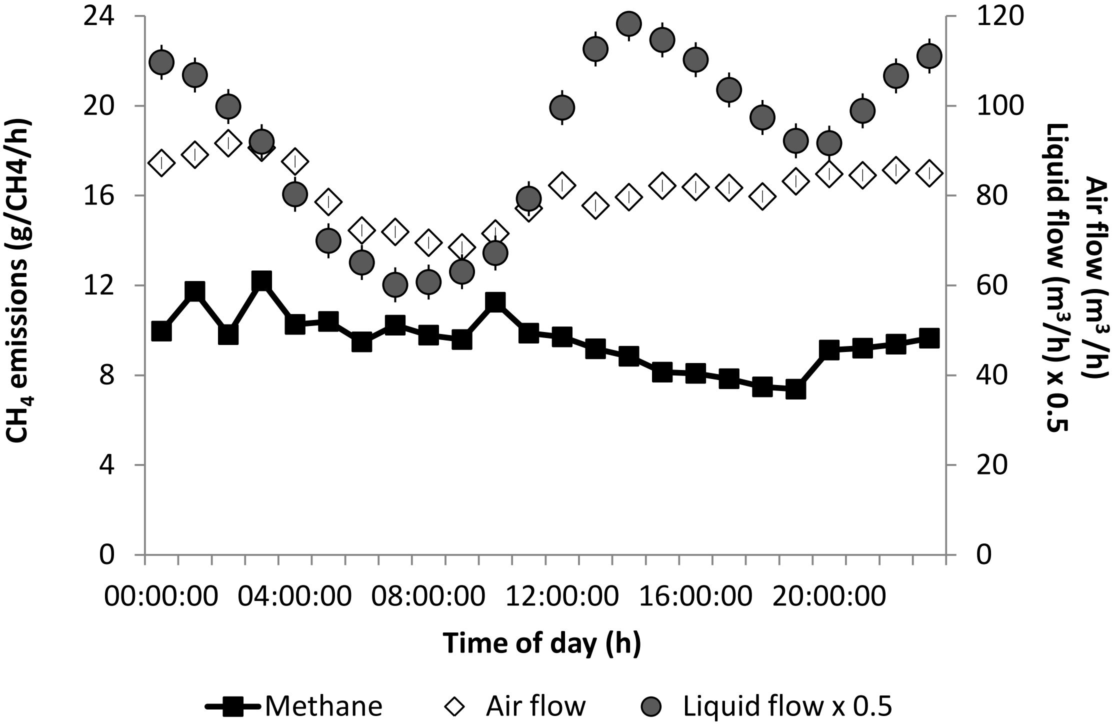


Figure 4.5: Comparison between diurnal variability in CH_4 emissions and influent liquid flow and airflow rates. Figures show emissions (gCH_4/h) with standard error bars. Liquid flow rate is multiplied by a factor of 0.5 for easier visibility.

The airflow rate drops around 03:00, whereas CH_4 emissions see a drop around 02:00 and increase again at 03:00, and continue to drop irregularly after that. The airflow increases around 10:00, during which there is a peak in emissions. Between midday and 18:00 the airflow shows a more irregular trend, with a somewhat steady increase between 14:00 to 17:00 but with occasional abrupt drops, around 13:00 and 18:00 in the afternoon. The irregular airflow trend in the afternoon is consistent with the influent peak flow (Fig. 4.5). After midday, CH_4 emissions continue to drop, reaching an all-low around 19:00, before increasing again after 20:00. This is accompanied by an increase in airflow (after 19:00 in the evening), with both trends increasing until about 01:00 in the morning.

The temperature of the wastewater did not change considerably throughout the monitored period, ranging between 17.9 ^{0}C and 18.1 ^{0}C. Although an important influencing factor to CH_4 emissions, in this study, the changes in temperature were too small to be relevant.

4.3.3. Greenhouse gas emissions versus aeration

Spatial distribution of off-gas emissions, namely CH_4, N_2O and CO_2, show a similar trend in average values for all gases in zones within the same aeration passes and airflow rates within those zones (Fig. 4.6). In the first aeration pass, which includes zones 1 and 2, the airflow rates are amongst the highest seen in the lane, averaging around 139 and 133 m^3/h during monitoring of zones 1 and 2 respectively (rates in the pass ranged between 90 to 170 m^3/h), leading to some of the highest GHG emissions seen, particularly for CO_2 and N_2O. Airflow, as well as emissions, drop considerably in the second aeration pass, zones 3 to 5. The lowest airflow rate seen in the lane is during monitoring of zone 3 (average of 32 m^3/h), although rates do not increase by much during monitoring of the other zones (zone 4 = 35 m^3/h and zone 5 = 37 m^3/h). Airflow increases again in the final aeration pass (ranging between 60 to 100 m^3/h and averaging around 95, 88 and 88 m^3/h during monitoring of zones 6, 7 and 8 respectively), which is accompanied by an increase in all GHG emissions, with the highest CH_4 emissions seen in this aeration pass.

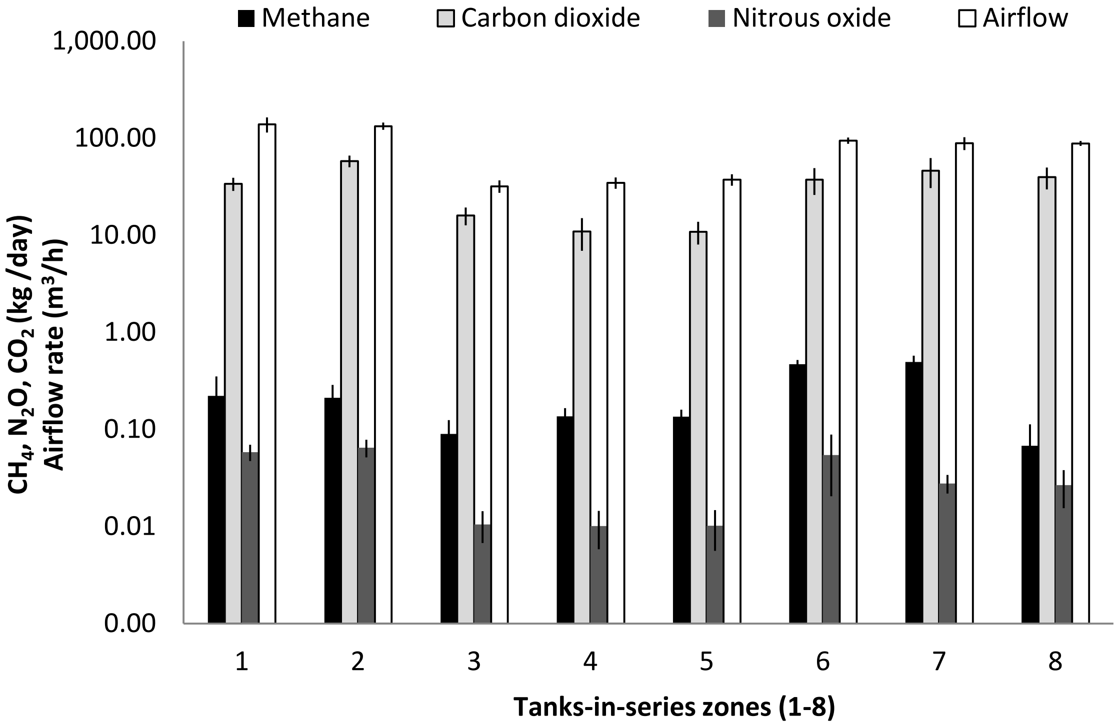


Figure 4.6: Comparison of spatial variability in off-gas emissions of CH_4, CO_2 and N_2O (averages in kg/day) versus average airflow rates (m^3/h) in each monitored tanks-in-series zone. For comparison purposes (to fit all bars in the same graph), the methane figures have been multiplied times 100, nitrous oxide time 1000 and airflow rate divided by 100.

4.3.4. Methane emissions and carbon impact

The average methane (CH_4-C) emission factor both as a percentage of influent COD into the lane and as COD removed was found to be 0.07 %, with emissions ranging from 0.04 % to 0.1 % for influent COD and between 0.04 % to 0.11 % for COD removed.

The CH_4 emissions from this particular nitrifying lane make up a total of about 667 $kgCH_4$/year, which translates as just over 14,000 $kgCO_2$ equivalents ($kgCO_2e$) per year.

This represents a 5 % increase in the carbon footprint associated with the electricity required to run the aeration lanes, which make up at total of 234,225 kgCO$_2$e/year (Table 4.1).

Table 4.1: Carbon impact of off-gas CH$_4$ emissions to carbon footprint of the nitrifying process

Description	Value	Units
Annual methane mass emitted	667	Kg year^{-1}
Methane global warming potential	21[a]	
Annual process emissions	14,012	KgCO$_2$e year^{-1}
Annual energy requirements for aeration	430,560	kWh year^{-1}
Conversion factor from grid electricity to carbon equivalents	0.544[b]	KgCO$_2$e kWh^{-1}
Annual operational carbon footprint	234,225	CO$_2$e year^{-1}
Total annual operational carbon emissions	268,368	CO$_2$e year^{-1}
Carbon impact of methane emissions	**5 %**	

[a] 1.0 kg of CH$_4$ = 21 CO$_2$ equivalents (IPCC, 2006)

[b] 1.0 kWh = 0.544 kgCO$_2$ equivalents (UKWIR, 2008)

4.4. Discussion

4.4.1. Factors influencing methane emissions

The diurnal pattern of emissions, whilst variable hour-on-hour and highly specific to each zone, was consistent throughout the lane, whereby repeated measurements throughout the monitoring week for each zone resulted in small standard deviations from the mean value. These low standard deviation values suggest similar conditions were achieved at specific times of the day (e.g., 6:00 shows a standard deviation of 0.2 gCH$_4$/h; Fig. 4.5) and as such, insight into the impacting factors on CH$_4$ emissions can be gained.

At this treatment works, influent flow tightly matches the influent load; that is, a higher flow rate is synonymous with a higher loading rate and vice-versa. Thus, as the influent flow increases, the residual DO in the nitrifying lane drops due to higher oxygen demand in the bulk liquid. This in turn works with a feedback loop controlled by the aeration control system, whereby when DO drops below the set-point of 1.5 mg/L in the lane, it triggers the blowers to increase the air supply. Therefore, as it can be seen in Figs. 4.4 and 4.5, at high influent flow the airflow rate is also higher, to a maximum achievable. As the airflow begins to increase, emissions increase as well (Fig. 4.4), suggesting the dissolved CH$_4$ in the bulk liquid is air-stripped. However, the airflow continues higher for a prolonged period of time to coincide with peak loadings, although emissions eventually drop suggesting that the dissolved CH$_4$ has been fully stripped out.

The aeration control and equipment employed at this treatment works have a significant effect on the range of DO concentrations that are found in the bulk liquid. Indeed, the highly dynamic DO profile in this ASP lane, where measured values ranged between <0.15 and >7.0 mg/L, suggests that anoxic and aerobic conditions can co-exist, with different “sites” within the same process where oxygen availability changes considerably (Tallec et al. 2008). This in turn can have a profound effect on the oxygen transfer from the liquid phase into the sludge floc (Ahn et al. 2001; Zeng et al. 2003; Zhen et al. 2011). Aeration, loading and resulting residual DO are all linked to CH_4 emissions from this lane, either by promoting release or enabling CH_4 formation within an aerobic treatment process.

4.4.2. Methane production or release?

The production of CH_4 in anaerobic conditions in the sewer network (Guisasola et al. 2009) and strictly anaerobic zones within a WWTP (Daelman et al. 2012) is generally well documented and expected, as methanogens require a source of organic carbon and anaerobiosis to establish. Thus, the logical explanation for CH_4 emissions in an aerobic lane as reported in the present study, could be attributed to air-stripping of dissolved methane (previously formed in the sewer network and/or primary tanks), from the bulk liquid to the atmosphere as a side effect of forced aeration to increase DO levels in the lane. Indeed, compared to N_2O (Henry's law constant, K_H, for solubility in water at 298.15 K for N_2O = 0.024 mol/kg*atm; Wilhelm et al., 1977), CH_4 has low water solubility (K_H for CH_4 = 0.0014 mol/kg*atm; Wilhelm et al., 1977), and is easily stripped off once in contact with air (Speight, 2004). Without measurements of dissolved CH_4 however, this hypothesis cannot be fully tested. Nevertheless, by comparing the spatial distribution of CH_4 with other monitored off-gas emissions in the lane (Fig. 4.6), namely CO_2 and N_2O, it is possible to see that they all seem to follow the same general pattern: the first aeration pass (zones 1 and 2) sees a peak in all the off-gas emissions, which drops in the middle pass (zones 3 to 5) and increases again in the final pass (zones 6 to 8). Because the same pattern is also seen for the airflow rates (Fig. 4.6), it is therefore feasible to conclude that the off-gas emissions seen in the zones within the aeration passes follow the same trends due to the effect of air-stripping caused by the aeration.

A less likely, but still possible explanation for the observed emissions in the present study is the formation of CH_4 within the nitrifying lane itself, as a direct result of the DO control system and resulting DO profiles. The consistency (i.e., low standard deviation) of emissions at 20–24 gCH_4/h in zones 6 and 7, when compared against the 5–8 gCH_4/h in zones 3 to 5, suggests that the higher values, observed further downstream in the process, could be a result of in-lane production, rather than increased levels of dissolved methane entering the lane from elsewhere during the monitoring campaign.

Under oxygen transfer diffusion limitations, an outer aerobic region may be created within the floc, which benefits from an immediate interface with the bulk DO, where therefore nitrification is most likely to take place (Zhen et al. 2011). An inner floc region is also created, where anoxic conditions prevail, because most of the oxygen is removed by the outer floc, allowing heterotrophic microorganisms to denitrify (Ahn et al. 2001; Zeng et al. 2003). Potentially, a core anaerobic microenvironment is thus formed, which could sustain a population of methanogens. Lens et al. (1995) for example, investigated the presence of methanogens and sulphate reducing bacteria in a selection of full and lab-scale aerobic wastewater treatment systems, from biofilm reactors to ASPs. They found that several types of strictly anaerobic microorganisms, both of the sulphate reducing and CH_4 producing kind, were present in a wide range of oxic reactors (with the exception of an ASP tank aerated with pure oxygen at 40 mg/L). The findings are explained by the existence of anoxic microenvironments inside a biofilm or activated sludge floc, or by the physiological versatility of these strictly anaerobic bacteria. Although the floc sizes in their experiments were higher (diameter = 1.6 mm) than normally found in conventional ASPs, the authors advise that the presence of anoxic micro-sites in full-scale environments cannot be ruled out.

Gray et al. (2002) reported on the presence of methanogenic *Archaea* and CH_4 production under anoxic conditions, in activated sludge samples. Methanogens, although inactive during optimal oxygen concentrations, would nevertheless quickly resume activity once conditions became anoxic. This suggests that methanogens may be exposed to, and even capable of surviving periods of oxygenation, during which they remain inactive until conditions are appropriate for methanogenesis to ensue. Therefore, these microorganisms do not necessarily need to reside in permanently anoxic zones in activated sludge flocs. It should be noted however, that the plants studied by Gray et al. (2002) were operated under intermittent aeration. This, they suggest, may be a viable factor in maintaining survival of methanogens. The dynamic DO profile in this nitrifying lane, where transient DO in the bulk liquid often drops to closely anoxic conditions (<0.2 mg/L), could make it viable for these microorganisms to nestle themselves in microenvironments within the flocs.

However, the low availability of biodegradable organic fraction in the nitrifying ASP would hinder methanogenesis, as well as the competition for carbon uptake, which occurs when denitrifiers and methanogens share the same habitat (Andalib et al. 2011). Conversely, it has been reported in previous studies that substrate competition is not the main obstacle in suppressing CH_4 production (Andalib et al. 2011; Klüber and Conrad 1998; Roy and Conrad 1999; Tugtas and Pavlostathis 2007). In fact, it is the presence of nitrogen oxides, nitrate (NO_3^-) and nitrite (NO_2^-) in particular, that has been associated with causing a complete, but largely reversible, inhibitory effect of methanogenesis, due to a redox potential effect (Banihani et al. 2009; Klüber and Conrad 1998). Indeed, the presence of NO_3^- in the last aeration pass of the tank, when nitrification has mostly taken place, is high (average = 12 mgN/L), despite also showing the highest CH_4 emissions; NO_{2-} on the other hand, was low (<1.0 mgN/L). Another nitrogen compound which inhibits methanogenesis is N_2O, which was also found in this aeration pass, particularly in zone 6 (average N_2O in bulk liquid = 79.9 g/day), as well as across the nitrifying tank (Aboobakar et al. 2013a). Indeed, both off-gas CH_4 and N_2O have been monitored in this study and shown to be emitted in similar fashion within the aeration passes of the lane (Fig. 6), although only dissolved N_2O was measured. Based on these measurements, it was concluded that N_2O was not only emitted but also produced within the nitrifying lane (Aboobakar et al., 2013a). However, due to the inhibitory effect that nitrogen has on CH_4, and given the aerobic conditions of the aeration tank as well as low availability of organic carbon sources, it seems improbable that strictly anaerobic methanogens could thrive in this environment. Considering all these conditions, it is likely that CH_4 emissions in the nitrifying tank are mainly a result of air-stripping rather than in-lane production, but further research is required to confirm this.

4.4.3. Methane emissions and carbon impact

Global anthropogenic CH_4 emissions account for 14 % of all GHG emissions, second only to CO_2 (GMI, 2010). For 2010, CH_4 emissions resulting from human activities worldwide were estimated at 6,875 million tonnes of CO_2 equivalents ($MtCO_2e$), with wastewater treatment corresponding to 594 $MtCO_2e$, about 9 %, of that value (GMI, 2010; USEPA, 2006; Yusuf et al., 2012). When compared to wastewater CH_4 emission values from 1990 (446 $MtCO_2e$), this represents an increase of over 33 % (Yusuf et al. 2012). Indeed, the contribution of wastewater treatment to the global CH_4 emissions is a growing trend, forecasted to rise by 12 % by 2020 (GMI, 2010; USEPA, 2006) and nearly 18 % by 2030 (USEPA, 2012). However, the reported values are based on projections, with some data not incorporated into these estimations due to time and method limitations, thereby adding to a significant uncertainty (USEPA, 2012).

In the United Kingdom, the average value of CH_4 emissions coming from ASPs, as estimated by the Environment Agency (George et al., 2009), is derived from a study carried out by Czepiel et al. (1993), where measured CH_4 corresponded to 39 gCH_4/person/year. When allowing a 245 L of wastewater treated per person per day, this gives an estimation of 0.4 $kgCH_4$ per megalitre of wastewater treated, or 0.0004 $kgCH_4/m^3$ per day (George et al., 2009). However, this value has an assumed overestimation since the measurements include emissions from primary sedimentation. The average per day in the present study over the monitored eight-week period was 0.0003 $kgCH_4/m^3$ per day, which is very close to the UK estimation, especially considering it represents the emissions solely from the aerobic biological treatment process.

The emission factor of 0.07 % (of influent and removed COD) is lower than reported by other full-scale studies (Table 4.2), although similar to that found by Wang et al., (2011a) of 0.08 %. However, unlike in other studies, the emissions measured here are derived solely from the aerobic treatment process, without any input from anaerobic digestion facilities. Therefore, if the overall site was to be accounted for, it is likely that CH_4 emitted in other parts of the WWTP would add to the reported value.

Table 4.2: Normalised methane emission factors for this and other full-scale studies

Author	**$kgCH_4/kgCOD$ load (%)**	**Comments**
Czepiel et al., (1993)	0.34 [a]	Durham WWTP, New Hampshire, United States. Grab samples method.
Daelman et al., (2012)	1.13 [b]	Kralingseveer WWTP, Netherlands. Online measurements of CH_4 off-gas. Dissolved CH_4 also measured.
Wang et al., (2011a)	0.08	Jinan WWTP, China. Grab samples method. Dissolved CH_4 measured.
This study	0.07	Coleshill WWTP, England. Online measurements of CH_4 off-gas. Spatial and diurnal profiling of emissions across a nitrifying lane only.

[a] *Originally expressed as 0.16 % as kg CH_4/kg BOD_5. Conversion factor from Grady et al. (1999) where: COD ≈ (2.1) (BOD_5) used to convert to kg CH_4/kg COD*

[b] *Includes an anaerobic digestion facility*

The discrepancies between estimated and measured emission factors highlight the need for a global emission inventory based on real, full-scale measurements, whereby site-specific operational conditions must be taken into account, since these are key in shaping emission profiles.

More importantly, with a global warming potential 21 times stronger than that of CO_2, (IPCC, 2006), a small CH_4 emission factor can nevertheless have an impact on the total carbon footprint of a sewage treatment works. In this particular study, the mass of measured CH_4 emissions represent a total of around 667 $kgCH_4$-C/year, which equates to an annual 14,000 $kgCO_2e$, or 5 % (Table 1), added to the energy requirements associated with the operation of the lane (embodied carbon calculations not considered).

As reported by the Environment Agency (the environmental regulatory body in England and Wales), the water industry was responsible for 5 $MtCO_2e$ in 2007/2008, which corresponded to 0.8 % of the annual UK GHG emissions (Environment Agency, 2009). Of those, 56 %, or 2.8 $MtCO_2e$ came from wastewater treatment. By comparison, the carbon impact measured in this study is much lower. However, the implications could be significant, particularly in the current legislative scenario: the UK has a challenging framework under the Climate Change Act of 2008, which sets out a reduction of the overall carbon emissions from all sectors by 80 %, below the 1990s levels, by 2050. Indeed, legislation requiring the mandatory reporting of GHG emissions by companies is currently being introduced (DEFRA, 2009).

4.5. Conclusions

A highly dynamic trend of CH_4 emissions both in time and space, was found in the nitrifying lane. Data from this and other full-scale research, suggest that emissions are mostly air-stripped in the aeration tank and that methane is produced elsewhere, in the sewer or in zones in WWTPs where anaerobic conditions prevail. Because of the transient conditions recorded in the lane, the possibility of methanogens surviving within anoxic/anaerobic microenvironments within the flocs is made viable. However, low availability of biodegradable organic fraction, competition for carbon uptake with heterotrophs and the presence of nitrogen oxides, have all been identified as inhibiting methanogenesis. Further investigation into the mechanisms of CH_4 production and emission are needed to explain the findings from this study.

A CH_4 emission factor of 0.07 % of influent and removed COD was determined, and found to be lower than reported by other full-scale studies. This equated to a carbon impact of 5 % added to the energy requirements associated with the operation of the lane. Although a small increase in carbon emissions, may still have a huge impact on the overall emissions for a water company as a whole, particularly as the industry moves towards a carbon-reducing future. An adequate profiling of full-scale GHG emissions is thus critical for future proofing the existing treatment technologies.

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CHAPTER 5

PAPER 3: NITROUS EMISSIONS UNDER DIFFERENT DISSOLVED OXYGEN SET-POINTS IN A FULL-SCALE NITRIFYING ACTIVATED SLUDGE TREATMENT PLANT

IN PREPARATION: paper in finalised draft and potential journal for publication is currently under discussion.

5. NITROUS EMISSIONS UNDER DIFFERENT DISSOLVED OXYGEN SET-POINTS IN A FULL-SCALE NITRIFYING ACTIVATED SLUDGE TREATMENT PLANT

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Abstract

This study was designed to quantify nitrous oxide (N_2O) emissions during full-scale wastewater treatment in a nitrifying activated sludge plant (ASP), under different dissolved oxygen (DO) set-points (1.5 and 2.0 mg/L), using an online methodology, in order to investigate the effect of DO in triggering N_2O production. The study also included a lab investigation to answer the following questions: is there a specific low ammonia (NH_4^+) threshold by which N_2O production stops? And what is the main biological pathway of N_2O production in the final stages of a nitrifying ASP?

Nitrous oxide emissions were higher at DO set-point of 2.0 mg/L than at 1.5 mg/L, with emission factors (EF) at 0.58 % and 0.05 % of influent total nitrogen (TN) respectively. This was unexpected, since the higher set-point also resulted in higher DO concentrations and N_2O has been shown to drop at higher DO concentrations, somewhat contradicting the current findings. However, increase in emissions at higher set-point, and within zones for both set-points, were found to be driven by an increase in DO variability. Therefore, increase in operational fluctuations, particularly DO, imposes stress onto the biological process, thereby increasing N_2O production. Low NH_4^+ nitrification lab tests showed that N_2O is produced even at very low concentrations (0.5 mgNH_4-N/L), thus explaining the emissions seen in the final stage of the full-scale ASP, where NH_4^+ levels were consistently low. And since N_2O production was always accompanied by nitrite (NO_2^-) peaks, it suggests that autotrophic nitrifier denitrification, via reduction of NO_2^-, is the main triggering mechanism under aerobic and low DO conditions, although off-gas emissions dropped considerably due to absence of aeration under low DO. Denitrification batch tests at low C/N ratios also showed that heterotrophic incomplete denitrification is taking place in the nitrifying ASP, with emissions from this pathway shown to be higher in the lab than for the nitrification tests. Finally, the emission factor was shown to be dependent on the nitrogen fraction, thereby raising questions as to the relevance and reliability of a generic EF.

***Keywords**: nitrous oxide, dissolved oxygen, activated sludge, nitrification, denitrification, wastewater treatment.*

5.1. Introduction

Nitrous oxide (N_2O) is a greenhouse gas (GHG) with a 100-year global warming potential (GWP) about 310 times stronger (IPCC, 2006) than that of carbon dioxide (CO_2) and therefore represents a major environmental issue. It is also predicted to be the most significant ozone-depleting substance to be emitted in the 21st century (Ravishankara et al., 2009). Despite a relatively small contribution to the overall global emissions (Thomson et al., 2012), N_2O from wastewater treatment plants (WWTPs) is on the rise, currently estimated at 2.8 % (IPCC, 2007); and because of its strong GWP, N_2O emissions from this sector are of great concern, as they are estimated to increase by approximately 13 % between 2005 and 2020 (Gupta and Singh, 2012). Furthermore, it has been estimated that even a low emission factor (EF) such as 0.5 % in conventional activated sludge plants (ASP) or biological nutrient removal plants (BNR), could be equivalent to the same amount of indirect carbon emissions associated with energy consumption (De Haas, 2004; Ye et al., 2014).

The release of N_2O is mainly attributed to microbiological processes, particularly from nitrification and denitrification (Colliver and Stephenson, 2000; Tallec et al., 2006; 2008) in BNR plants, to remove nitrogen from wastewater. However, the specific contributions of each process to N_2O production is still debatable, as limited information is available as to how this GHG is emitted in WWTPs. Presently, the tools used to report on emissions from WWTPs rely on over-simplified estimations, which do not include influencing factors (Ye et al., 2014). Nevertheless, data from full-scale studies are beginning to emerge, focusing mainly on two issues: the huge variability seen in EF, which tend to be site-specific (Aboobakar et al., 2013a; Ahn et al., 2010a; Foley et al., 2010a), and the significant effect of operating conditions on N_2O production and emission. This also highlights the importance of quantifying N_2O from reliable and methodical approaches, which integrate both the impact of operational conditions and plant design settings on N_2O formation and emission.

Indeed, one operational factor considered to be key in controlling N_2O production (Kampschreur et al., 2008a; 2009; Tallec et al., 2006; Zheng et al., 1994) is dissolved oxygen (DO), since low DO conditions in the nitrifying process result in localised oxygen depletions in the tank, leading to process disturbances, which in turn promote N_2O production, mostly via the nitrifier denitrification pathway (Kampschreur et al., 2009a; Tallec et al., 2006). It follows therefore, that N_2O is generated – and subsequently emitted – as a stress response by nitrifiers to disruptions in the oxygen supply (Burgess et al., 2002a; Sivret et al., 2008). It has been shown that at DO concentrations below 1 mg/L, N_2O production can account for 10 % of the nitrogen load (Goreau et al., 1980), and that increased emissions correlate with drops in DO concentrations (Aboobakar et al., 2013a). Because of the significant impact of DO on N_2O emissions, a more appropriate control over nitrification may result in lower emissions, and indeed the monitoring of off-gas N_2O has been suggested as a process control tool for aeration supply and early warning of nitrification failure (Burgess et al., 2002a; Butler et al., 2005; 2009; Sivret et al., 2008). Moreover, it has been shown that N_2O emissions increase with increasing airflow (Kampschreur et al., 2008b), particularly with accumulation of N_2O in the bulk liquid. This indicates that the production of N_2O is a concentration-driven process (Kampschreur et al., 2009a) and can therefore be reduced by minimising aeration, as long as oxygen availability is not limited.

Changes to ammonia (NH_4^+) concentrations also influence N_2O production during nitrification, particularly during NH_4^+ oxidation (Burgess et al., 2002a; b; Kampschreur et al., 2008a; Kim et al., 2010). Sudden high concentrations or shock loadings of ammonia, ranging from 50–2440 mg/L (Burgess et al., 2002a; b; Kim et al., 2010; Law et al., 2012; Tallec et al., 2006) have been shown to trigger an increase in oxygen demand, thus reducing DO availability in the wastewater, which in turn results in N_2O being produced via nitrifier denitrification. The production of N_2O via this pathway has been linked to the accumulation of nitrite (NO_2^-), predominantly under reduced DO (Tallec et al., 2006; Wunderlin et al., 2012) and high NH_4^+ concentrations (Wunderlin et al., 2012). However, we have recently reported on N_2O production in the final stages of a full-scale nitrifying ASP, where NH_4^+ concentrations were consistently low (Aboobakar et al., 2013a), although it was not clear from the findings, whether this was due to nitrification or denitrification pathways. Indeed, because of the mixed populations inherent to an ASP environment, the presence of heterotrophic denitrifying microorganisms in a fully aerated ASP cannot be ruled out. Low oxygenation and low carbon to nitrogen ratios (C/N) are the main factors attributed to N_2O production by incomplete heterotrophic denitrification (Itokawa et al., 2001; Kishida et al., 2004; Tallec et al., 2006). Therefore, if both these conditions co-exist in a nitrifying ASP they could trigger a significant release of N_2O, as previous findings reported a 20–30 % of influent nitrogen converted to N_2O where incomplete denitrification prevailed (Itokawa et al., 2001).

However, very little data is available on full-scale research plants that confirms many of these findings (Kampschreur et al., 2009a). This highlights the need for further research, not only in order to quantify emissions but also for a greater knowledge of the mechanisms of production during nitrogen removal from wastewater and how operational conditions can influence that production; more so when changes to DO settings may equally impact on ASP performance as well as trigger N_2O emissions.

This study therefore, was designed to quantify N_2O emissions during full-scale wastewater treatment in an ASP, under different DO set-point control settings, whilst applying an online methodology, to monitor detailed profiles of off-gas and dissolved N_2O, as well as operating conditions. The following research questions are to be answered: is there a specific low NH_4^+ threshold by which N_2O production stops? And what is the main pathway of N_2O production in the final stages of a nitrifying ASP: nitrification under low NH_4^+ concentrations or heterotrophic incomplete denitrification due to low C/N ratios?

5.2. Materials and methods

5.2.1. Monitoring site

A full-scale wastewater treatment site in the Midlands, UK, serving a 210,000 population equivalent, was chosen for this study. The monitored process consisted of a three-pass aeration lane, in a plug-flow nitrifying ASP, preceded by an anoxic zone treating 10 % of the daily incoming flow. The lane was designed to provide an eight-hour hydraulic retention time (HRT) and 10-day solid retention time (SRT), at average flow rate of 185–300 m^3/h in the aeration tank, and a HRT of 30 minutes in the anoxic zone. The aeration control consisted of blowers in duty/assist/standby modes. Two DO control set-points were tested, at baseline set-point of 1.5 mg/L and a higher set-point of 2.0 mg/L. Stress response tests were carried out by operating the lane at a lower set-point of 0.5 mg/L for two weeks and during 36 events of intermittent aeration.

5.2.2. Full-scale measurement campaign

An online methodology was used to monitor operating conditions and emissions continuously during eight-week periods for DO set-points 1.5 and 2.0 mg/L respectively and two weeks for DO set-point of 0.5 mg/L. Off-gas N_2O was captured using a gas-collecting floating hood (surface area = 0.34 m^2; Water Innovate, UK), suspended over the wastewater and connected to a PTFE tubing sampling line. Off-gases were pumped through via an infra-red gas analyser with an integrated sample pump, moisture trap, auto-calibration system and data-logging unit, recording concentrations every minute (N-TOX®, Water Innovate, UK). Dissolved N_2O was detected every minute, using a modified Clark electrode probe (N_2O-R mini-sensor, Unisense A/S, Denmark) connected to a picoammeter and data-logging laptop. A rugged DO probe LDO probe with Sc100 monitor (Hach Lange, Germany), was used to monitor DO concentrations in the bulk liquid every 15 minutes and placed next to the gas analyser and floating hood.

In order to produce a spatial profile of emissions in the lane, a tanks-in-series (TIS) model for plug-flow was used which produced eight equally-distributed sampling "zones" in the nitrifying lane (Aboobakar et al., 2013a), with zone 1 at the inlet of the aeration lane, immediately after the anoxic zone, and zone 8 at the outlet of the lane just before the weir. The first two zones (zones 1 and 2) were in the first aeration pass, with zones 3 to 5 in the middle and zones 6 to 8 in the last aeration pass of the plug-flow lane. The equipment was deployed in each of these zones for a period of one week per DO set-point, giving a total of eight weeks of monitoring for each set-point (except for the low set-point of 0.5 mg/L, when the monitoring took place over a two-week period, in the first aeration pass only). The airflow rate was monitored continuously, using an insertion-type airflow meter (VPFlowScope, Omni Instruments, UK), with readings taken every 15 minutes. Two online NH_4^+ monitors (STIP PBS1, Envitech, UK) were also used, with one capturing influent NH_4^+ to the aeration lane (in zone 1) and another recording NH_4^+ two-thirds down the lane (in zone 6), where most of the NH_4^+ had been nitrified.

A sampling campaign was also carried out every two weeks in parallel with the online monitoring, during which 24-hour discrete samples were collected from settled sewage and final effluent, and grab samples from the returned activated sludge (RAS) at peak and low loadings. Samples were analysed for NH_4^+, nitrate (NO_3^-), NO_2^-, total nitrogen (TN) and chemical oxygen demand (COD) using colorimetric test kits (Hach-Lange, Germany) and for solids (total and volatile suspended solids, TSS and VSS respectively) according to Standard Methods (APHA, 2005). A nitrogen mass balance of the combined data was used to determine the EF, based on the percentage of influent NH_4^+ and TN emitted as N_2O.

5.2.3. Batch experiments

Reactors with a working volume of 2.0 L were operated under different DO conditions to test for N_2O profiles under a range of low NH_4^+ concentrations (nitrification) and low C/N ratios (denitrification). The reactors were seeded with 0.25 L of sludge from the full-scale ASP and 1 L of synthetic feed and operated at room temperature (20–22 ^{0}C). The contents were kept in suspension by mixing with a magnetic stirrer, while air was supplied with a fish tank pump via a fine bubble diffuser (1.5 L/min). The adapted synthetic wastewater (OECD, 2001) was made by adding reagent grade phosphorous, sulphur, and trace elements in quantities needed to support biological growth, based on Grady et al. (1999).

Three-litre stock solutions were prepared by dissolving the following ingredients in deionised water: calcium chloride dehydrate ($CaCl_2$*$2H_2O$), disodium hydrogen orthophosphate dodecahydrate (Na_2HPO_4*$12H_2O$), iron (III) chloride hexahydrate ($FeCl_3$*$6H_2O$), magnesium sulphate heptahydrate ($MgSO_4$*$7H_2O$), potassium chloride KCl), sodium bicarbonate ($NaHCO_3$) and sodium chloride (NaCl). For the nitrification experiments, 0.23 g of ammonium chloride (NH_4Cl) were added to the synthetic feed to make up a 20 mgNH_4-N/L NH_4^+ concentration, whilst no NO_3^- or carbon sources were added in order to prevent denitrification. The stock solution was used as feed for the control reactors and further diluted to low NH_4^+ concentrations for the batch tests.

For the denitrification experiments, no NH_4^+ was added in order to prevent nitrifier activity, and the stock solution was prepared with a concentration of 40 mgCOD/L (37 mg/L of the carbon source), using 0.1 g of dextrose anhydrous ($C_6H_{12}O_6$), 1.9 mL of 1.0 M acetic acid (CH_3COOH) and 2.2 g of potassium nitrate (KNO_3) to make up a NO_3^- concentration of 8.9 mgNO_3-N/L (OECD, 2001). This solution was used for the control reactors (COD/NO_3-N ratio of 4.5). For the batch tests, the COD concentration was kept at 40 mgCOD/L and the required low C/N ratios were achieved by adjusting for different concentrations of nitrate nitrogen (NO_3-N, Table 5.1). All chemicals were purchased from Fisher Scientific UK Limited (United Kingdom). Experiments started once the feed was added.

Table 5.1: Batch test experiments

Reactor	Label	Concentration (mg/L)[a]	DO conditions	C/N ratio[b]
Experiment 1 - nitrification reactors				
1	Control 1 *Full nitrification*	20.0	Aerobic (target DO 6 mg/L)	N/A
2	Control 2 *No nitrification – no DO*	20.0	Air off	
3	Control 3 *No nitrification - no ammonia*	0.0	Aerobic	
4	Control 4 *No nitrification, no ammonia or DO*	0.0	Low DO (target DO 0.5 mg/L)	
5	Test 1	5.0	DO 8 mg/L (condition 1) DO 0.5 mg/L (condition 2)	
6	Test 2	2.5		
7	Test 3	1.9		
8	Test 4	1.0		
9	Test 5	0.5		
Experiment 2 - denitrification reactors				
1	Control 1 *Optimal denitrification*	8.9	Anoxic	4.5
2	Control 2 *No denitrification (high DO)*	8.9	Aerobic	4.5
3	Control 3 *Denitrification after aeration stops*	8.9		4.5
4	Test 1	14.5	Intermittent (15 min on, 45 min off)	2.8
5	Test 2	16.5		2.4
6	Test 3	18.0		2.2
7	Test 4	21.6		1.9
8	Test 5	28.0		1.4

[a] *Refers to the concentrations of nitrogen species: Experiment 1 in mgNH_4-N/L. Experiment 2 in mgNO_3-N/L (the COD concentration is constant in Experiment 2 = 40 mgCOD/L).*

[b] *Only applicable to Experiment 2 – testing for different C/N ratios*

Nitrifying batch tests

Activated sludge was collected in the morning from the monitored site before total nitrogen and COD peak loads, and kept under experimental conditions (airflow, DO, pH and temperature) for up to two hours prior to the experiments (Wunderlin et al., 2012). Samples were taken for liquid species (nitrogen and COD) and solids (TSS and VSS), during this period. The experiments were started by adding the synthetic feed according to the requirements of each batch reactor. Nitrification was tested under a range of five NH_4^+ concentrations and four control reactors (Table 5.1). Two DO conditions were tested: high (> 6.0 mg/L) and low (0.5 mg/L) concentrations, in order to compare N_2O profiles under low NH_4^+, with optimal and sub-optimal oxygenation. Experiments stopped when NH_4^+ was fully oxidised.

Denitrifying batch experiments

Sludge collected on-site was stored in a batch reactor overnight, and conditions kept anoxic in order to remove any remaining nitrogen species (Wunderlin et al., 2012). Denitrification experiments were then carried out under a range of five low C/N ratios and intermittent DO conditions (Table 5.1), which were achieved by aerating the reactors for 15 minutes and switching the air off for the remainder of the experiment. Experiments stopped when NO_3^- was fully reduced.

Analytical procedures

Samples were collected from all reactors during the experimental period, for liquid and solid analysis. Dissolved as well as off-gas N_2O, DO, pH and temperature were monitored online. Both off-gas and dissolved N_2O were monitored using the same equipment as described in section 5.2.2., for the full-scale measurement campaigns. Dissolved oxygen and pH were monitored using lab-scale probes (HQ40d multi-meter with pH gel probe and standard DO probe; Hach-Lange, Germany). Liquid grab samples for nitrogen species and COD were filtered and analysed using commercial colorimetric test kits (Hach-Lange, Germany).

Statistical analysis was also carried out to determine the differences in diurnal variation under each set-point, using two-way, repeated measures ANOVA, using STATISTICA v12 software (StatSoft Inc, Oklahoma, USA).

5.3. Results

The treatment works achieves over 95 % removal rates, with average (settled sewage) influent concentrations of 38 mg/L for NH_4^+, 125 mg/L for TSS and 450 mg/L for COD. The final effluent concentrations average 0.25, 25 and 13 mg/L for NH_4^+, TSS and COD respectively, which is within the expected levels and well below the effluent NH_4^+ discharge consent of 5.0 mg/L.

The NH_4^+ load into the activated sludge lane averaged 55.5 ($\underline{+}$1 standard deviation) kgNH$_4$-N/day and 54 ($\underline{+}$1) kgNH$_4$-N/day during the monitoring periods at DO set-points of 1.5 and 2.0 mg/L respectively, showing little change from one set-point to another.

The average load during the two-week period at DO set-point of 0.5 mg/L was 50 (±1.1) kgNH_4-N/day. The DO depletion levels seen during this low set-point had a negative impact on nitrification, with NH_4^+ removal rates dropping from 95 to less than 45 %.

The average inlet NH_4^+ concentrations into the aerated tank (zone 1) were 13.2 (±4.5), 15.3 (±5.1) and 9.4 (±4.2) mgNH_4-N/L for set-points 0.5, 1.5 and 2.0 mg/L, respectively. The average NH_4^+ concentrations in the settled sewage (i.e., prior to mixing with the RAS stream) were: 38 (± 5) and 28.9 (±6.7) mgNH_4-N/L for set-points 1.5 and 2.0 mg/L respectively, and 35.8 (±4.5) mgNH_4-N/L for the lowest set-point of 0.5 mg/L.

The in-lane sampling of nitrogen species during each monitored period, showed no statistical differences between the set-points of 1.5 and 2.0 mg/L, with most nitrification taking place in the first two thirds of the lane, for both set-points, and with NH_4^+ leaving the lane (zone 8) averaging at 1.1 and 1 for set-points 1.5 and 2.0 mg/L. Nitrate concentrations also remained similar at 15 and 16 mgNO_3-N/L for set-points 1.5 and 2.0 mg/L. The main difference between the two set-points rested with in-lane NO_2^-, which averaged at 0.3 mgNO_2-N/ for set-point 1.5 mg/L, with the highest concentration seen in zone 6, at 0.5 mgNO_2-N/L. For set-point 2.0 mg/L, the average doubled in comparison to the lower set-point, at 0.6 mgNO_2-N/L, with the highest value seen in zone 3, at 1.42 mgNO_2-N/L. No in-lane sampling was carried out during the monitoring of set-point 0.5 mg/L. The influent liquid flow rates from the settled sewage averaged as follows: 4,300 (±1500), 4,770 (±2,130) and 7,300 (±2,500) m^3/day for set-points 0.5, 1.5 and 2.0 mg/L respectively.

5.3.1. Nitrous oxide profile

The data showed high spatial variability in both off-gas (Fig. 5.1A) and dissolved N_2O (Fig. 5.1B), in each of the monitored zones within the lane, for DO set-points 1.5 and 2.0 mg/L. The highest value for dissolved N_2O, was seen in zone 2, during the two weeks in which DO set-point of 0.5 mg/L was monitored, at just over 2.3 kgN_2O-N/day per kgNH_4-N/day. This was a significant increase, compared to the highest dissolved N_2O peaks seen for the other two set-points, at 0.0013 (zone 6) and 0.32 (zone 2) kgN_2O-N/day per kgNH_4-N/day for 1.5 and 2.0 mg/L respectively.

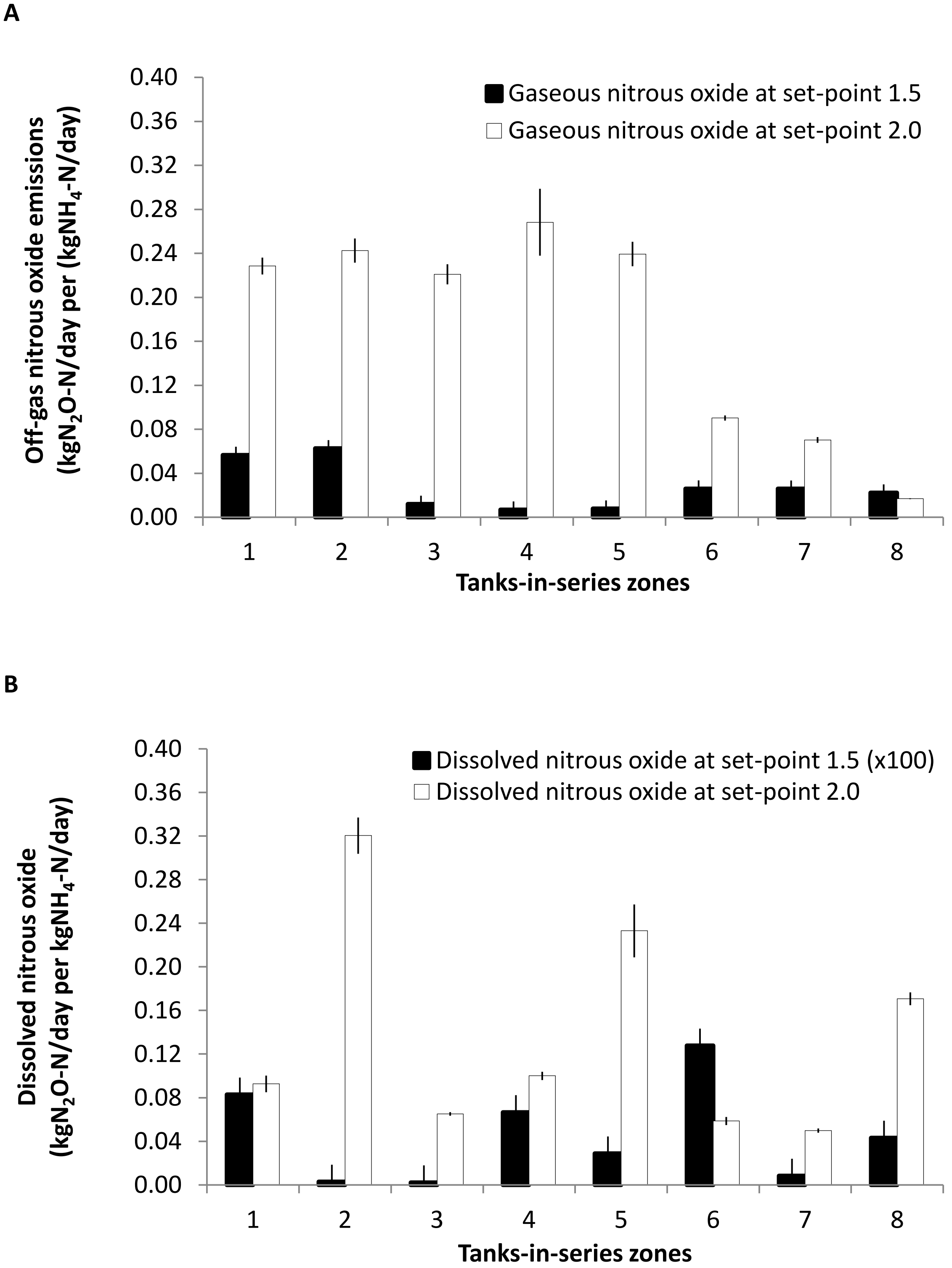


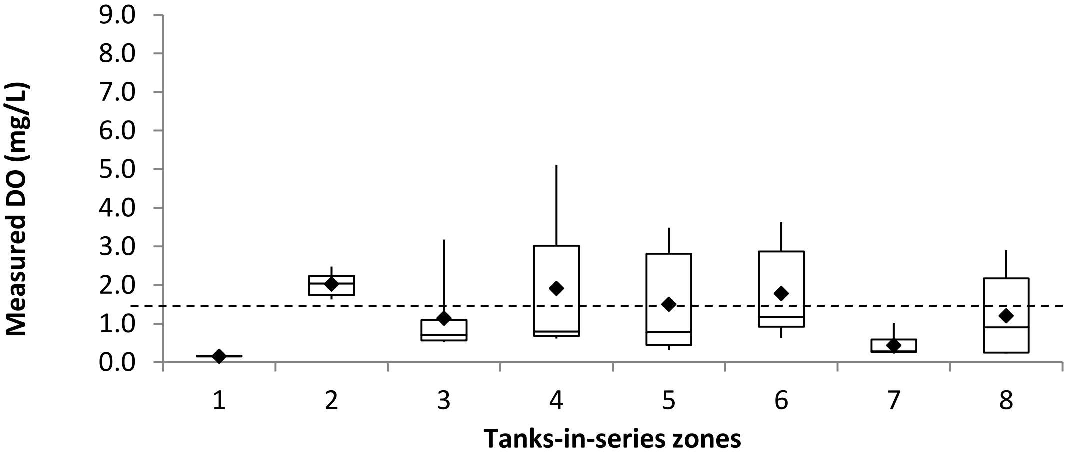
Figure 5.1: Spatial comparisons of off-gas (A) and dissolved (B) N_2O for DO set-points 1.5 and 2.0 mg/L

Off-gas N_2O on the other hand (Fig. 5.1A) was, on average, lower than the values seen for dissolved N_2O, with the highest trends recorded for the set-point of 2.0 mg/L, particularly in zone 4 (middle aeration pass), at 0.27 kgN_2O-N/day per kgNH_4-N/day, which was about 4.5 times higher than the highest peak seen during set-point 1.5 mg/L, at 0.06 kgN_2O-N/day per kgNH_4-N/day in zone 2 (first aeration pass). Nitrous oxide was emitted from zone 1 (closer to the anoxic zone) up to zone 8 (back end of the lane).

5.3.2. Dissolved oxygen profiles

Similarly to N_2O emissions, the DO measurements showed high variability (Fig. 5.2), whereby the recorded DO concentrations in the nitrifying lane changed considerably from 1.5 to 2.0 mg/L control set-points. Fluctuations occurred on a daily basis, with measured averages drifting away from the targeted set-points, revealing not only a distinct spatial profile in each zone but also in different days within the same monitoring zone. For set-point 2.0 mg/L, the average DO shifted towards higher measured concentrations, with the only values below 1 mg/L seen in zones 1 and 6, compared to the baseline set-point of 1.5 mg/L, where values <1.0 mg/L were seen in all zones, except in zone 2, where the lowest DO concentration was 1.7 mg/L. Notably, in the set-point 1.5 mg/L, there was a dip in DO average concentration from zone 7 to zone 8 (Fig. 5.2A), which did not occur in the set-point 2.0 mg/L (Fig. 5.2B), where DO continued to rise from zone 6 up to zone 8. The higher set-point however, triggered fluctuations in measured DO (Fig. 5.2B), and as a result, more variability was seen from zone to zone. Statistically, the zones remained the same ($p = 0.91$), therefore confirming that the variability in DO distribution was not caused by localised effects within zones, but was instead triggered by changing the set-points from 1.5 to 2.0 mg/L.

A



B

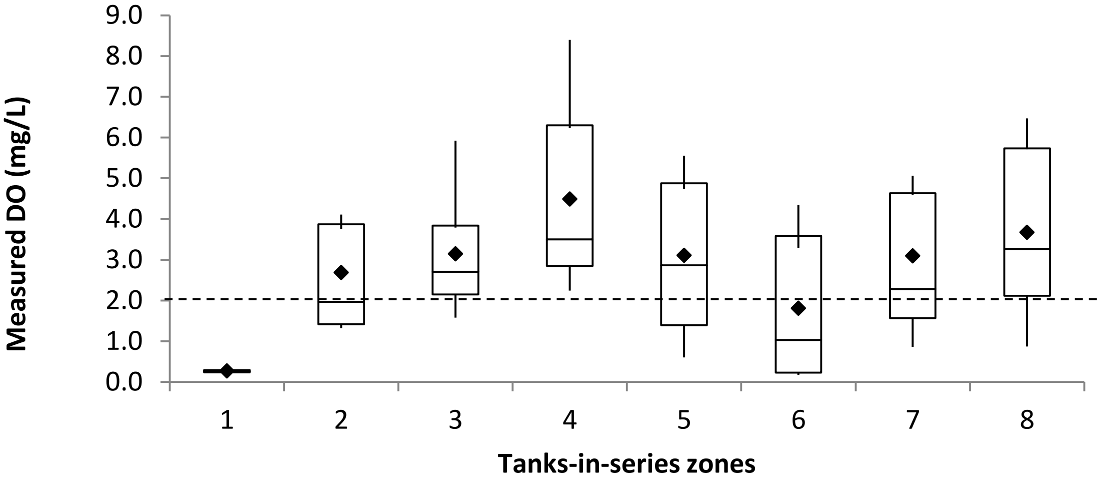


Figure 5.2: Box and whisker plot of spatial variability in measured DO distribution for set-point 1.5 (A) and 2 (B) mg/L, where the median is represented by the horizontal line, the mean by the closed diamond marker, as well as the 25th and 75th percentiles (box) and min and max (whiskers). The broken line represents the DO set-point.

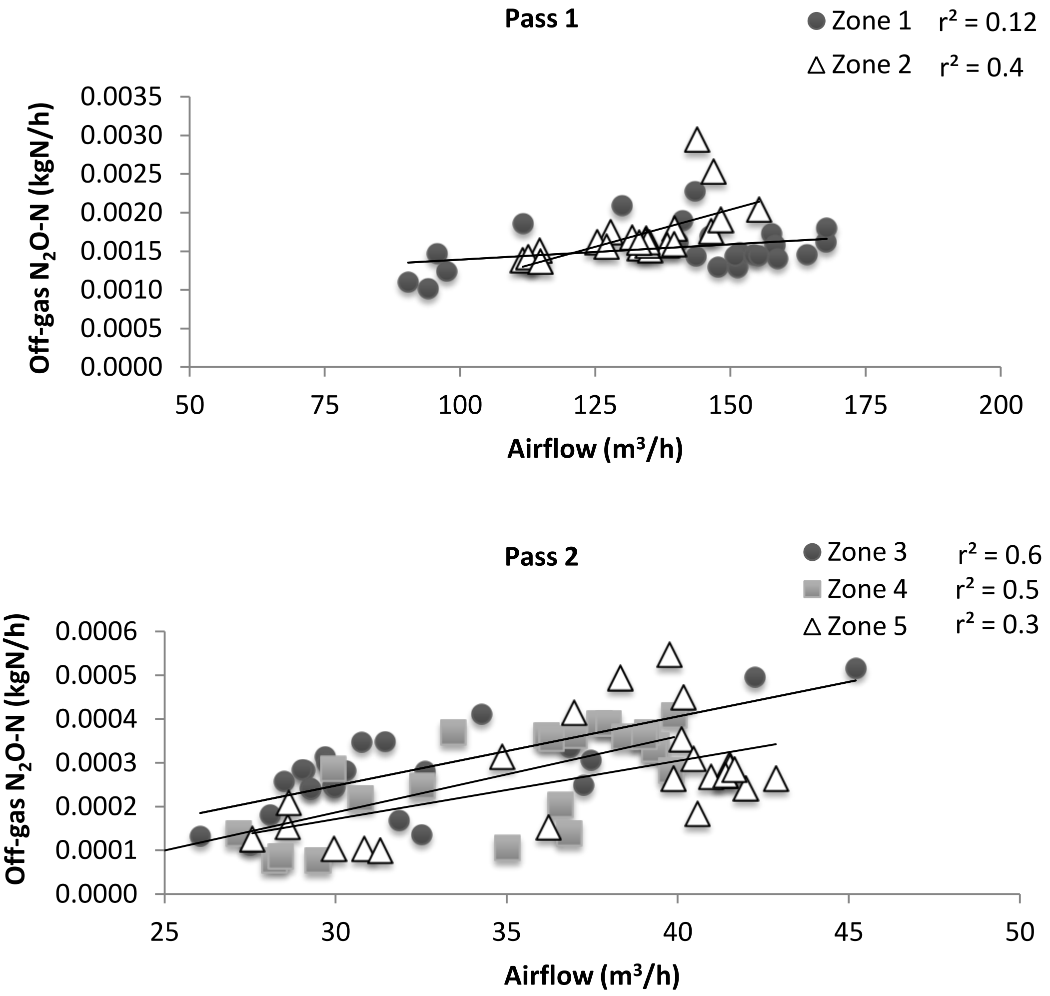
5.3.3. Nitrous oxide emissions and aeration

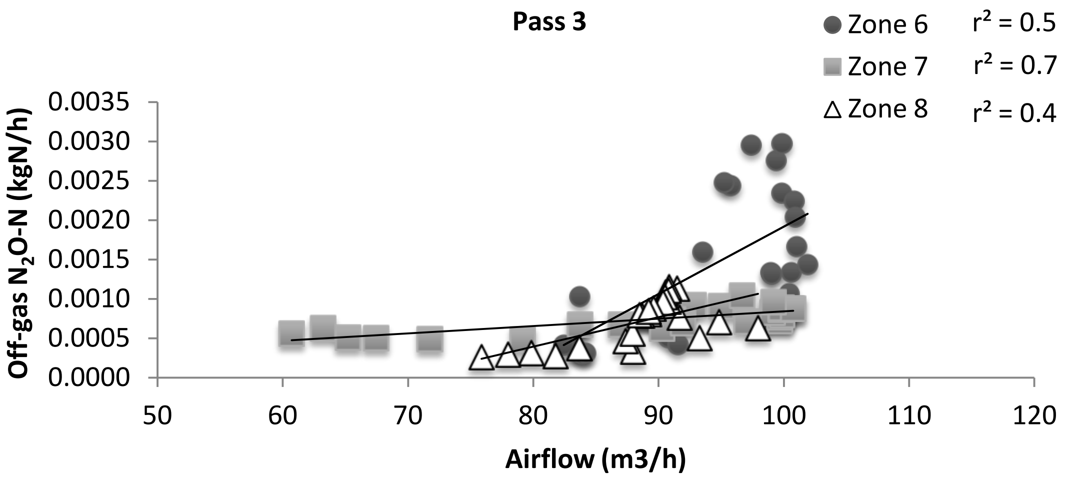
The relationship between aeration and N_2O emissions (N_2O in the off-gas) was depicted for both set-points in each of the aeration passes (Fig. 5.3A and 5.3B). The correlation was overall positive for the set-points, with the exception of zone 8 during set-point 2.0 mg/L which showed a negative correlation (drop in N_2O with increase in airflow). At the lower set-point, some correlation between aeration and emissions was seen in the first aeration pass (Fig. 5.3A), particularly in zone 2 (r^2 = 0.1 and 0.4 for zones 1 and 2 respectively). Correlations were stronger in the middle pass (r^2 = 0.6, 0.5, 0.3 for zones 3, 4 and 5 respectively) and continued within the same range in the final aeration pass (r^2 = 0.5, 0.7, 0.4 for zones 6, 7 and 8). For the set-point of 2.0 mg/L, values changed dramatically within the first aeration pass (Fig. 5.3B), with zone 1 exhibiting the weakest correlation between airflow and emissions in the lane (r^2 = 0.01) and zone 2 the strongest (r^2 = 0.8).

Similarly, the relationship between DO and N_2O was very strong in zone 2 during set-point 2.0 mg/L (supplementary material, S1). The middle aeration pass showed some correlation within the zones (r^2 = 0.4, 0.1 and 0.2 for zones 3, 4 and 5), which was stronger at the start of the pass, in zone 3. In the last pass, the strongest correlation was in zone 7 (r^2= 0.3, 0.6 and 0.4 for zones 6, 7 and 8).

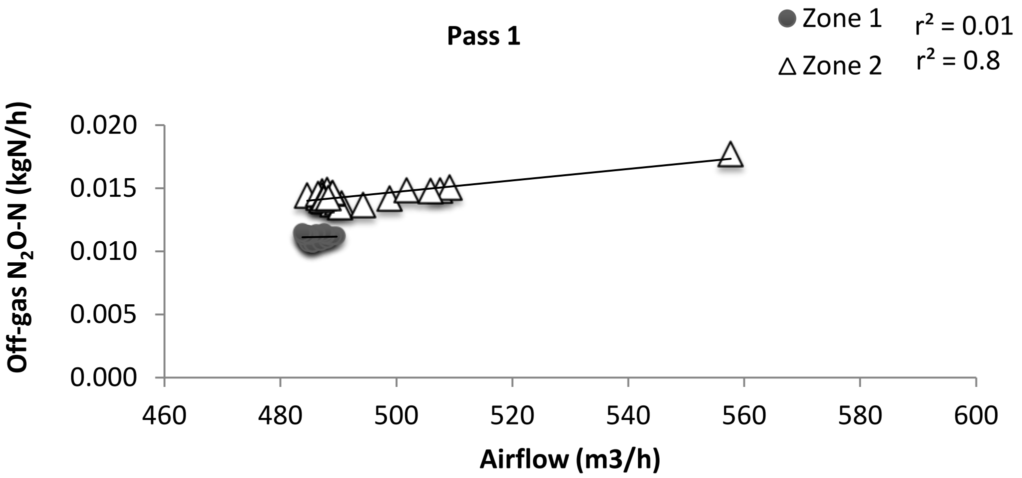
Overall, the process was much more aerated at set-point 2.0 mg/L than at 1.5 mg/L, which translated as an increase in average airflow of 340 %. The relationship between DO and combined N_2O (off-gas and dissolved) under the different set-points was variable, with generally weak correlations (r^2 <0.5) throughout (supplementary material, S1). At the higher set-point of 2.0 mg/L, significant correlations were found in zones 2 to 5, where most of the nitrification took place.

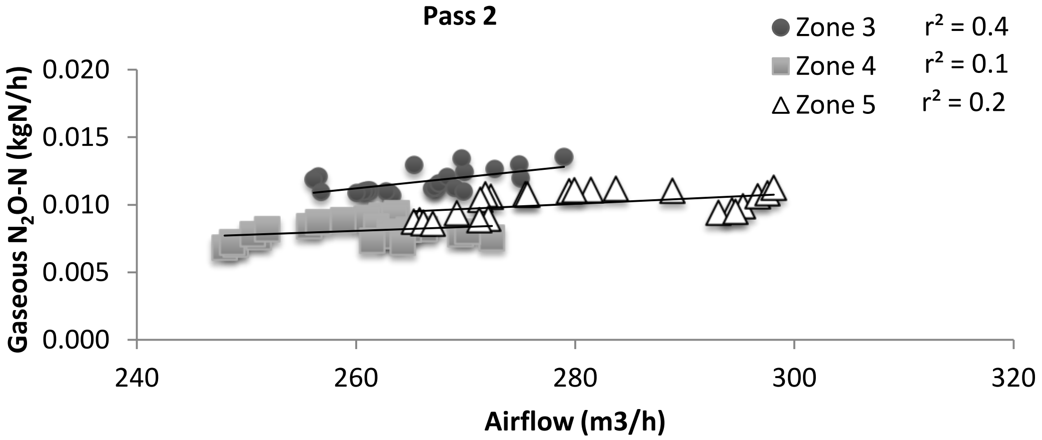
A




Pass 3
Zone 6 r² = 0.5
Zone 7 r² = 0.7
Zone 8 r² = 0.4
Off-gas N₂O-N (kgN/h)
0.0035
0.0030
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
50
60
70
80
90
100
110
120
Airflow (m3/h)

B


Pass 1
Zone 1 r² = 0.01
Zone 2 r² = 0.8
Off-gas N₂O-N (kgN/h)
0.020
0.015
0.010
0.005
0.000
460
480
500
520
540
560
580
600
Airflow (m3/h)


Pass 2
Zone 3 r² = 0.4
Zone 4 r² = 0.1
Zone 5 r² = 0.2
Gaseous N₂O-N (kgN/h)
0.020
0.015
0.010
0.005
0.000
240
260
280
300
320
Airflow (m3/h)

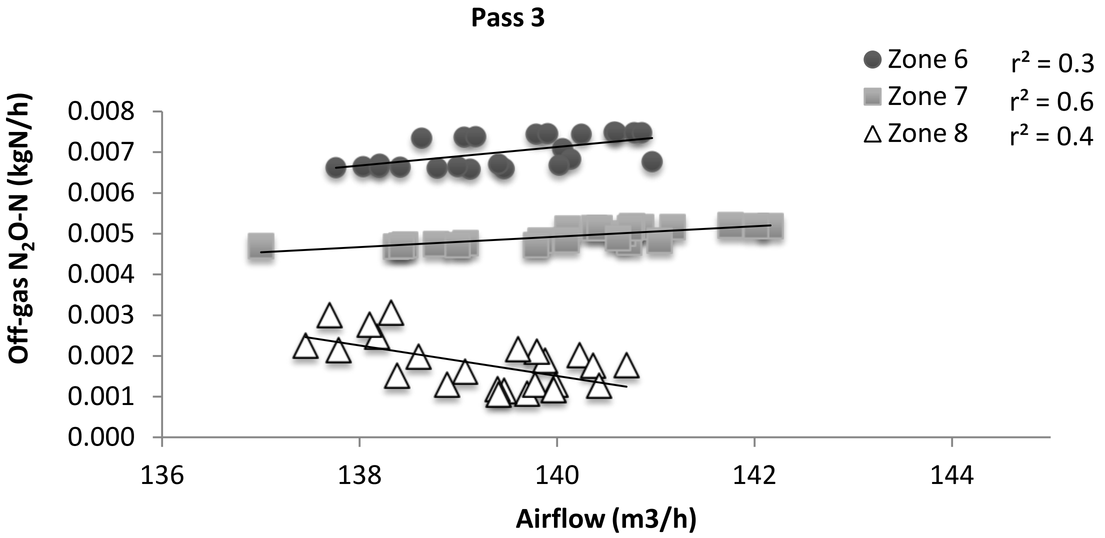


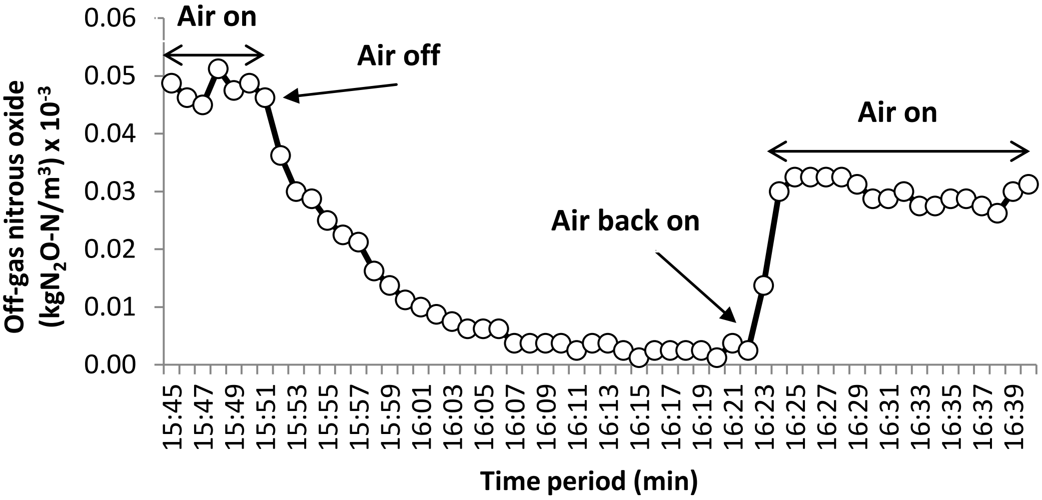
Figure 5.3: Correlations between off-gas N_2O airflow rates (zones split per aeration pass) for set-points 1.5 mg/L (A) and 2.0 mg/L (B). The r^2 for each zone is shown on the top right hand corner next to the labels.

Aeration stress events

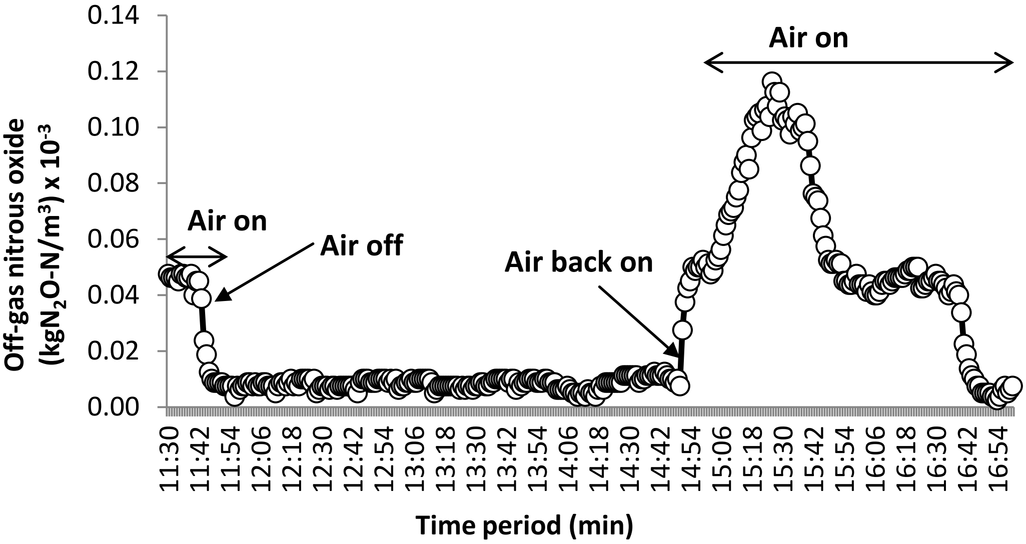
Stress events were carried out whereby aeration to the nitrifying tank was interrupted and conditions monitored. A specific pattern in the off-gas N_2O concentrations was observed in most of the stress events, with concentrations dropping abruptly when aeration stopped and increasing suddenly with the re-introduction of air (Fig. 5.4A to C). Prolonged interruption of airflow resulted in accumulation of dissolved N_2O in the bulk liquid, which led to more air-stripping of N_2O in the off-gas once aeration was resumed. A mass balance of the monitored zone where the stress tests were carried out (zone 4), showed that dissolved N_2O, up to an hour before aeration was interrupted, averaged 0.0001 kg/h, with off-gas emissions averaging at 0.03 kg/h (flows normalised to surface area per zone and assuming that volume of liquid did not change in that zone during the monitored period). During the non-aerated period, the dissolved N_2O accumulated to an average of 0.0015 kg/h, with off-gas N_2O dropping to nearly zero. Once aeration was resumed, there was a rapid drop of N_2O in the bulk liquid, reaching close to zero within minutes (Fig. 5.4C). By comparison, the amount of air-stripped off-gas N_2O averaged at 0.001 kg/h, suggesting that the dissolved N_2O formed during the non-aerated period was mostly stripped out (nearly 70 %) during the aerated periods.

The DO depleted fairly quickly during these events (<0.2 mg/L). And, upon return of aeration, the DO remained low for several hours, particularly when the non-aerated stress events were carried out repeatedly and for longer periods of time.

A


Air on
Air off
Air on
Air back on
Off-gas nitrous oxide (kgN$_2$O-N/m^3) x 10^{-3}
0.06
0.05
0.04
0.03
0.02
0.01
0.00
15:45
15:47
15:49
15:51
15:53
15:55
15:57
15:59
16:01
16:03
16:05
16:07
16:09
16:11
16:13
16:15
16:17
16:19
16:21
16:23
16:25
16:27
16:29
16:31
16:33
16:35
16:37
16:39
Time period (min)

B


Air on
Air on
Air off
Air back on
Off-gas nitrous oxide (kgN$_2$O-N/m^3) x 10^{-3}
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
11:30
11:42
11:54
12:06
12:18
12:30
12:42
12:54
13:06
13:18
13:30
13:42
13:54
14:06
14:18
14:30
14:42
14:54
15:06
15:18
15:30
15:42
15:54
16:06
16:18
16:30
16:42
16:54
Time period (min)

C

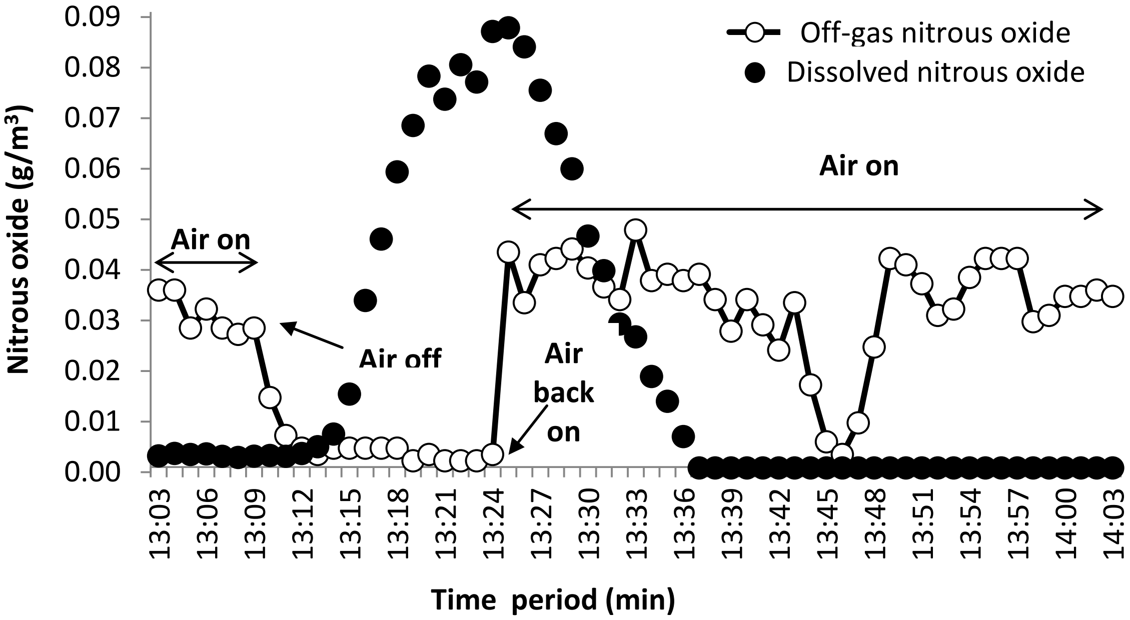


Figure 5.4: Stress events caused by interrupted aeration to the nitrifying lane, showing: a typical trend of off-gas N_2O during a short event (A); the same trend for a longer non-aerated period, capturing an increase in N_2O once the aeration returned (B); and an event during which dissolved N_2O was also being monitored, showing accumulation in the bulk liquid during the non-aerated phase (C).

5.3.4. Emission factors

The EF was found to differ, depending on whether it was based on influent or removed nitrogen fraction (Table 5.2), particularly for set-point 2.0 mg/L, in which the highest EFs were also obtained. During set-point 1.5 mg/L however, the lowest EF was of 0.05 % of both influent NH_4^+ and TN. The highest EF for this set-point came at 0.2 % of removed NH_4^+, which was still lower than the lowest EF for the 2.0 mg/L set-point, at 0.58 % of influent TN.

Table 5.2: Emission factors based on different nitrogen fractions under DO set-points of 1.5 and 2 mg/L

	Set-point 1.5 mg/L	Set-point 2 mg/L
Emission factors (%) [a]		
N_2O-N/TN load	0.05	0.58
N_2O-N/NH_4-N load	0.05	0.72
N_2O-N/TN removed	0.13	1.59
N_2O-N/NH_4-N removed	0.20	3.90

[a] *Emission factor = (off-gas N_2O in all zones + dissolved N_2O zone 8) x 100 / N fraction*

$$\text{Emission factor} = \frac{\text{off-gas } N_2O \text{ in all zones} + \text{dissolved } N_2O \text{ zone 8}}{\text{N fraction}} \times 100$$

5.3.5. Factors influencing emissions after ammonia depletion

Aerobic low ammonia nitrifying tests

Data from the aerobic tests showed that N_2O, both dissolved and in off-gas, increased upon addition of NH_4^+ for all tested concentrations, even at 0.5 mgNH_4-N/L (Fig. 5.5A). The tendency was for the mass of N_2O to increase with increasing NH_4^+ concentration, with the percentage of N_2O emitted as a fraction of the NH_4^+ removed ranging from 0.1 to 0.15 % (Table 5.3).

Additionally, sludge collected from site and brought to the lab was firstly monitored and aerated without adding synthetic wastewater and before starting tests. Data from this sludge showed high values in both dissolved (0.027 mgN_2O-NgVSS//h) and in off-gas (0.308 mgN_2O-N/gVSS/h) N_2O, despite the low NH_4^+ (=<0.1 mg/L). Once aerated, the N_2O values in the fresh sludge dropped to zero within about 30 minutes. No N_2O was observed upon subsequent addition of synthetic wastewater without NH_4^+ (control reactor = 0.0 mgNH_4-N/L), until further NH_4^+ was added according to the required concentrations (Fig. 5.5A).

An initial peak in NO_2^-, accompanied by the peak in N_2O, was also observed in all NH_4^+ tests (Fig. 5.5), which subsided as nitrification carried forward with NH_4^+ depletion; the higher the NH_4^+ concentration, the higher the NO_2^- peak, with the highest value seen for control reactor at 20 mgNH_4-N/L, at 0.364 mgNO_2-N/L (Fig. 5.5). This trend was not seen in the negative control (i.e., "no NH_4^+") aerated batch reactor, where NO_2^- remained consistently close to zero.

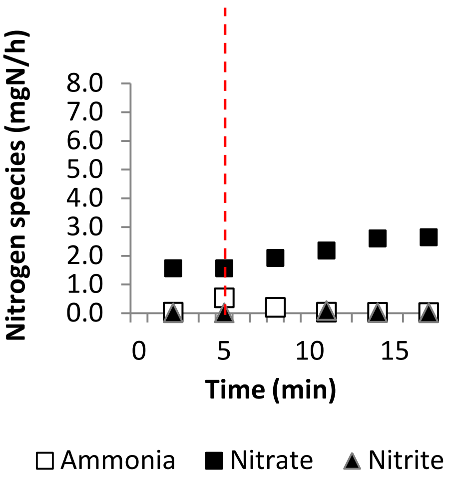
Low DO and low ammonia nitrifying tests

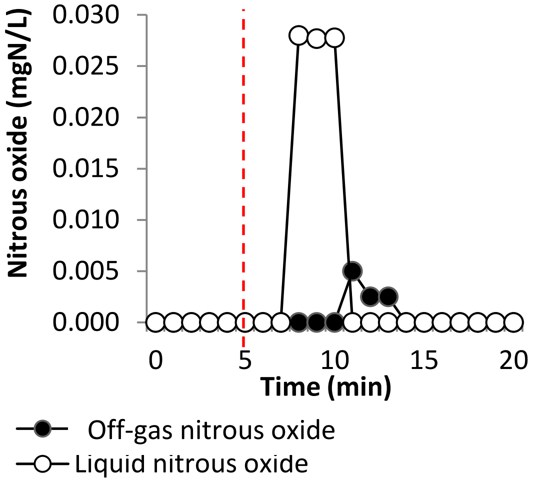
The batch tests with low DO showed that mostly, N_2O was seen in the dissolved phase and very little emitted as gas (Fig. 5.5). Nitrous oxide from four of the five batch tests showed the same value of 0.0005 mgN/gVSS/h, with only the highest NH_4^+ concentration under low DO condition generating a higher value of 0.001 mgN/gVSS/h (Table 5.3). All reactors under low DO showed lower N_2O in comparison to the higher DO tests. The exception was the 0.5 mgNH_4-N/L test, whereby more NH_4^+ was converted to N_2O at low (0.25 %), than at optimal DO (0.1 %). Additionally, accumulation of dissolved N_2O (Fig. 5.5B) occurred under low DO, which was not seen in the optimal DO tests. Some dissolved N_2O was observed in the control reactor without NH_4^+ (Fig. 5.5C, Table 5.3).

Nitrification activity was still observed at low DO, with NH_4^+ removal efficiencies from 30–85 %. However, because of the sub-optimal conditions, the rate of nitrification was lower and full nitrification not observed during the experimental period. The appearance rates for NO_3^- + NO_2^- (Table 5.3) became smaller than the NH_4^+ disappearance rates with increasing NH_4^+ concentrations, which was not observed in the previous batch tests (DO > 6 mg/L). Nitrite started to increase once NH_4^+ was added and particularly as conditions turned anoxic (Fig. 5.5B and 5.5C), which was observed in all the batch tests under low DO, including the control reactor with no NH_4^+.

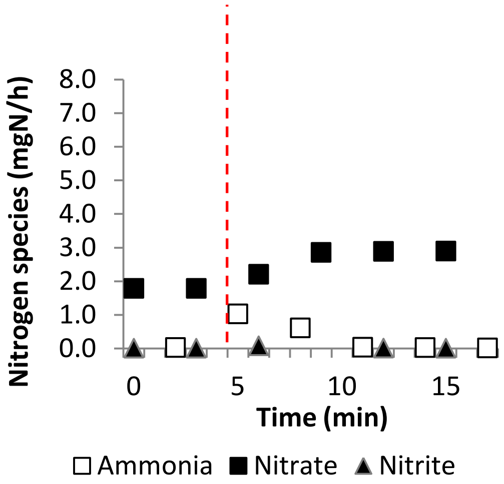
A Nitrification batch tests: low NH_4^+ + optimal DO

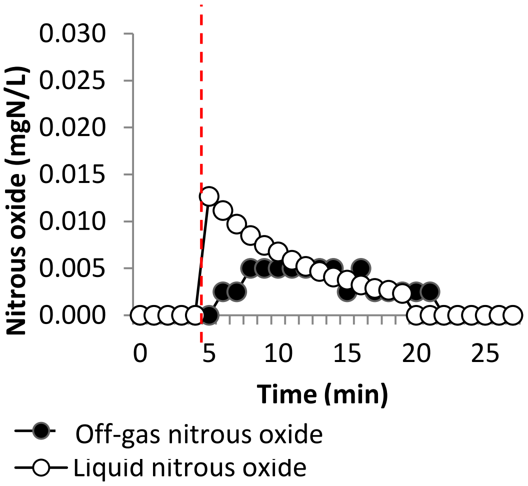
Test: 0.5 mgNH_4-N/L



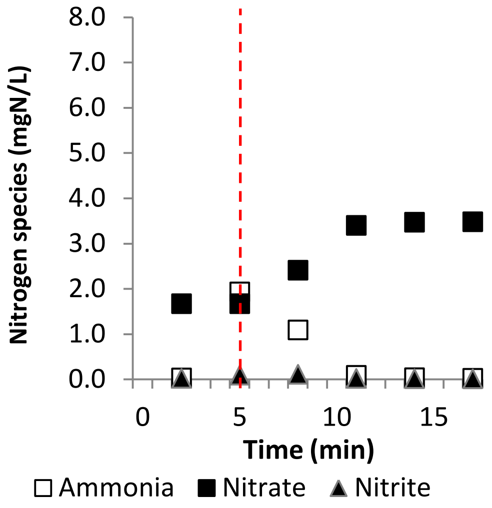


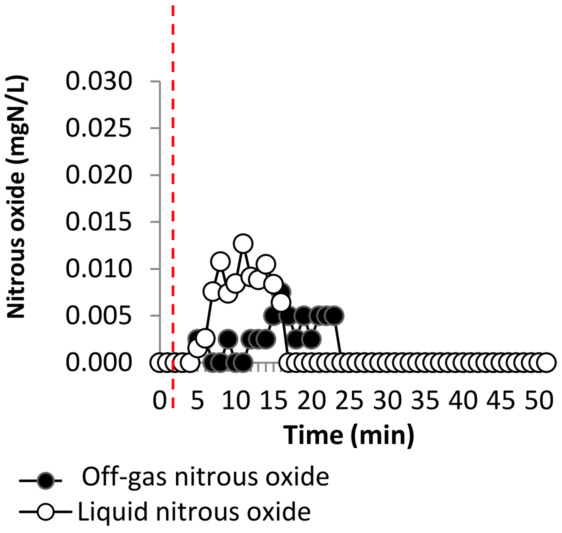
Test: 1 mgNH_4-N/L



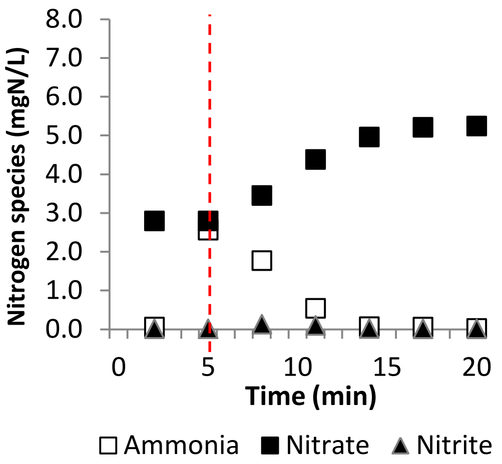


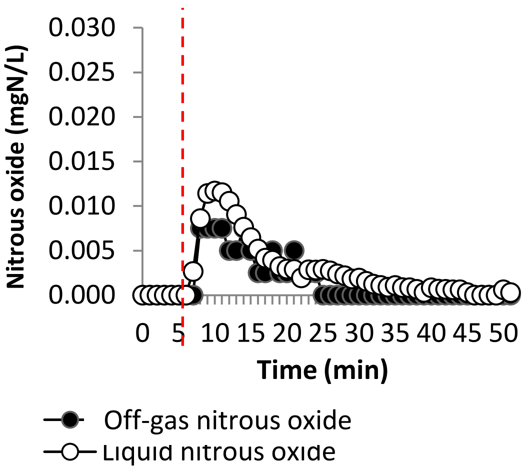
Test: 1.9 mgNH_4-N/L



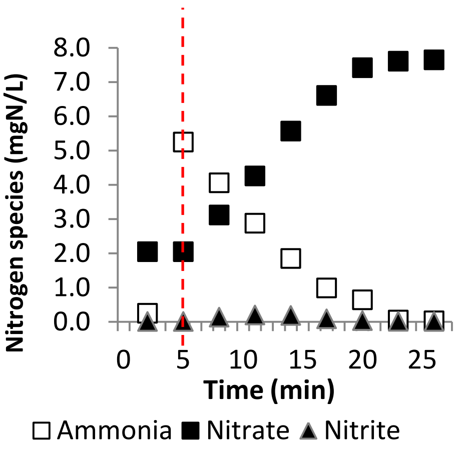


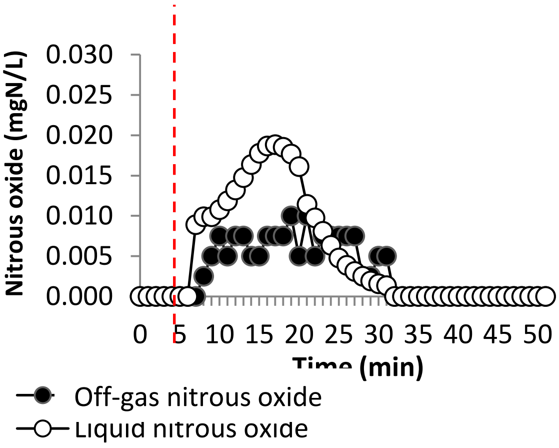
Test: 2.5 mgNH_4-N/L





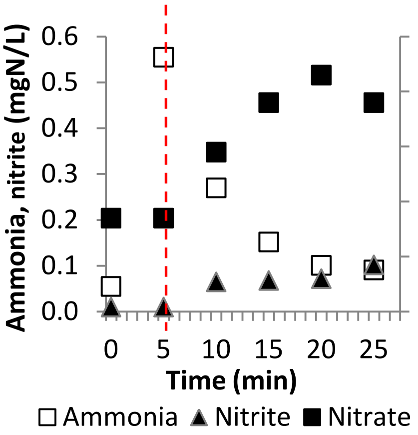
Test: 5.0mgNH_4-N/L

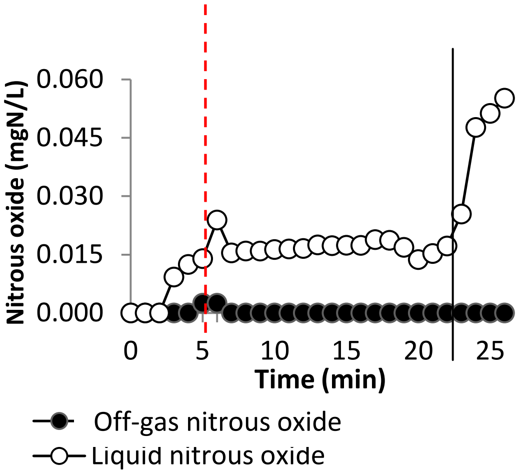




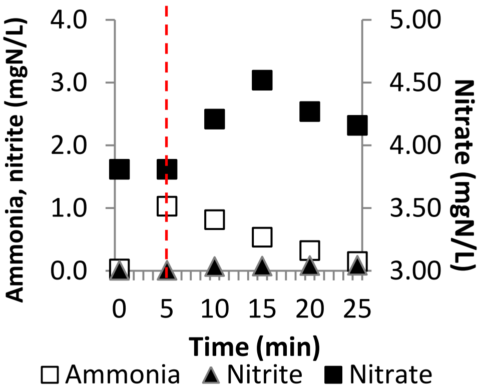
B Nitrification batch tests: low NH_4^+ + low DO

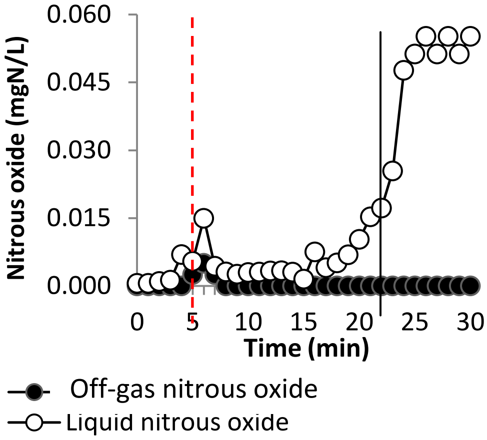
Test: 0.5 $mgNH_4$-N/L



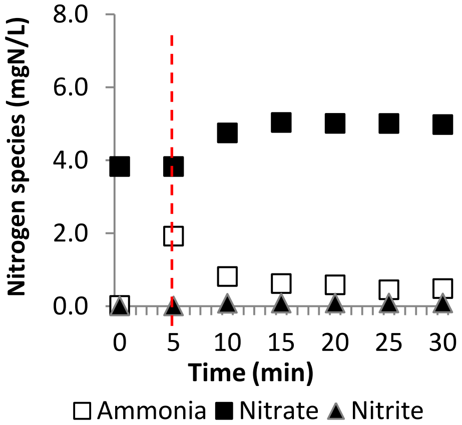


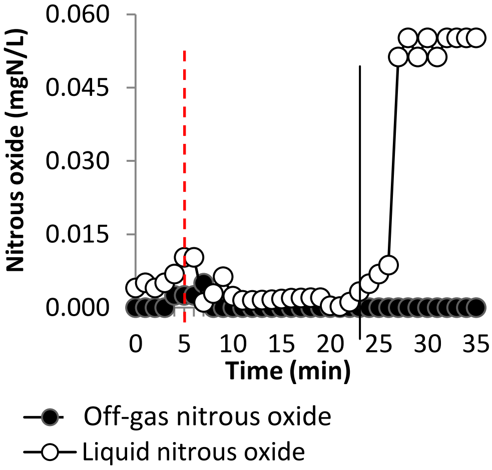
Test: 1 $mgNH_4$-N/L



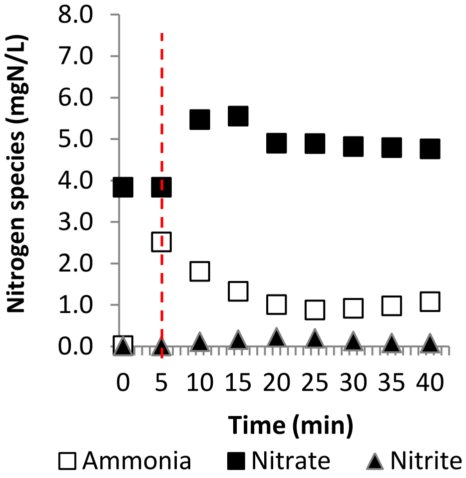


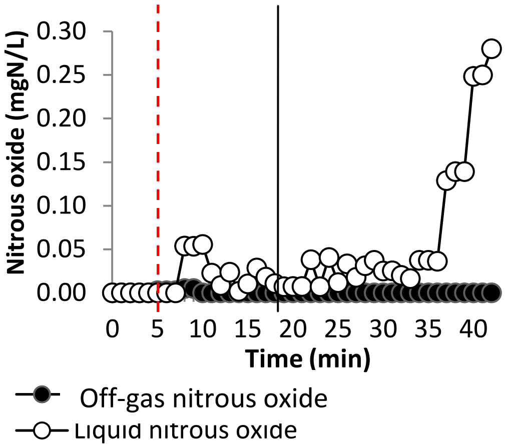
Test: 1.9 $mgNH_4$-N/L



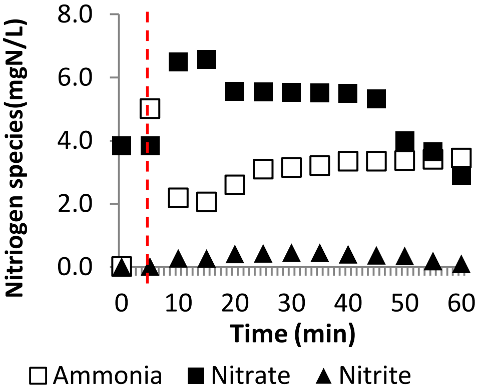


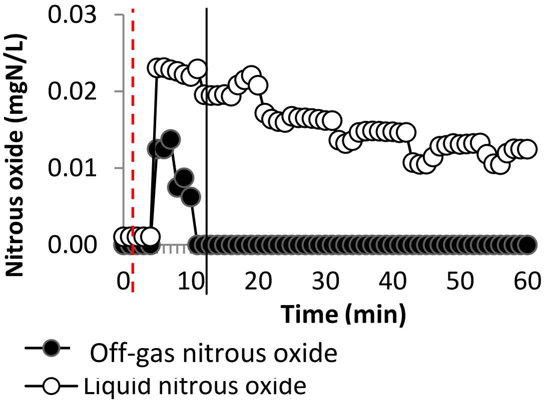
Test: 2.5 mgNH$_4$-N/L





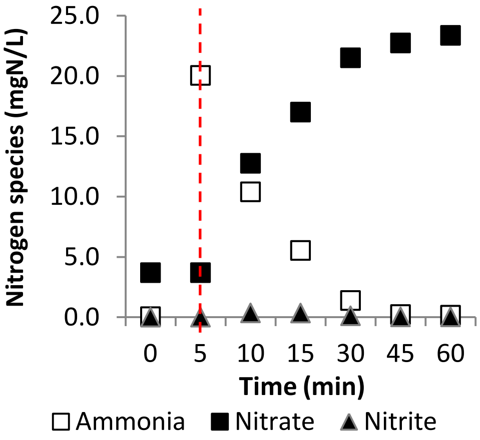
Test: 5.0 mgNH$_4$-N/L

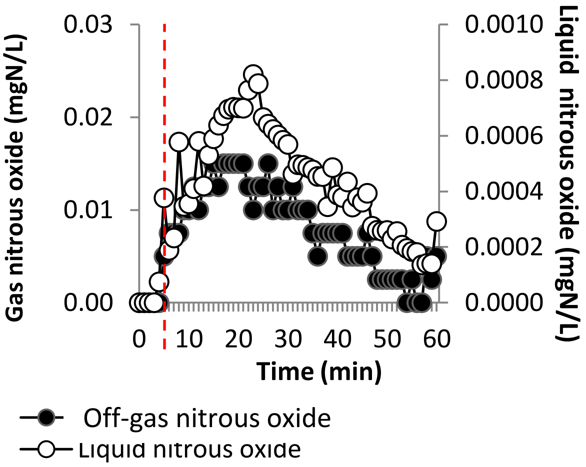




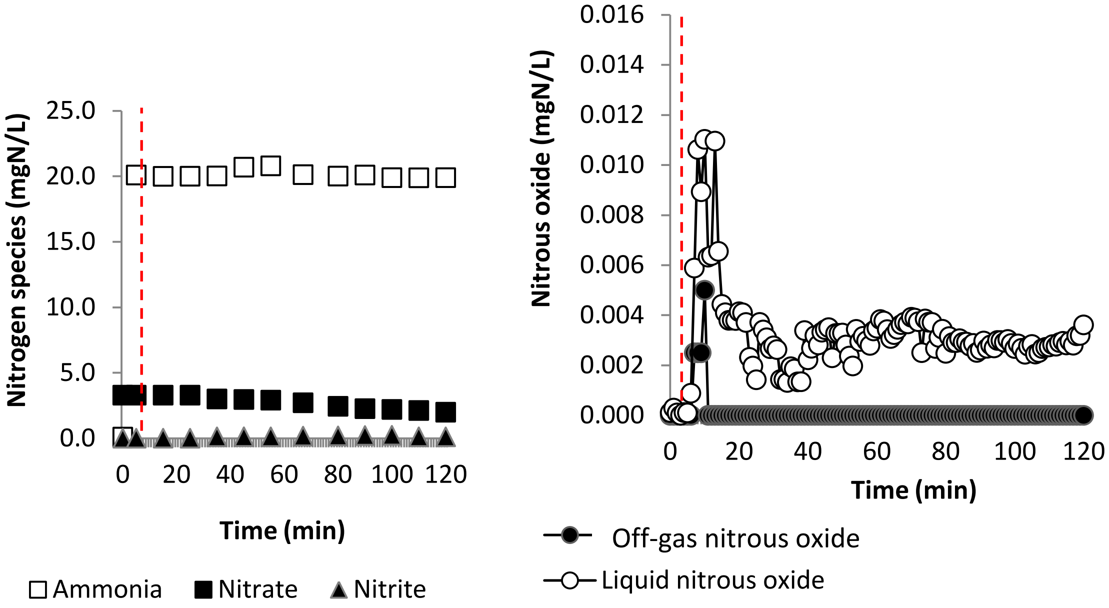
C Nitrification batch tests: control reactors

Control: 20 mgNH$_4$-N/L + aerated





Control: 20 mgNH$_4$-N/L + no air



Control: 0 mgNH$_4$-N/L + low DO

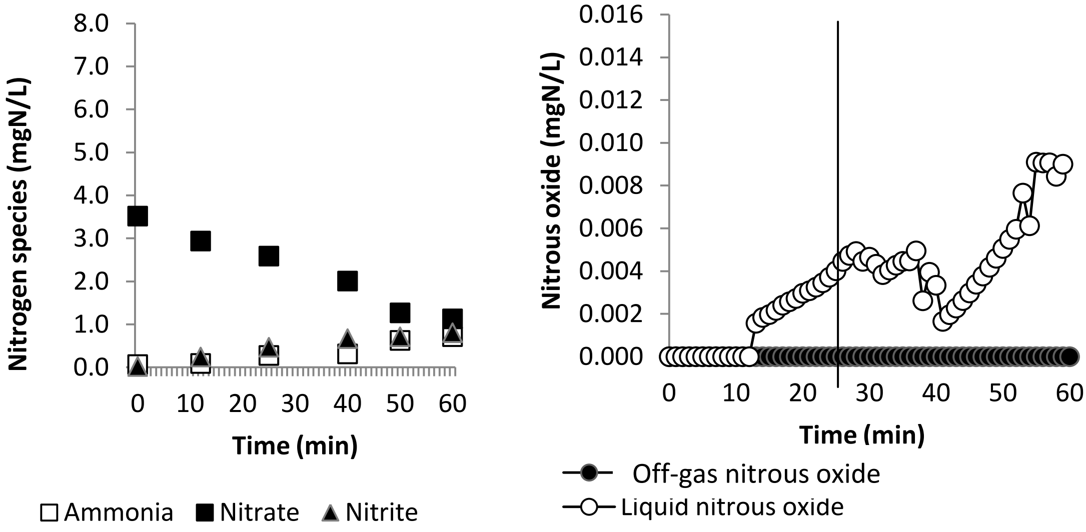


Figure 5.5: Lab-scale nitrification tests, with nitrogen concentrations under different low NH_4^+ concentrations and different DO conditions. Figure 5.5A trends under optimal DO conditions (DO average >= 6 mg/L). Figure 5.5B shows the same trend but under low DO conditions (<0.5 mg/L). Figure 5.5C shows the trends for control reactors. Graphs are arranged by increasing NH_4^+ concentrations from first to last: 1.9, 2.5, 5.0 mgNH$_4$-N/L and controls. The broken (red) line indicates when NH_4^+ was added. The black vertical line indicates when conditions turned anoxic (<0.02 mg/L).

Incomplete denitrification tests

The batch tests showed that under low C/N ratio and cessation of aeration, there was a time-dependent accumulation of N_2O (Fig. 5.6A), which increased with lower C/N, at 0.021 and 0.028 mg for C/N ratios 2.8 and 2.4 respectively (Table 5.3). Under the optimal C/N of 4.5 however (control tests, Fig. 5.6B), although N_2O production ensued with the introduction of air, particularly at intermittent aeration, the values were nevertheless lower than for low C/N tests (0.007 and 0.001 mg for intermittent and fully aerated control reactors respectively).

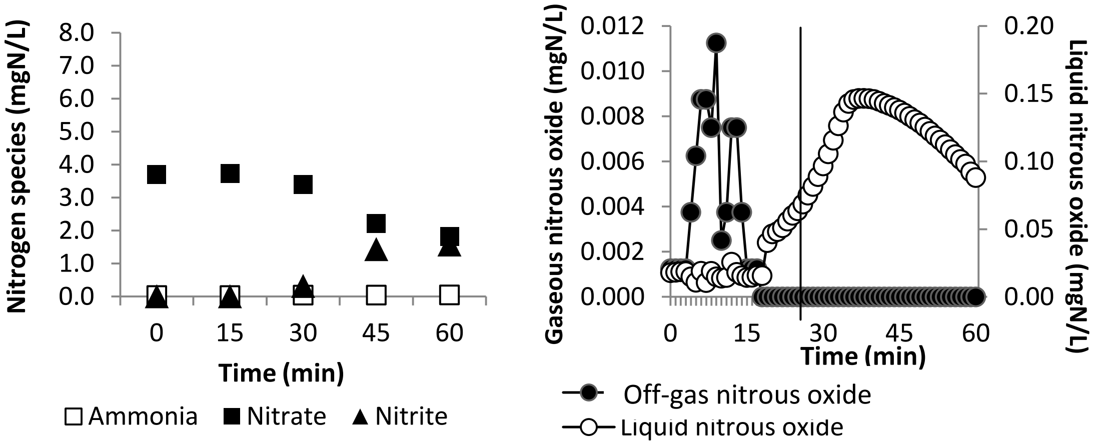
During aerated periods, very little dissolved N_2O was seen in the low C/N tests, as it was mostly stripped in the gaseous phase (Fig. 5.6A). Accumulation in the bulk liquid started mainly after aeration stopped (at time = 15 minutes), with no off-gas N_2O released therein.

However, the control reactors under optimal C/N (Fig. 5.6B) produced different profiles, with the fully aerated reactor showing initial peak in off-gas N_2O and any residual gas mostly depleted after five minutes. In the intermittently aerated control reactor, both dissolved and off-gas N_2O were observed during the aerated period, although interruption of air saw a drop in off-gas emissions with continuous accumulation of dissolved N_2O. As the DO continued to drop however, the dissolved N_2O in the reactor also dropped, about 50 minutes into the experiment. No N_2O was observed in the control reactor where conditions were kept anoxic under optimal C/N (Fig. 5.6B).

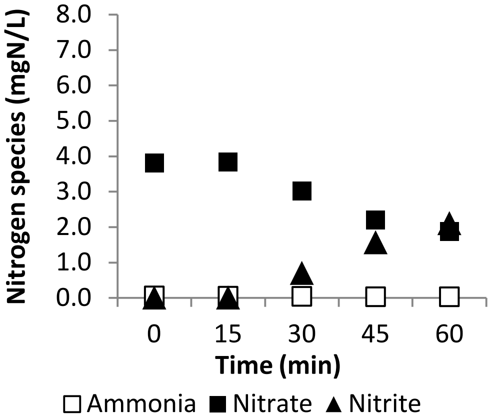
A Denitrification batch tests: low C/N + intermittent aeration

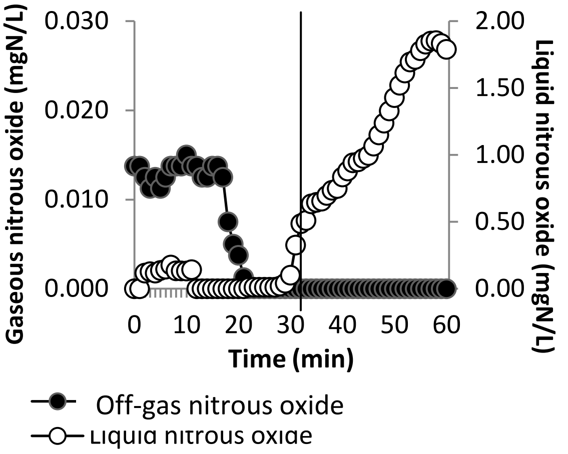
(Aeration stopped at t = 15min)

Test: C/N = 2.8



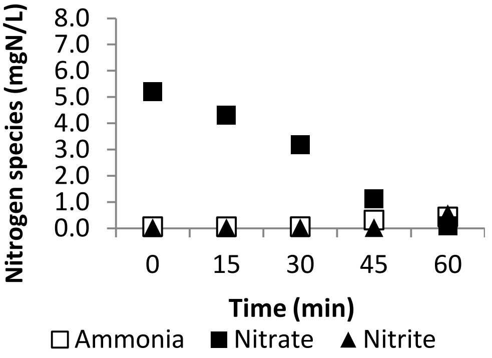
Test: C/N = 2.4

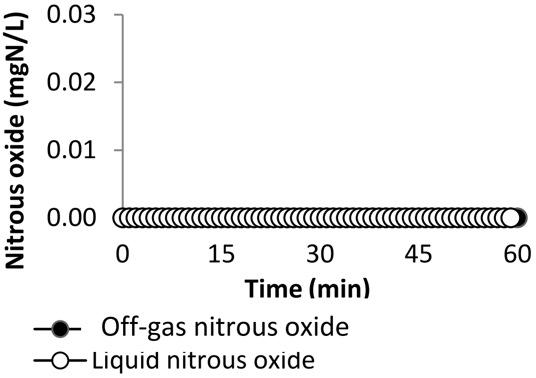




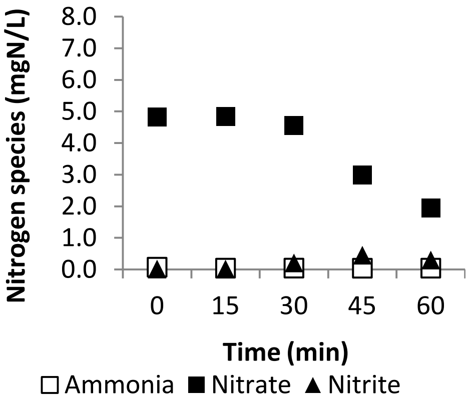
B Denitrification batch tests: control reactors with optimal C/N

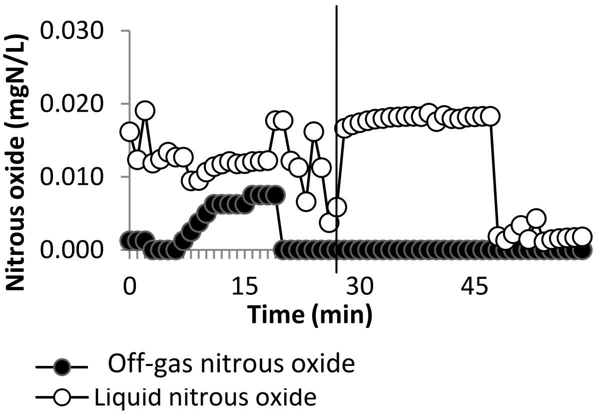
Test: C/N 4.5 + anoxic





Test: C/N = 4.5 + intermittent aeration (aeration stopped at t = 15min)





Test: C/N = 4.5 + air

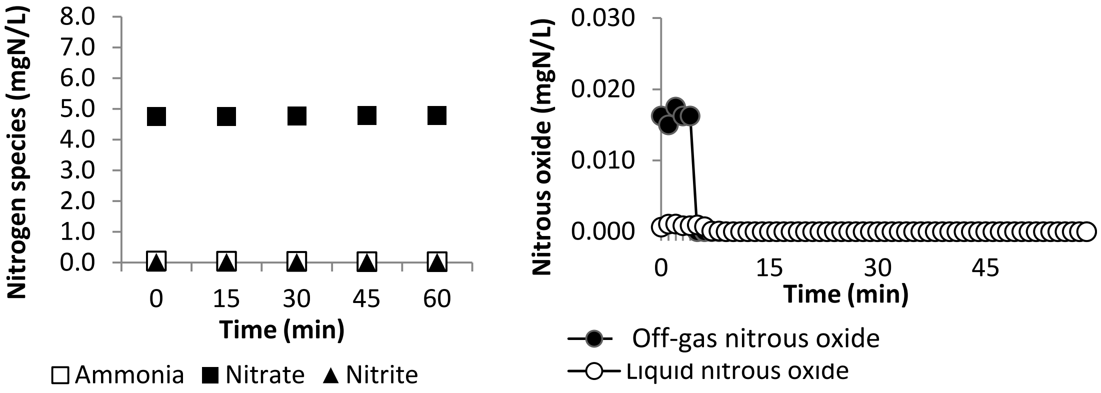


Figure 5.6: Lab-scale denitrification tests, with nitrogen concentrations under different low C/N ratios and intermittent aeration. Figure 5.6A shows trends for low C/N tests. Figure 5.6B shows the trends for control reactors under optimal C/N. The black vertical line shows when conditions became anoxic (DO <0.02 mg/L)

Emission factors: full-scale (final aeration pass) versus batch tests

Batch tests with low NH_4^+ concentrations and optimal DO showed EFs ranging between 0.19 to 0.15 % of the NH_4^+ removed (Table 5.3), whereas the low DO tests ranged between 0.06 to 0.25 %. The full-scale final aeration pass showed EFs of 0.25 % (0.01 mgN_2O-N/gVSS/h) and 1.38 % (0.04 mgN_2O-N/gVSS/h) for set-points 1.5 and 2.0 mg/L respectively.

The EF for the DO set-point of 1.5 mg/L compares to the one found at lab-scale for the NH_4^+ concentration test of 0.5 $mgNH_4$-N/L under low DO, both at 0.25 % of the NH_4^+ removed. The full-scale set-point of 2.0 mg/L however, showed a much higher EF in the final aeration pass than values seen in all the nitrification batch tests, although it remained lower than those obtained for the denitrification tests under low C/N (Table 5.3), which increased with lower C/N ratio (2.4 and 4.1 % for C/N ratios 2.8 and 2.4 respectively).

Table 5.3: Mass balance and associated rates of the different nitrogen fractions during the nitrification batch tests with low NH_4^+ and denitrification batch tests with low C/N

Batch tests	***Mass balance (mg) ± std. dev.***							***Specific rates (mgN/gVss /h) [b] ± std. dev.***			***Emission factor (%) [d]***
	NH_4-N or TN [a]		**NO_3-N**		**NO_2-N**		**N_2O**	**NH_4-N**	**NO_3-N +**	**N_2O**	
	In	**Out**	**In**	**Out**	**In**	**Out**	**Produced**	**or TN [a]**	**NO_2-N [c]**	**Emissions**	
Nitrification: low concentrations (mgNH_4-N/L) + optimal DO (> 6 mg/L)											
0.5	1.06	0.04	3.12	4.14	0.02	0.02	0.001	-0.45	0.44	0.0004	0.10
	±0.3	±0.01	±1.10	±1.4	±0.008	±0.008	±0.00004	±0.32	±0.13	±0.0001	
1.0	2.06	0.04	3.58	5.58	0.02	0.02	0.003	-0.63	0.62	0.0009	0.14
	±0.7	±0.01	±1.2	±1.7	±0.007	±0.007	±0.0001	±0.46	±0.17	±0.0001	
1.9	3.86	0.04	3.34	7.16	0.18	0.02	0.005	-0.69	0.69	0.0008	0.12
	±0.4	±0.02	±1.1	±1.5	±0.06	±0.007	±0.0002	±0.18	±0.04	±0.0001	
2.5	5.11	0.04	5.59	10.59	0.02	0.02	0.007	-0.92	0.90	0.0013	0.14
	±0.9	±0.01	±1.7	±2.2	±0.008	±0.007	±0.0002	±0.24	±0.09	±0.0001	
5.0	10.5	0.06	4.10	14.50	0.02	0.02	0.012	-1.89	1.88	0.0028	0.15
	±0.7	±0.02	±1.4	±1.1	±0.008	±0.008	±0.0003	±0.40	±0.15	±0.0002	
Nitrification: low concentrations (mgNH_4-N/L) + low DO (~ 0.5 mg/L)											
0.5	1.11	0.18	7.54	7.96	0.02	0.20	0.001	-0.20	0.13	0.0005	0.25
	±0.3	±0.06	±2.8	±2.0	±0.005	±0.07	±0.0	±0.07	±0.06	±0.0001	
1.0	2.06	0.30	7.62	8.32	0.02	0.18	0.001	-0.64	0.33	0.0005	0.07
	±0.02	±0.1	±2.7	±2.9	±0.007	±0.06	±0.0001	±0.41	±0.03	±0.0001	
1.9	3.85	0.97	7.66	9.96	0.02	0.18	0.002	-0.89	0.76	0.0005	0.06
	±0.02	±0.3	±2.7	±3.5	±0.007	±0.007	±0.00006	±0.06	±0.10	±0.00008	
2.5	5.04	2.16	7.68	9.53	0.02	0.16	0.003	-0.52	0.38	0.0005	0.09
	±0.01	±0.7	±2.7	±3.4	±0.008	±0.005	±0.0002	±0.21	±0.09	±0.0001	
5.0	10.03	6.90	7.66	5.82	0.03	0.20	0.008	-0.57	-0.30	0.0010	0.18
	±0.5	±0.4	±2.7	±2.0	±0.001	±0.007	±0.0003	±0.27	±0.39	±0.0001	

Batch tests	*Mass balance (mg) ± std. dev.*							*Specific rates (mgN/gVss /h)* [b] *± std. dev.*			*Emission factor (%)* [d]
	NH_4-N or TN [a]		**NO_3-N**		**NO_2-N**		**N_2O**	**NH_4-N or TN** [a]	**NO_3-N + NO_2-N** [c]	**N_2O Emissions**	
	In	**Out**	**In**	**Out**	**In**	**Out**	**Produced**				
Nitrification: control reactors											
20 + optimal DO	40.10 ±0.05	0.34 ±0.7	7.40 ±1.3	46.74 ±0.7	0.02 ±0.005	0.07 ±0.004	0.0357 ±0.0004	-7.19 ±1.14	6.34 ±0.48	0.0065 ±0.0004	0.09
20 + no air	40.20 ±0.09	39.80 ±1.0	6.60 ±2.7	4.00 ±2.1	0.03 ±0.01	0.24 ±0.009	0.0027 ±0.0006	-0.04 ±0.18	-0.22 ±0.17	0.0002 ±0.00003	0.68
0 + low DO	0.19 ±0.01	1.43 ±0.08	5.88 ±0.96	2.26 ±1.1	0.49 ±0.14	1.62 ±0.01	0.0004 ±0.00001	0.24 ±0.27	-0.58 ±0.12	0.0001 ±0.00001	0.03
Denitrification: low C/N ratios + intermittent aeration											
C/N 2.8	8.25 ±0.02	7.64 ±0.04	7.40 ±2.6	3.64 ±1.3	0.02 ±0.007	3.16 ±1.1	0.021 ±0.0002	-0.11 ±0.04	-0.11 ±0.22	0.0027 ±0.0001	2.41
C/N 2.4	8.21 ±0.04	7.74 ±0.03	7.62 ±2.5	3.75 ±1.5	0.02 ±0.007	3.88 ±1.3	0.028 ±0.001	-0.09 ±0.04	-0.08 ±0.12	0.0036 ±0.0008	4.14
Denitrification: control reactors											
C/N 4.5 + anoxic	10.65 ±0.05	2.19 ±0.3	10.42 ±2.6	0.19 ±0.07	0.05 ±0.01	1.11 ±0.2	0.000 ±0.0	-1.55 ±0.04	-1.66 ±0.02	0.0000 ±0.0	0.00
C/N 4.5 + intermit. air	9.85 ±0.05	4.60 ±0.03	9.66 ±2.4	3.90 ±1.6	0.03 ±0.008	0.60 ±0.007	0.007 ±0.0002	-0.95 ±0.03	-0.94 ±0.43	0.0014 ±0.0001	0.14
C/N 4.5 + air	10.57 ±0.04	9.68 ±0.02	9.50 ±1.4	9.58 ±1.4	0.02 ±0.007	0.02 ±0.007	0.001 ±0.0004	0.16 ±0.09	0.01 ±0.03	0.0002 ±0.0003	0.12

[a] *Refers to ammonia for nitrification tests and total nitrogen (TN) for denitrification tests*

[b] *Average concentrations of volatile suspended solids (VSS) = 2,765 mg/L (±27.1)*

[c] *Negative values represent disappearance (removal) rates and positive values represent appearance (production) rates*

[d] *Emission factor (%) = N_2O specific emission rates/NH_4-N specific removal rates (nitrification) or TN specific removal rates (denitrification) x 100*

5.4. Discussion

5.4.1. Linking DO to nitrous oxide

The findings showed that N_2O emissions were higher at DO set point 2.0 mg/L than at 1.5 mg/L (Fig. 5.1). This was unexpected, since the higher set-point resulted in higher measured DO concentrations in the bulk liquid (Fig. 5.2). Although both set-points showed DO fluctuations between sub-oxic to highly aerobic, for the set-point of 2.0 mg/L there were fewer occasions when DO dropped below 1.0 mg/L, which has been previously suggested as the threshold for increased emissions (Aboobakar et al., 2013a; Cébron et al., 2005; Goreau et al., 1980; Tallec et al., 2006). And indeed, as reported in literature, N_2O formation and subsequent emissions are reduced at higher DO concentrations (Law et al., 2012; Rassamee et al., 2011; Tallec et al., 2006; Yu et al., 2010), somewhat contradicting the findings from this study.

However, the increase in DO set-point also resulted in higher DO variability, with the available oxygen between zones ranging from very low to very high, thus suggesting that the fluctuations in this case, rather than the actual DO threshold values, may be key in triggering N_2O emissions. The statistical analysis further confirmed that the differences in DO trends between the two set-points, in this case the increase in DO fluctuation seen when changing from 1.5 to 2.0 mg/L, was indeed triggered by the effects of changing the set-points. The production of N_2O can occur not only during transient low DO (Kampschreur et al., 2008a), but also during recovery from low DO, when conditions are much more aerobic (Yu et al., 2010). Therefore, the introduction of more variability at the higher set-point led to an increase in emissions, irrespective of the fewer drops below 1.0 mg/L in DO concentrations. An example that clearly illustrates this is shown by comparing the N_2O and DO trends for the first aeration pass, more so in zone 2 (Figs. 5.1 and 5.2 respectively), under both set-points. For 1.5 mg/L, the rate of dissolved N_2O in zone 2 was particularly low (0.000028 kgN_2O-N/$kgNH_4$-N per day), following an initial peak in zone 1 (0.00083 kgN_2O-N/$kgNH_4$-N per day). This peak could be due to the proximity with the anoxic zone, whereby some N_2O may be carried over to the nitrifying lane and subsequently stripped without necessarily being produced therein. The stripping continued into zone 2 (Fig. 5.1A), which was followed by a decline in the dissolved N_2O. However, for the 2.0 mg/L set-point, zone 2 showed the highest dissolved N_2O seen in the lane for any zone under both settings (0.32 kgN_2O-N/$kgNH_4$-N per day), much higher indeed than in the previous zone (0.09 kgN_2O-N/$kgNH_4$-N per day). What also changed in this zone, from one set-point to another, was the DO profile: at 1.5 mg/L the average DO was not only within optimal values (2.0 mg/L), but also showed very little variability (Fig. 5.2A). However, for set-point 2.0 mg/L, the average measured DO in the same zone, although slightly higher (2.7 mg/L) than the previous set-point, varied considerably (Fig. 5.2B). Additionally, in zone 2, the relationship between DO and combined N_2O, at set-point 1.5 mg/L, contrasted greatly with set-point 2.0 mg/L, with the latter showing a strong, positive correlation (r^2 = 0.9) between the two parameters (Supplementary Fig. S1), particularly with dissolved N_2O. This suggests that during the higher set-point, increase in oxygen variability was strongly related to an increase in N_2O production. This could also be related to a recovery period in the biological process, from a very low DO in the first zone, to a generally higher DO in zone 2 (ranging between 1.3 to 5.5 mg/L). But this change in DO from zones 1 to 2 was also observed for the 1.5 mg/L set-point without however, the ensuing higher N_2O production. It seems therefore, that during set-point 2.0 mg/L, it was the higher DO variability within zone 2, rather than the changes from zones 1 to 2, that may have led to the increase in N_2O production. This agrees with the observation that the more fluctuation is introduced to the process, especially abrupt or rapidly changing from very low to aerobic DO conditions, the more it can lead to N_2O being generated (Rassamee et al., 2011), which is triggered as an immediate transient response by activated sludge populations (Burgess et al., 2002a; Kampschreur et al., 2008a; 2009a; Tallec et al., 2006; Vanrolleghem et al., 2004).

Not surprisingly, the correlation between N_2O emissions and aeration was high for set-point 2.0 mg/L, particularly in zone 2 (Fig. 5.3B). This means that dynamic changes in DO levels which induce N_2O production, can lead to N_2O being released to the atmosphere, since the more aeration is introduced to increase the transient DO concentrations in the bulk liquid, the more N_2O will be air-stripped. If these conditions are met within dynamic scenarios (for example, sudden changes in DO and vigorous aeration), autotrophic N_2O production and emission will occur even at more optimised DO levels, during a recovery period (Yu et al., 2010).

At the 1.5 mg/L set-point however, the more stable DO profile (ranging between 0.16 to 2.5 mg/L) had less of an effect on produced N_2O, which is supported by the fact that zone 2 had the second lowest amount of N_2O found in the bulk liquid for this set-point (only zone 3 comes slightly lower at 0.000022 $kgN_2O\text{-}N/kgNH_4\text{-}N$ per day). The off-gas emissions in this zone however, were the highest for this set-point (0.063 $kgN_2O\text{-}N/kgNH_4\text{-}N$ per day), although these were equally high for set-point 2.0 mg/L. This is associated with the typically vigorous aeration rates seen at the beginning of nitrifying tanks, thus leading to most of the N_2O in these first zones being emitted due to air-stripping. At set-point 1.5 mg/L, zone 6 in the final aeration pass, showed the highest value for dissolved N_2O. This is a transition zone between aeration passes, with an increase in airflow from the middle to the final aeration passes giving rise to abrupt changes, potentially inducing further N_2O production and gas-stripping. This further supports the argument that changes to the system, particularly in DO and aeration, can lead to higher N_2O production and subsequent emission.

For the remainder of the last aeration pass (zones 7 and 8) however, N_2O continued to be generated (Fig. 5.1B), both under low DO averages, as seen in zone 7 for set-point 1.5 mg/L (Fig. 5.2A), but also under optimal DO as per zones 7 and 8 under set-point 2.0 mg/L (Fig. 5.2B). This can attributed to a number of factors: the residual N_2O in the bulk liquid came from the previous zones, where dissolved N_2O peaked (zone 6 for set-point 1.5 mg/L and zone 5 for 2.0 mg/L); changes in DO conditions from zone to zone, which at 1.5 mg/L dropped to very low averages from zone 6 to 7 before increasing again in zone 8; and for 2.0 mg/L, continued to show high variability, typical of the DO trend for this set-point. As established in the previous paragraphs, these changes could lead to N_2O being generated. Finally, the possibility of N_2O production coming from incomplete heterotrophic denitrification cannot be dismissed because of the mixed nature of activated sludge populations. The implications of this contention are further discussed in the next section.

Stress events, whereby aeration was interrupted for periods of time, further highlighted the impact of DO changes to N_2O. During non-aerated events, N_2O accumulated in the bulk liquid (Figs. 5.4), within minutes, whilst concentrations of off-gas N_2O declined. The reintroduction of aeration resulted in the accumulated N_2O being mostly stripped as off-gas, whilst accumulation of dissolved N_2O during the aerated period was minimal (Fig. 5.4C). The longer the period of DO depletion (i.e., the longer the non-aerated event), the more N_2O accumulated and the more was subsequently emitted (Fig. 5.4B). This suggests that at lower DO (whether caused by a lower set-point or by depletion during interrupted aeration), less N_2O will escape to the atmosphere as off-gas emissions due to the absence of active stripping (Law et al., 2012). However, more N_2O will accumulate in the bulk liquid and eventually be released, when conditions become suddenly aerobic. A prolonged aeration shut-off however, means a complete depletion of available oxygen to the activated sludge, which in turn leads to a decline in – or eventual failure of – nitrification. Further evidence of this was seen with the accumulation of dissolved N_2O in zone 2, during the low set-point of 0.5 mg/L, whereby N_2O peaked at just over 2.3 kgN_2O-N/$kgNH_4$-N per day, in comparison to the second highest value, seen during set-point 2.0 mg/L, at 0.3 kgN_2O-N/$kgNH_4$-N per day (also in zone 2). The measured DO concentrations during 0.5 mg/L set-point averaged 0.2 mg/L, seldom even reaching the set-point concentration and indeed with a significant drop in nitrification rates.

Most investigations investigating at N_2O production and emissions as a response to dynamic conditions, have been mainly based at lab-scale (Kampschreur et al., 2009a). With the current study however, a comparison between different set-points and the effect on emissions within the same process was made at full-scale, thus offering a detailed insight into the relationship between changes in DO and the impact on N_2O.

5.4.2. Impact of ammonia and low C/N ratios on N_2O

Observations at the end of the nitrifying lane, where nitrification had mostly occurred, showed that N_2O was emitted under both set-points, even at very low NH_4^+, with discharge concentrations averaging at 1.1 and 1 for set-points 1.5 and 2.0 mg/L respectively, and minimum values equal or below 0.5 $mgNH_4$-N/L. Nitrous oxide emissions under high NH_4^+ concentrations have been well documented: Kim et al. (2010) used concentrations between 90–350 mg/L, Law et al. (2012) tested concentrations between 50–500 mg/L, Tallec et al. (2006) concentrations between 15–49 mg/L and Wunderlin et al. (2012) carried out nitrification tests with 25 mg/L of NH_4^+. However, emissions at NH_4^+ concentrations below 5.0 mg/L, have never been reported. Further investigations were therefore carried out at lab-scale to assess the effect of low NH_4^+ concentrations on N_2O emissions, in order to correlate with the emissions at full-scale, particularly in the final aeration pass. Under a fully aerated control batch test, without the addition of NH_4^+, no N_2O was observed once the initial N_2O in the sludge was fully stripped out, and residual NH_4^+ and NO_2^- fully oxidised. This agrees with the findings by Kim et al., (2010) and Rassamee et al. (2011), which showed that no emissions were seen in fully aerated tests without the addition of NH_4^+ or hydroxylamine (NH_2OH) as substrates, thereby linking NH_4^+ oxidation with N_2O production.

However, in the fully aerated batch tests (DO >6 mg/L), the addition of NH_4^+ even at 0.5 mg NH_4-N/L, saw an initial peak in dissolved and off-gas N_2O, as well as in NO_2^-, which declined rapidly to zero once the NH_4^+ was oxidised. The peak was always accompanied by a dip in DO (average from 6.0 to 4.5 mg/L, which quickly increased to >6.0 mg/L during optimal DO tests). The drop in DO followed by NO_2^- peaks (an intermediate during nitrification) upon added NH_4^+, is expected, as it is concurrent with an increase in oxygen demand during typical nitrification activity. This happens not just at high NH_4^+ concentrations, but also at low concentrations, as shown in the current study. Because the trend was seen on both the optimal and low DO batch tests, it suggests that N_2O production is related to the NH_4^+ oxidation, even at very low concentrations, which will always trigger a dip in DO and a peak in NO_2^-, independently of anoxic or aerobic conditions. In the optimal DO tests it was during this dip in oxygenation that N_2O and NO_2^- peaked, whereas in the low DO tests, both NO_2^- and N_2O accumulated as conditions became anoxic, thus suggesting that DO is a key trigger for N_2O production under nitrification (Rassamee et al., 2011).

Furthermore, once NH_4^+ was added to the low DO tests, it was difficult to maintain the concentration in the reactors at ~0.5 mg/L. Nitrification was not as effective under low DO but still measurable, and as NH_4^+ concentrations increased, the appearance rates of NO_3^- + NO_2^- were lower than the disappearance rate of NH_4^+ through oxidation (Table 5.3), which is suggestive of two possible pathways: nitrifier denitrification pathway by autotrophic bacteria; whereby, due to limited oxygenation, the reduction of NO_2^- as the final electron acceptor instead of oxygen leads to less NO_3^- being produced (Tallec et al., 2006); or by denitrification, which may occur under low DO, thus leading to some NO_2^- and NO_3^- reduction (Tallec et al., 2008). Despite no addition of an external carbon source to the synthetic feed, the presence of some COD from the fresh sludge was inevitable (average 18.5 mg/L); which combined with the NO_3^- also present in the sludge (seen as initial nitrate in the mass balance, Table 5.3), could still instigate incomplete heterotrophic denitrification due to low C/N ratios. This is further confirmed by the denitrification experiments, whereby EFs were shown to be much higher for the low C/N ratio tests when compared to the nitrification experiments. Therefore, limited DO conditions in nitrifying ASPs, may give rise to simultaneous nitrification and denitrification mechanisms, and as previously suggested (Wunderlin et al., 2012), incomplete denitrification, particularly under low C/N, can be the dominating pathway of N_2O production in this case.

The presence of heterotrophic denitrifiers in the full-scale nitrifying tank was confirmed, as seen by the control reactor with no NH_4^+ and low DO, whereby up to 0.009 mg/L of dissolved N_2O accumulated (followed by an increase in NO_2^- and decrease in NO_3^-), even without any NH_4^+ (Fig. 5.5C). It should be noted however, that this accumulation was lower than those seen in the batch tests with NH_4^+ and DO ~0.5 mg/L, again linking N_2O to NH_4^+ oxidation.

It seems, therefore, that as long as NH_4^+ is present, even at very low concentrations, as seen in the fresh sludge (<0.1 mgNH_4-N/L) as well as in the batch tests (0.5 to 5.0 mgNH_4-N/L), N_2O production will follow. And, since this production is always accompanied by NO_2^- peaks, this suggests that autotrophic nitrifier denitrification, via reduction of NO_2^-, is the main triggering mechanism under aerobic conditions. Under low DO conditions, this pathway also leads to N_2O production, although off-gas emissions drop considerably due to absence of aeration. Even though high levels of NO_2^- have been linked with an increase in N_2O (Desloover et al., 2011; Kampschreur et al., 2009a; Law et al., 2012; Wunderlin et al., 2012), it has been shown with this study that N_2O will increase, albeit at low NO_2^- concentrations. Overall, NO_2^- must be present for N_2O production either by autotrophic or heterotrophic denitrification mechanisms (Rassamee et al., 2011), and very little is required. Indeed, at full-scale, NO_2^- levels were consistently low, although always present (between 0.01 to just below 1.0 mg/L, averaging at 0.3 mg/L) in the final aeration pass.

Furthermore, under low DO and anoxic conditions, incomplete heterotrophic denitrification is concurrently taking place because of low C/N, thus contributing to higher N_2O production. At optimised DO levels however, most of the NH_4^+ is still converted to NO_3^-, although with some N_2O still present (in Fig. 5.5A), implying that the formation of N_2O is inherently linked with nitrification, even under steady-state conditions.

Heterotrophic denitrification may be an important triggering mechanism in N_2O emissions from a nitrifying activated sludge, as shown by the lab studies, where the highest EFs came from the low C/N tests. Therefore, incomplete denitrification may be key to explaining some of the emissions seen in the final stages of the full-scale nitrifying lane, more so during low DO periods. Indeed, the EF seen at full-scale could only be achieved in the lab when incomplete heterotrophic denitrification was also considered; nitrifier denitrification alone was insufficient to generate the emissions observed at full-scale. Additionally, process disturbances and dynamic changes to conditions, more so when related to aeration and DO, can cause N_2O production and subsequent emissions.

Finally, the batch tests showed that under full aeration N_2O only builds up initially, upon addition of NH_4^+. Therefore, if the full-scale nitrifying tank is kept under consistently stable and optimised airflow and DO concentrations, in order to promote complete nitrification, N_2O production and emissions may occur in smaller pulses rather than in prolonged accumulation periods. These periods led to higher N_2O

production in the denitrification experiments as well as accumulation of N_2O in the low DO nitrification tests, as observed in this study. When aerobic conditions prevail, heterotrophs will continue to preferentially use molecular oxygen rather nitrate as a terminal electron acceptor in respiration, thus minimising N_2O formation through denitrification. The EFs from the batch tests were comparable to those from previous findings (Rassamee et al., 2011; Tallec et al., 2006).

5.4.3. Impact of nitrogen fractions on emission factors

The conventional understanding that N_2O emissions are potentially minimised by an increase in DO set-point, are contradicted by the findings from this study. Indeed, the N_2O EFs were found to be 0.05 and 0.58 % of influent TN for set-points 1.5 and 2.0 mg/L respectively (Table 5.2). The EF for 1.5 mg/L set-point was much lower than the value reported by the UK Water Industry Research Limited of 0.2 % (UKWIR, 2008); for the higher set-point however, it was nearly three times higher than that, despite the quality of the effluent remaining similar under both set-points during the monitored period. Historically, EFs have relied heavily on estimations, rather than on direct measurements, and the discrepancies and uncertainties related with these estimations have been discussed at length elsewhere (Aboobakar et al., 2013a; Ahn et al., 2010b; Foley et al., 2010a; GWRC, 2011; Kampschreur et al., 2009a).

Furthermore, the nitrogen fraction from which those factors are converted is a significant point to consider: the values based on influent NH_4^+ and TN, were incidentally the lowest by comparison to the NH_4^+ and TN removed fraction, which increased the emission factors by an order of magnitude, at 0.2 and 3.9 % of removed NH_4^+ for set-points 1.5 and 2.0 mg/L respectively. Clearly, values are very distinct depending on how they are computed, and could mean different things for different process configurations. For example, when considering BNR processes, it could be argued that influent or removed TN are more relevant than influent or removed NH_4^+, which are perhaps more applicable to nitrifying ASP instead. However, from a perspective whereby the impact on receiving water bodies is considered, effluent nitrogen fractions may be more important when converting N_2O EF. Nonetheless, care must be taken when choosing the right nitrogen fraction so that the amount of process emissions is highlighted, rather than hidden by an inadequate EF. This is particularly the case as regulation such as the EU Water Framework Directive (WFD) becomes more stringent, and nitrogen removal methods more efficient.

However, changes in effluent quality are not directly linked to increased emissions, as shown in this study. It may be argued that in such cases, an EF based on nitrogen removed is a true indicator of process emissions, since it highlights the shift in environmental pollution from the receiving water bodies to the atmosphere (Kampschreur et al., 2008a). This is therefore a risk worth considering by WWTPs when assessing nitrogen removal and process control. More so with the potential legislative move from estimated to directly measured – and compulsory – reporting of process emissions, which may become a reality in the near future.

5.5. Conclusions

The aim of this study was to quantify N_2O emissions and the relationship with operational DO in a full-scale nitrifying ASP, under different DO set-points of 1.5 and 2.0 mg/L. The study also aimed at investigating the effects of low NH_4^+ concentrations and low C/N ratios on triggering N_2O production and emission in the final stages of nitrification. The main findings were as follows:

- Changes to higher DO set-point control (1.5 to 2.0 mg/L) in a full-scale nitrifying ASP led to an increase in emissions across the lane as well as in EFs (0.05 to 0.58 % of influent TN). This was unexpected, because the higher set-point also increased the DO averages in the lane, which should have seen a drop in N_2O.

- However, although DO averages increased at the higher set-point, the variability also increased, leading to fluctuations in DO concentrations.

- Therefore, the data suggests that it was this increase in DO variability in the lane, brought about by the change in set-points, which triggered higher N_2O production. Additionally, the increase in airflow at set-point 2.0 mg/L also resulted in higher N_2O emissions due to air-stripping.

- It seems therefore, that greater fluctuations in operating conditions, particularly in DO, lead to higher N_2O being produced and subsequently emitted.

- Nitrous oxide was found to be produced even at the low NH_4^+ concentration of 0.5 mg/L, which had not been previously reported. This explains the N_2O emissions seen in the final stages of the full-scale nitrifying lane, where the NH_4^+ was consistently low.

- Additionally, heterotrophic incomplete denitrification was also shown to occur in the final stages of nitrification, leading to significant N_2O production, due to the low C/N ratios and intermittent low DO periods seen in the nitrifying ASP.

- This study showed a clear link between DO and N_2O production at full-scale, and confirms the negative effects of variability in operating conditions towards triggering emissions.

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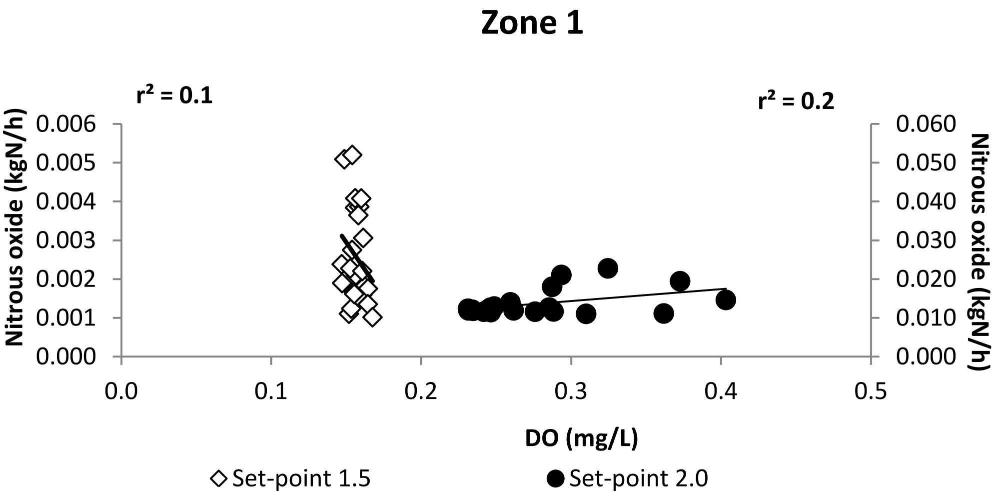
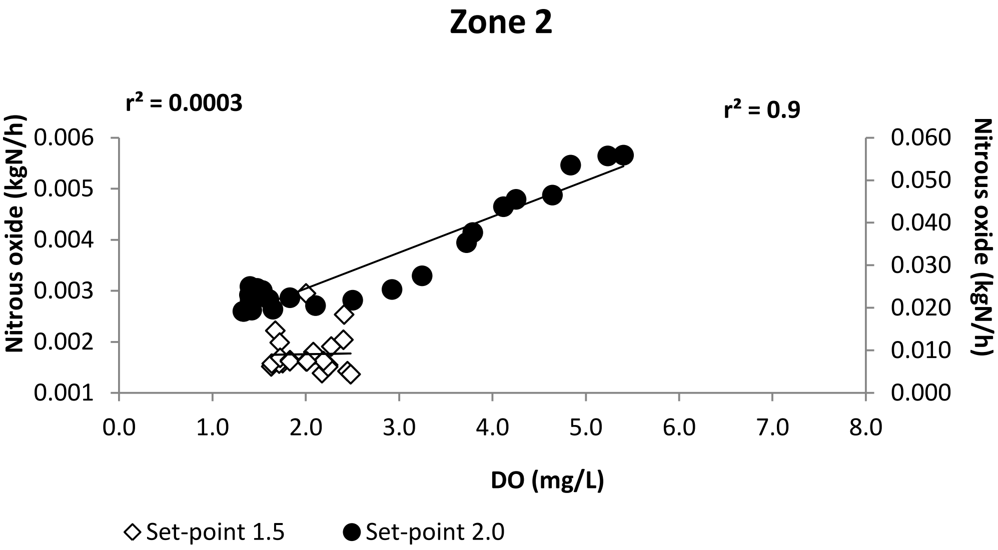
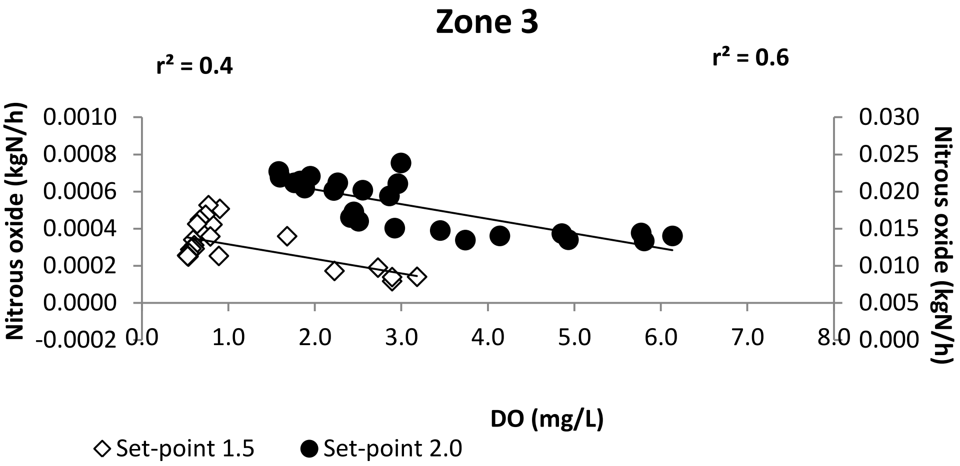
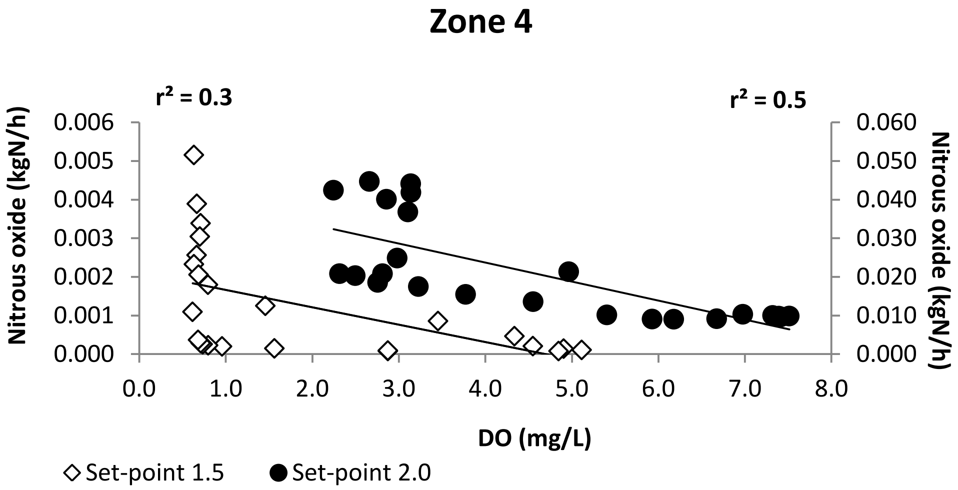
Supplementary information

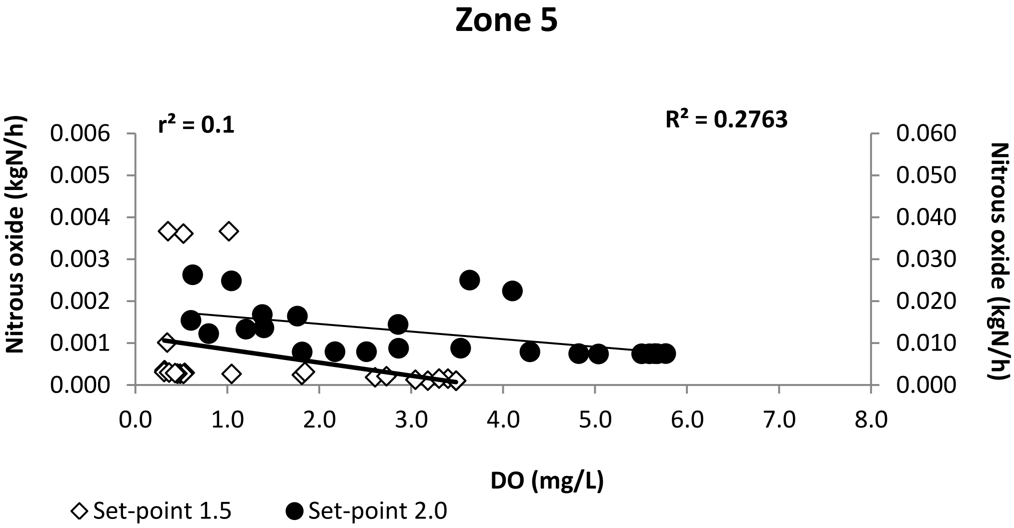
Figure S1: Correlations between N_2O emissions and DO in each zone, for the two DO set-points of 1.5 and 2.0 mg/L.

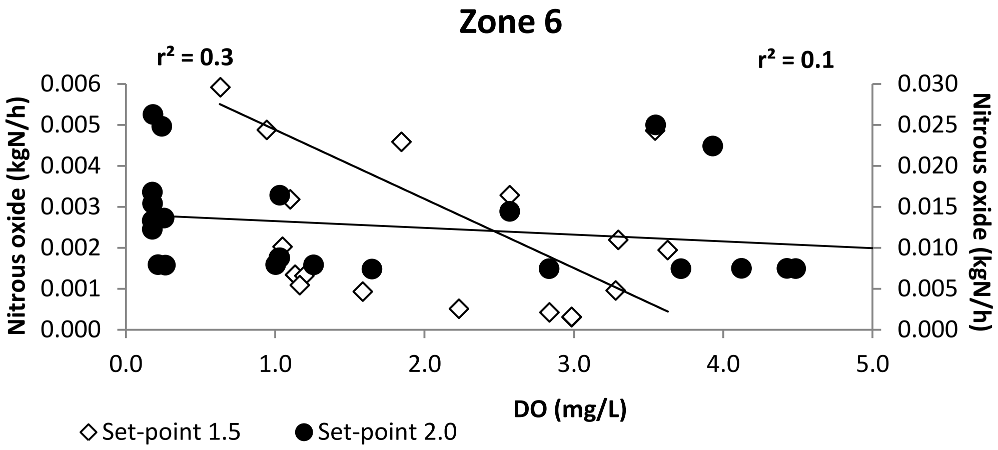


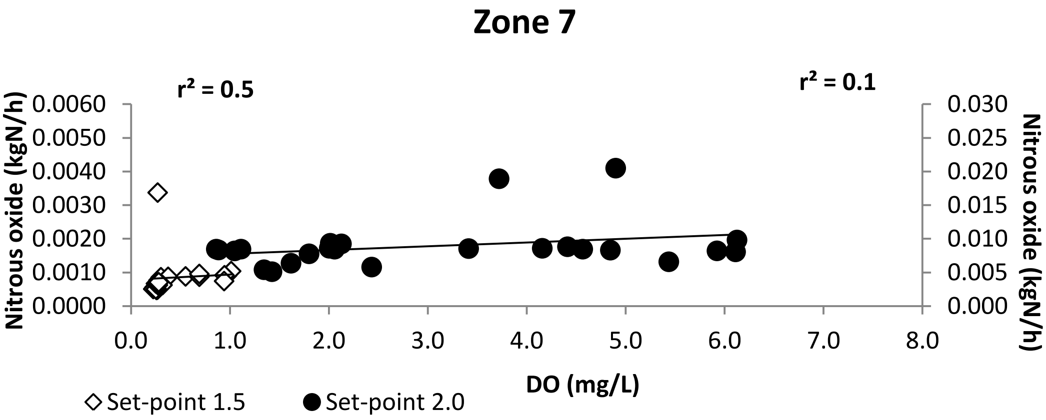


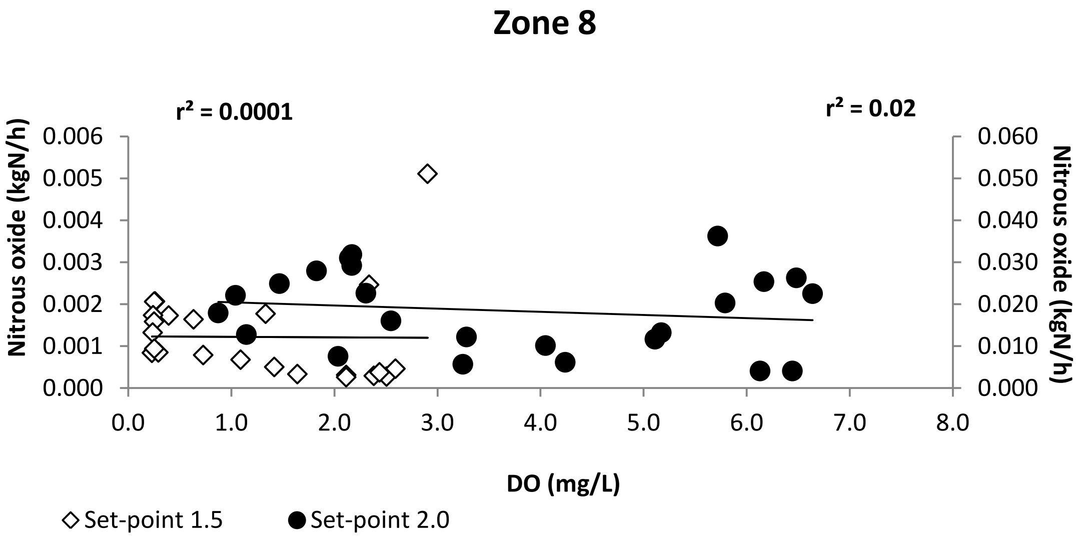

Zone 3
r² = 0.4
r² = 0.6
Nitrous oxide (kgN/h)
0.0010
0.0008
0.0006
0.0004
0.0002
0.0000
-0.0002
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
0.030
0.025
0.020
0.015
0.010
0.005
0.000
Nitrous oxide (kgN/h)
DO (mg/L)
◇ Set-point 1.5
● Set-point 2.0


Zone 4
r² = 0.3
r² = 0.5
Nitrous oxide (kgN/h)
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
0.060
0.050
0.040
0.030
0.020
0.010
0.000
Nitrous oxide (kgN/h)
DO (mg/L)
◇ Set-point 1.5
● Set-point 2.0


Zone 5
r² = 0.1
R² = 0.2763
Nitrous oxide (kgN/h)
0.006
0.005
0.004
0.003
0.002
0.001
0.000
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
0.060
0.050
0.040
0.030
0.020
0.010
0.000
Nitrous oxide (kgN/h)
DO (mg/L)
◇ Set-point 1.5
● Set-point 2.0


Zone 6
r² = 0.3
r² = 0.1
Nitrous oxide (kgN/h)
0.006
0.005
0.004
0.003
0.002
0.001
0.000
Nitrous oxide (kgN/h)
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0.0
1.0
2.0
3.0
4.0
5.0
DO (mg/L)
◇ Set-point 1.5
● Set-point 2.0


Zone 7
r² = 0.5
r² = 0.1
Nitrous oxide (kgN/h)
0.0060
0.0050
0.0040
0.0030
0.0020
0.0010
0.0000
Nitrous oxide (kgN/h)
0.030
0.025
0.020
0.015
0.010
0.005
0.000
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
DO (mg/L)
◇ Set-point 1.5
● Set-point 2.0


Zone 8
r² = 0.0001
r² = 0.02
Nitrous oxide (kgN/h)
0.006
0.005
0.004
0.003
0.002
0.001
0.000
Nitrous oxide (kgN/h)
0.060
0.050
0.040
0.030
0.020
0.010
0.000
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
DO (mg/L)
◇ Set-point 1.5
● Set-point 2.0

CHAPTER 6

PAPER 4: MINIMISING NITROUS OXIDE EMISSIONS FROM FULL-SCALE WASTEWATER TREATMENT PLANTS

IN PREPARATION: paper being prepared as final draft. Potential journal for publication is currently under discussion.

6. MINIMISING NITROUS OXIDE EMISSIONS FROM FULL-SCALE WASTEWATER TREATMENT PLANTS

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Abstract

Current knowledge around nitrous oxide (N_2O) emissions from full-scale wastewater treatment plants (WWTPs) is heavily reliant on estimations, which carry significant uncertainty. The objective of this study was to close that gap in knowledge, by quantifying N_2O emissions across different full-scale processes and the influence of operational changes, in order to identify the balance between reduction in carbon footprint and efficiency in nitrogen removal. The more fluctuations were introduced to the process, particularly to DO and aeration, the more N_2O was produced and released. This was seen by operating the same ASP lane under two different DO set-points (1.5 and 2.0 mg/L), whereby the lower set-point, with lower and more stable airflow rates (11–320 m^3/h) than the higher set-point (25–870 m^3/h), also produced a less fluctuating DO trend, thereby resulting in significant differences in emitted N_2O (0.09 and 1.6 kgN/day for set-points 1.5 and 2.0 mg/L respectively). Operating conditions were found to be dependent on control settings ($p < 0.05$), which in turn impacted on the ability of the process to generate and release N_2O. The highest and widest emission factors (EF) were seen in the lane operated at DO set-point of 2.0 mg/L (0.58–3.9 % across nitrogen fractions), whereas the most operationally stable process, the BNR lane, showed less variable and low EFs (0.08–0.1 %); the ASP lanes under the same DO set-point control of 1.5 mg/L, showed a similar range in EFs (0.05–0.2 % and 0.07–0.2 % for site A and B respectively), suggesting that operational process control is more important towards controlling emissions than loading rates. The more energy-efficient the process, the more N_2O emissions will contribute to the overall carbon footprint, as seen in the ammonia-controlled ASP, which contributed with the highest carbon footprint from process emissions (28 %), despite being the second most efficient process (80 m^3 of airflow and 5.0 kWh of energy input per kg of treated NH_4^+). However, a balance was achieved between low emissions, reduced carbon footprint and improved efficiency by operating at stable conditions, shown by the BNR lane. These conclusions are only feasible when obtained from a comprehensive online measurements of both N_2O and operating conditions, as the methodology adopted by this study.

Key words: nitrous oxide, carbon footprint, process efficiency, control settings, biological wastewater treatment

6.1. Introduction

Global warming has triggered concerns about the rising levels in atmospheric greenhouse gases (GHG) and the effects this may have on climate change, and therefore, attempts are being made at minimising GHG. In the United Kingdom (UK) for example, this is reflected by the introduction of the Climate Change Act. This is a legislative framework unique to the UK, aiming at reducing the net carbon account for all six Kyoto GHG by 80 % by 2050, with the necessary measures to achieve a minimum annual reduction of 1.4 % (OFWAT, 2010; Tribe, 2010). Most businesses in the UK, including wastewater treatment plants (WWTPs), are required to comply with this challenging target by reporting on their direct and indirect emissions, whilst also implementing measures to minimise their carbon footprint.

For WWTPs, compliance with the Climate Change Act may conflict with the requirements of another important piece of legislation: the Water Framework Directive (WFD). The focus of the WFD is on achieving “good ecological status” in inland and coastal waters (Ainger et al., 2009), pushing for better effluent quality and for more nitrogen removal from biological wastewater treatment. However, more nitrogen removal means more energy-intensive processes: currently, 56 % of GHG emissions from the water industry already derive from wastewater treatment (Reffold et al., 2008), and are likely to increase under the requirements of the WFD. This increase is mainly related to aeration systems required by activated sludge plants (ASPs) to treat ammonia (NH_4^+), since these processes account for 55 % of the energy consumption in WWTPs (George et al., 2009; Reffold et al., 2008; Cafoor, 2008). Therefore, carbon dioxide equivalent (CO_2e) emissions by WWTPs are expected to rise by 110,000 tonnes per year (George et al., 2009). The increase in CO_2e emissions however, does not only originate from energy consumption, but also from direct process emissions of non-CO_2 GHG, such as nitrous oxide (N_2O) and methane (CH_4). The global warming potentials (GWP) of these gases is higher than that of CO_2 (Listowski et al., 2011), particularly N_2O, with a GWP of 310 (IPCC, 2006).

Nitrous oxide is produced during nitrification and denitrification (Ahn et al., 2010a,b; Kampschreur et al., 2008a; Tallec et. al., 2006), the biological processes used to remove nitrogen from wastewater. Release of N_2O is enhanced with the introduction of anoxic zones and control strategies to reduce energy from aeration by dropping dissolved oxygen (DO) concentrations in WWTPs (Kampschreur et al., 2008a). Changes to DO conditions however, are key in influencing biological N_2O emissions, (Aboobakar et al., 2014a; Rassamee et al., 2011; Tallec et al., 2006).

Dissolved oxygen concentrations equal or below 1.0 mg/L (Aboobakar et al., 2013a; Tallec et al., 2006), have been shown to trigger N_2O production during nitrification by ammonia-oxidising bacteria (AOB), via a nitrite (NO_2^-) reduction pathway known as nitrifier denitrification (Colliver and Stephenson, 2000; Shaw et al., 2006). Additionally, during denitrification, low DO inhibits enzyme activity, leading to interrupted heterotrophic reduction of nitrate (NO_3^-) to dinitrogen gas (N_2), or incomplete denitrification, with N_2O as the final product (Kampschreur et al., 2009a; Otte et al., 1996). Dissolved oxygen may influence N_2O production during nitrification, not only during, but also in recovery from, low DO conditions (Yu et al., 2010), therefore highlighting the need for optimal DO conditions. Optimised levels however, must not be achieved at the cost of excessively aerated processes, because this in turn, not only releases N_2O into the atmosphere by air-stripping, but also impacts on carbon footprint. More importantly it seems, is that operational conditions must be as consistent as possible, since fluctuations in DO and airflows have been shown to trigger N_2O production and emissions, both under experimental and full-scale conditions (Aboobakar et al., 2014a; Kampschreur et al., 2008a; Rassamee et al., 2011). However, WWTPs are complex environments, with an inherent degree of variation in their operational conditions. Not surprisingly, emissions reported from full-scale monitoring have also shown significant variability (Aboobakar et al., 2013a; 2014; Ahn et al., 2010b; Foley et al., 2010a; Kampschreur et al., 2008b), not only from different processes, but also within the same processes (Aboobakar et al., 2013a). This makes it difficult to pin down one value for emission factor (EF), and indeed it challenges the validity of “one-size-fits-all” estimations, which carry a degree of uncertainty and fail to consider the variability shown by quantified data. For example, the average N_2O emission factor for the UK, estimated by the UK Water Industry Research (UKWIR) as originating from WWTPs (nitrification only), is of 0.2 % of the influent total nitrogen (TN), although this carries uncertainty levels between 30 to 300 % (UKWIR, 2009).

As the water industry moves towards a carbon-neutral future, the use of more sustainable and renewable carbon sources to reduce energy-associated emissions will be more common-practice (Water UK, 2008). This means that process emissions will become more relevant to the overall carbon footprint of a WWTP. Therefore, in order to develop reasonably effective carbon mitigation strategies, and find a balance between low emissions and high process efficiency, more information is required on how emissions evolve in wastewater treatment environments. The objective of this study is therefore, to close that gap in knowledge, by quantifying and characterising N_2O emissions across different full-scale processes, as well as investigating how those emissions are affected by changes in operational variables. Finally, the study was designed to identify the best compromise between low process emissions, reduction in operational carbon footprint and efficiency in nitrogen removal.

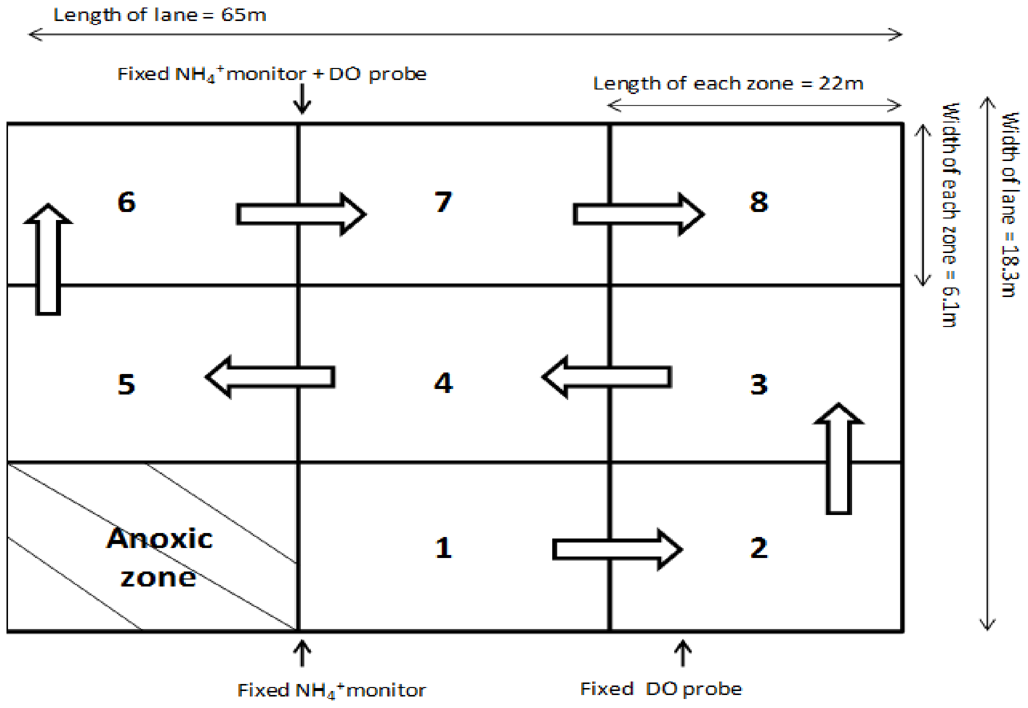
6.2. Materials and methods

6.2.1. Monitoring sites

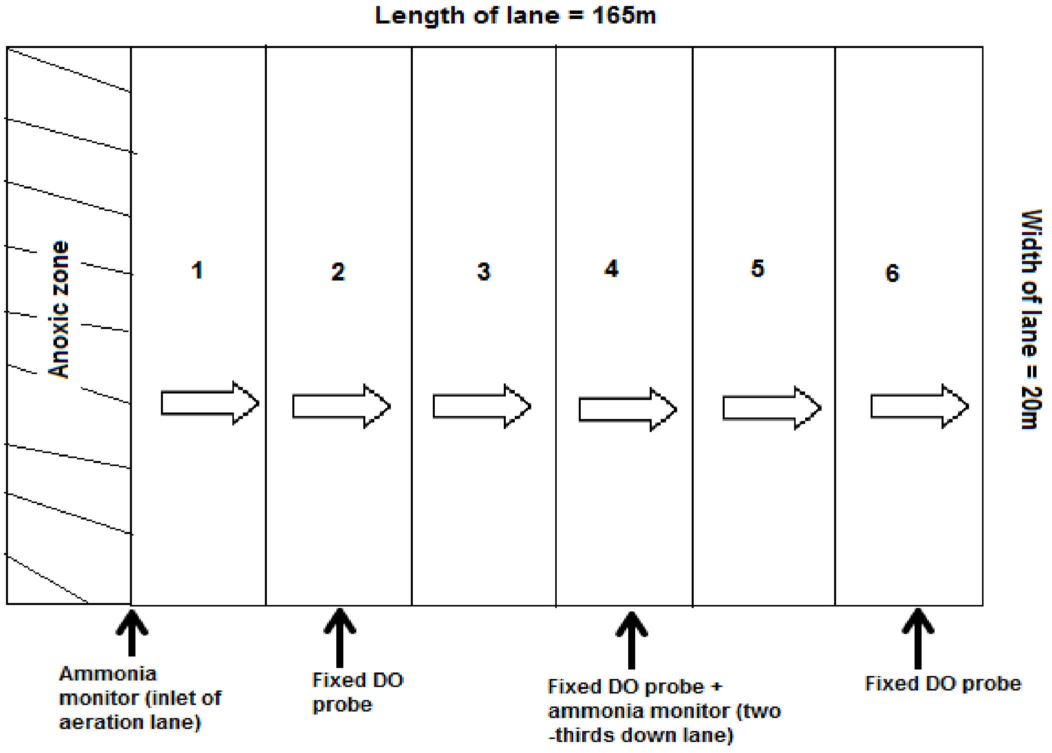
Two full-scale WWTPs in the Midlands, UK were chosen for this study (sites A and B). In site A (population equivalent of 210,000), the monitored process consisted of a nitrifying ASP, with a plug-flow configuration in a three-pass aeration lane preceded by an anoxic zone treating 10 % of the daily incoming flow, with eight-hour hydraulic and 10-day sludge retention times respectively, at incoming flow rate ranging between 185–300 m^3/h. The aeration control consisted of blowers in duty/assist/standby modes. Two DO control set-points were tested in the lane, first at the baseline set-point of 1.5 mg/L and then a higher set-point of 2.0 mg/L. At set-point 1.5 mg/L, average airflow rates ranged from 11–320 m^3/h, and from 25–870 m^3/h at set-point 2.0 mg/L.

In the second site (population equivalent 1,750,000), two processes were monitored: a nitrifying ASP and a biological nutrient removal (BNR) lanes, both operating in plug-flow, with each lane preceded by an anoxic zone (with an added anaerobic zone before the anoxic zone in the BNR lane), at an average flow rate of 1,450 m^3/h and 900 m^3/h per lane for the ASP and BNR respectively. The aeration control consisted of blowers also in duty/assist/standby modes, with airflow rates ranging from 0.7–760 m^3/h and 30–240 m^3/h across the ASP and BNR lanes respectively. Both lanes were run under an advanced process control setting, based on an NH_4^+ algorithm in feedback mode, controlled through an online NH_4^+ monitor installed two-thirds down the lane. The nitrifying ASP lane was also monitored under DO set-point control of 1.5 mg/L for a three-month period, where control was monitored via three DO probes in the lane (Fig. 6.1). The airflow rates for the ASP lane under DO 1.5 mg/L set-point control ranged from 18–363 m^3/h.

A


Length of lane = 65m
Fixed NH$_4^+$monitor + DO probe
Length of each zone = 22m
Width of each zone = 6.1m
Width of lane = 18.3m
6
7
8
5
4
3
Anoxic zone
1
2
Fixed NH$_4^+$monitor
Fixed DO probe

B


Length of lane = 165m
Anoxic zone
1
2
3
4
5
6
Width of lane = 20m
Ammonia monitor (inlet of aeration lane)
Fixed DO probe
Fixed DO probe + ammonia monitor (two -thirds down lane)
Fixed DO probe

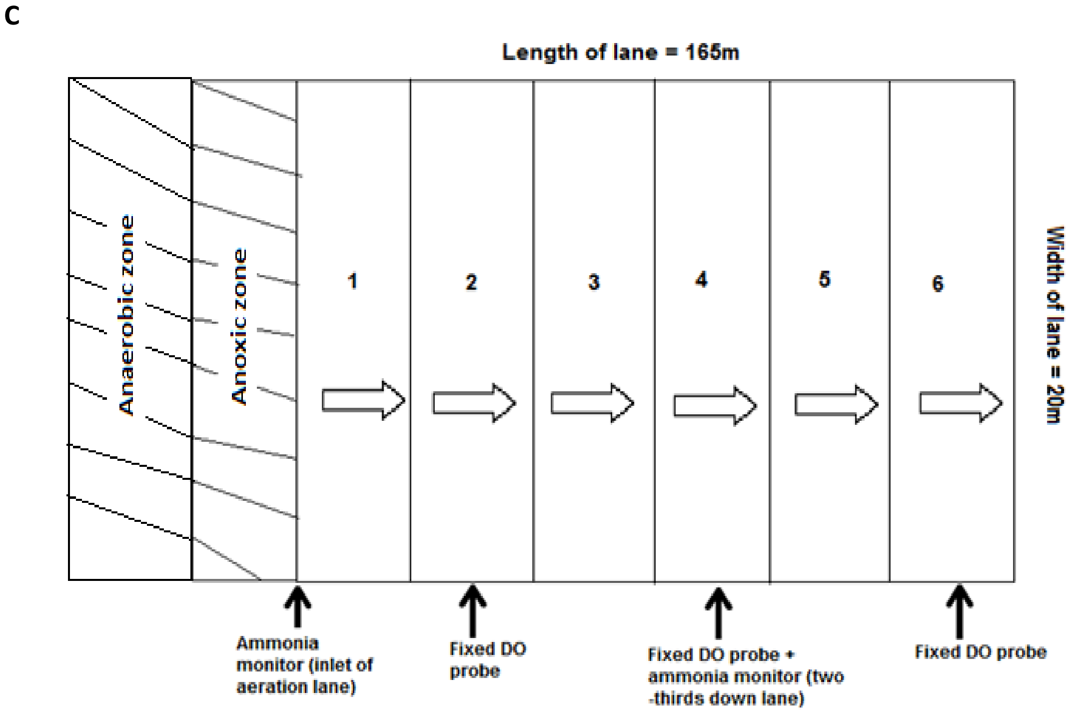


Figure 6.1: Configuration of the plug-flow nitrifying lanes (A = site A and B = site B, nitrifying ASP, C = site B, BNR) showing dimensions of the lane and of the monitored zones (numbered boxes) within the passes. The white arrows indicate the direction of flow. The fixed DO probes seen on the diagram (zones 2 and 6 and 2, 4, 6 for sites A and B respectively) are linked and controlled by the SCADA system. The fixed NH_4^+ monitor (zone 4) is also linked to SCADA, and controls the aeration based on NH_4^+ levels two-thirds down the lane under the NH_4^+ controlled ASP in site B. The monitored lane in site A is part of a two-lane ASP and in site B both the ASP and the BNR monitored lanes are part of a four-lane unit.

6.2.2. Full-scale monitoring campaign

Off-gas N_2O was captured using a gas-collecting floating hood (surface area of 0.34 m^2; Water Innovate, UK), suspended over the wastewater and connected to a PTFE tubing sampling line. Off-gases were then pumped through via an infra-red gas analyser with an integrated sample pump, moisture trap, auto-calibration system and data-logging unit, recording concentrations every minute (N-TOX®, Water Innovate, UK). Dissolved N_2O was detected every minute, using a modified Clark electrode probe (N_2O-R mini-sensor, Unisense A/S, Denmark) connected to a picoammeter and data-logging laptop. A rugged DO probe with Sc100 monitor (Hach Lange, Germany) was used to monitor DO concentrations in the bulk liquid every 15 minutes and placed next to the gas analyser and floating hood.

In order to produce a spatial profile of emissions in the lane, a tanks-in-series (TIS) model for plug-flow was used, which produced equally-distributed sampling "zones" in the nitrifying lane, with the first zone (zone 1) at the inlet of the aeration lane and the last zone (zone 8) at the outlet of the lane just before the weir (Fig. 6.1). The equipment was deployed in each one of these zones for a period of one week per zone, with a total of eight weeks of monitoring for each set-point in site A and six weeks per control setting in site B. The airflow rate was monitored continuously, using an insertion-type air flow meter (VPFlowScope, Omni Instruments, UK), with readings taken every 15 minutes. Two online NH_4^+ monitors (STIP PBS1, Envitech, UK) were used, with one capturing the NH_4^+ inflow to the aeration lane (placed in zone 1) and another recording the NH_4^+ two-thirds down the lane, whereby most of nitrification has taken place.

A sampling campaign was also carried out every two weeks in parallel with the online monitoring, during which 24-hour discrete samples from settled sewage and final effluent, and grab samples from the returned activated sludge (RAS) at peak and low load times were collected. Samples were analysed for NH_4^+, NO_3^-, NO_2^-, TN and chemical oxygen demand (COD) using colorimetric test kits (Hach Lange, Germany) and for solids (total and volatile suspended solids, TSS and VSS respectively) according to Standard Methods (APHA, 2005). A nitrogen mass balance of the combined data was used to determine the EF, based on the percentage of influent and removed NH_4^+ and TN emitted as N_2O.

To measure the non-aerated zones in site B, a methodology was adapted from the Gas Analysis Protocol developed by Baker et al. (2003), adopting recommendations reviewed by Mosier (1989), to address key issues related to chamber techniques for flux measurement when collecting gas samples from soil. The floating hood was sealed and deployed on non-aerated zones, with the sampling line connected to the inlet of an air pump. Gas samples were collected from the headspace of the hood, into a 0.3-litre gas bag, attached to the outlet of the air pump. Samples were taken at regular intervals and measured on-site, immediately after sampling, by using the N-TOX® analyser. A total of five gas samples were collected over one-hour periods, taken at the same time (mid-morning and mid-afternoon) over three days. The measurement of off-gas N_2O was done in parallel with the N_2O monitoring, by deploying the N_2O-R probe on the non-aerated zone at the same time as the gas sampling (about an hour before starting gas measurements), and leaving it for an extended 24-hour period, in order to provide a diurnal profile of the non-aerated zones.

6.2.3. Energy and statistical analyses

An energy and efficiency analysis was carried out for both sites. The data was gathered from the airflow delivered to the monitored lane, plus the energy required to run the blowers aerating the lanes. Process efficiency was then calculated for each monitored lane based on airflow (m^3/day) and energy input (kWh/day) required to treat 1.0 kg of NH_4^+. The energy data for site A was obtained from a monitoring study previously conducted at the site in 2009. For site B, the energy data was obtained from the Supervisory Control and Data Acquisition (SCADA) system during the monitored period.

Statistical analysis was carried out using a two-way, repeated measures analysis of variance (ANOVA) to determine the differences in diurnal variability for each aeration pass, process control settings, and for all monitored lanes. Data analysis was conducted with STATISTICA v12 (StatSoft Inc, Oklahoma, USA) and considered significant at $\alpha = 0.05$.

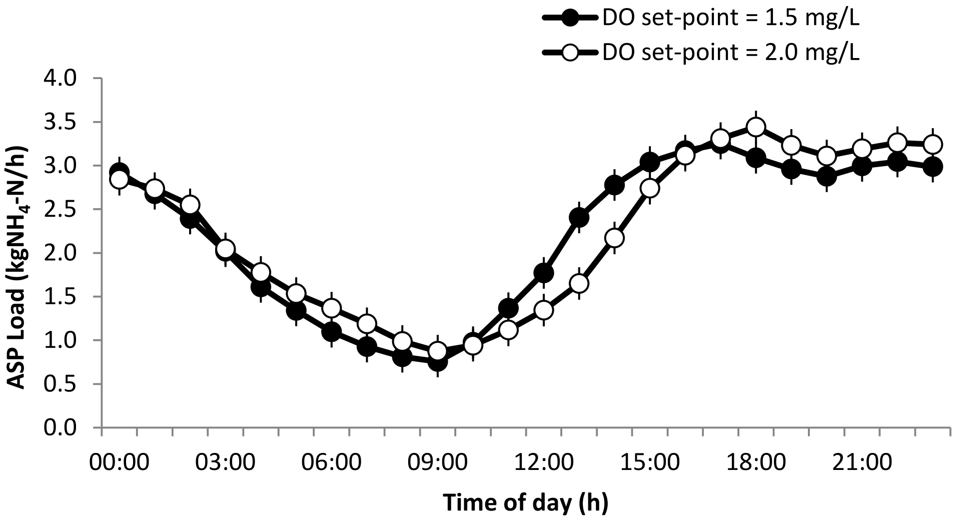
6.3. Results

6.3.1. Operating conditions

Based on the load trends (Fig. 6.2), conditions in each site were similar during the monitored periods within each process. All monitored processes treated NH_4^+ well below the relevant discharge consents (Fig. 6.3), with site B treating even less than half of the required NH_4^+ discharge consent for that site (discharge consent = 3.0 mg/L). The small increase in set-points at site A, had a remarkable impact on the airflow rates (Fig. 6.4A), particularly in the first (zones 1 and 2) and second (zones 3 to 5) aeration passes, with rates increasing four times in zones 1 and 2 and almost eight times in zones 3 to 5 from set-point 1.5 to 2.0 mg/L. Despite showing the most effective NH_4^+ removal (Fig. 6.3), the airflow profile in the nitrifying ASP in site B under NH_4^+ control was more variable than for the same ASP under set-point control (Fig. 6.4B) or even the BNR process. The DO in the anoxic and anaerobic zones was consistently below 0.2 mg/L during measurement campaigns of the non-aerated zones.

The DO profiles for site A (Fig. 6.5A), revealed a marked variability in both set-points, although the variability range increased for the higher set-point, most likely due to the changes observed in the airflow rates (Figure 6.4A). Similarly for site B, the more fluctuating airflow trend seen for the NH_4^+ controlled ASP (Fig. 6.4B) had a significant effect on the DO profile, particularly in zone 5, making it the lowest average seen in the lane (Fig. 6.5B). The airflow supply under NH_4^+ set-point control was maintained via an online NH_4^+ monitor two-thirds down the aeration tank (Figure 6.1). Most of the NH_4^+ was treated by the time it reached this zone, therefore resulting in very low average readings (0.3 $mgNH_4$-N/L for the NH_4^+ controlled ASP). This explains why although the airflow rates in the nitrifying ASP under NH_4^+ control started as the highest in all of monitored processes in site B, aeration was dramatically decreased from zone 4, leading in turn, to the low airflow rates seen in the following zone 5 (Fig. 6.4B).

A



B

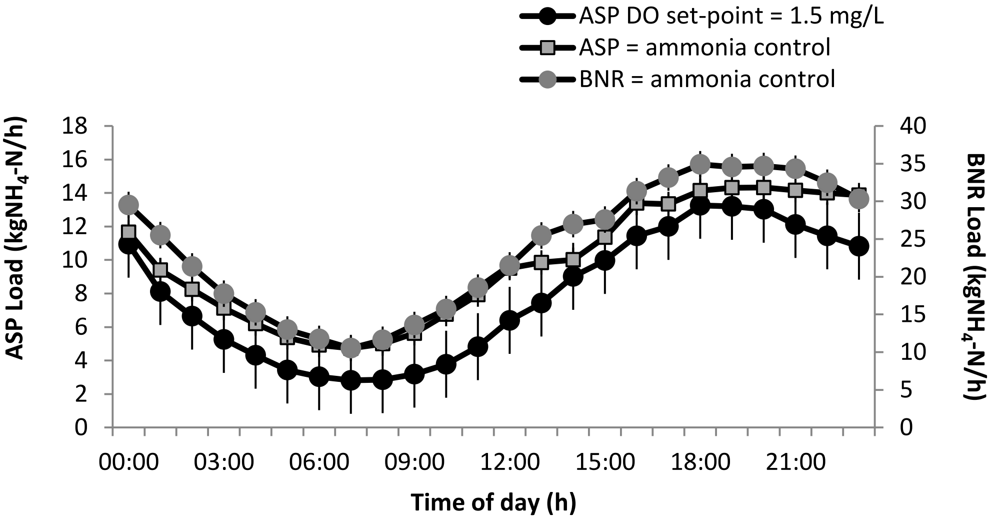


Figure 6.2: Comparison of diurnal load trends during different process controls within sites A and B (represented by A and B before each graph)

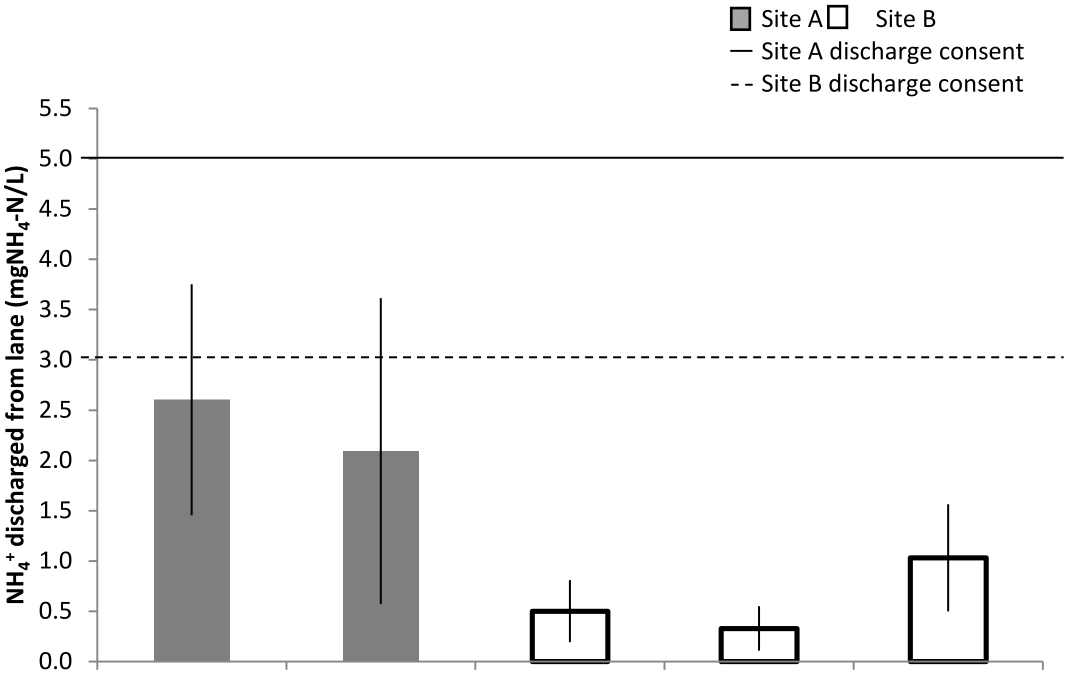
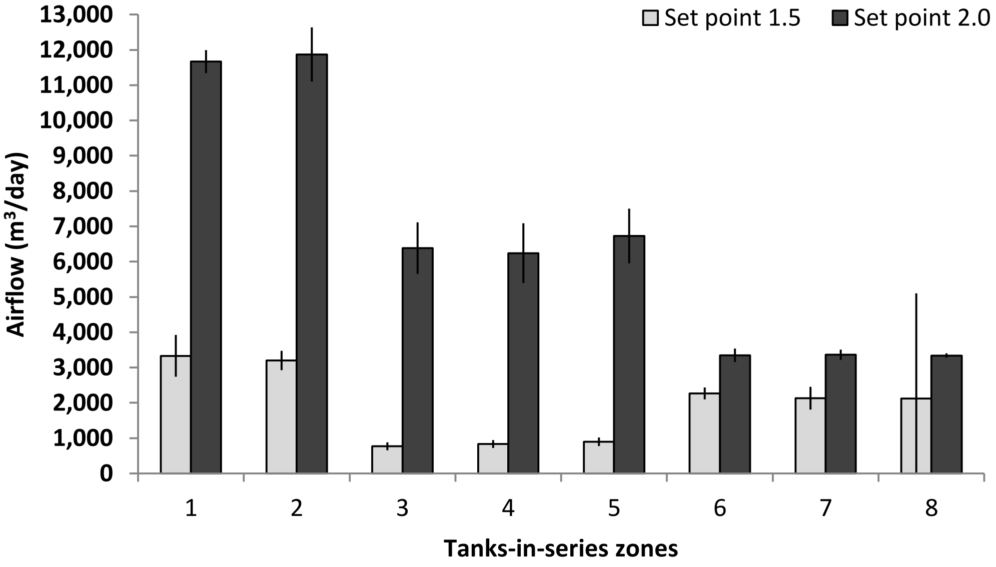


Figure 6.3: Comparison of average NH_4^+ discharged from the monitored lanes in each process for sites A and B (NH_4^+ discharge consent = 5.0 and 3.0 mg/L respectively)

A



B

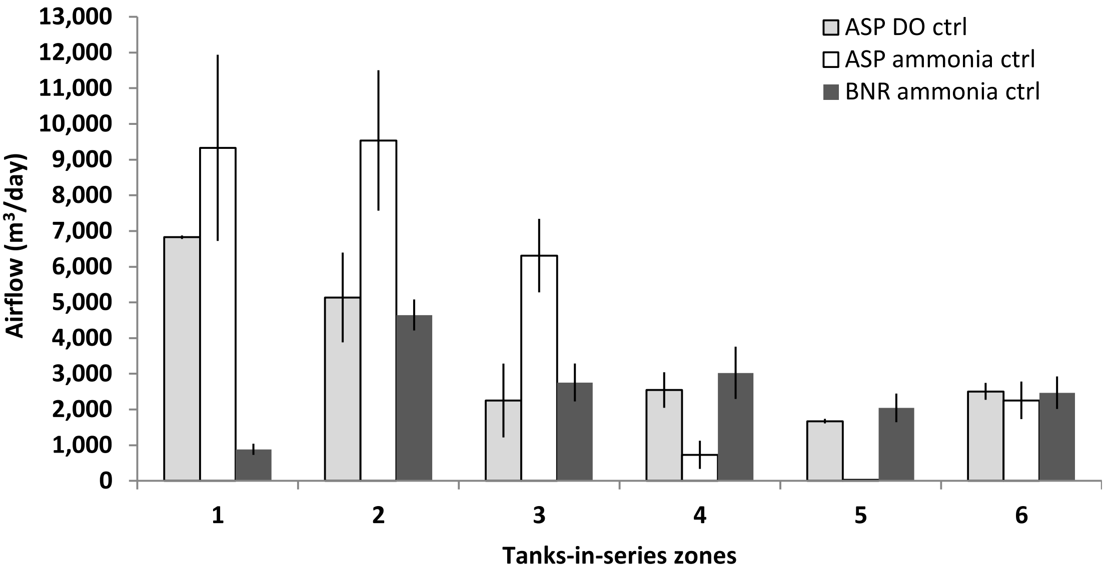
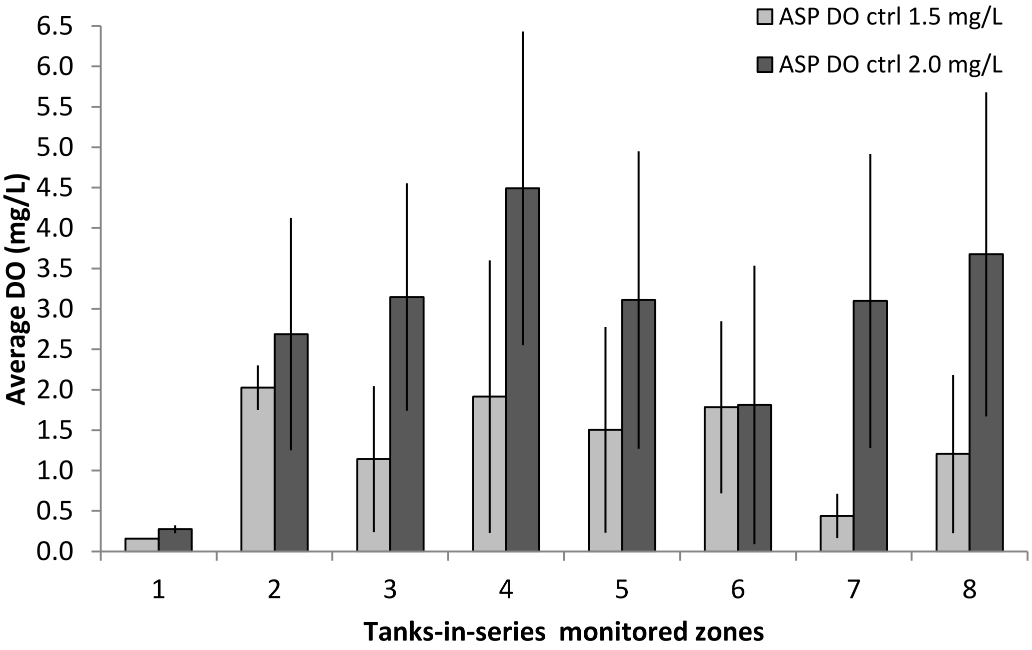


Figure 6.4: Comparison of spatial airflow trends during different process controls within sites A and B (represented by A and B before each graph)

A



B

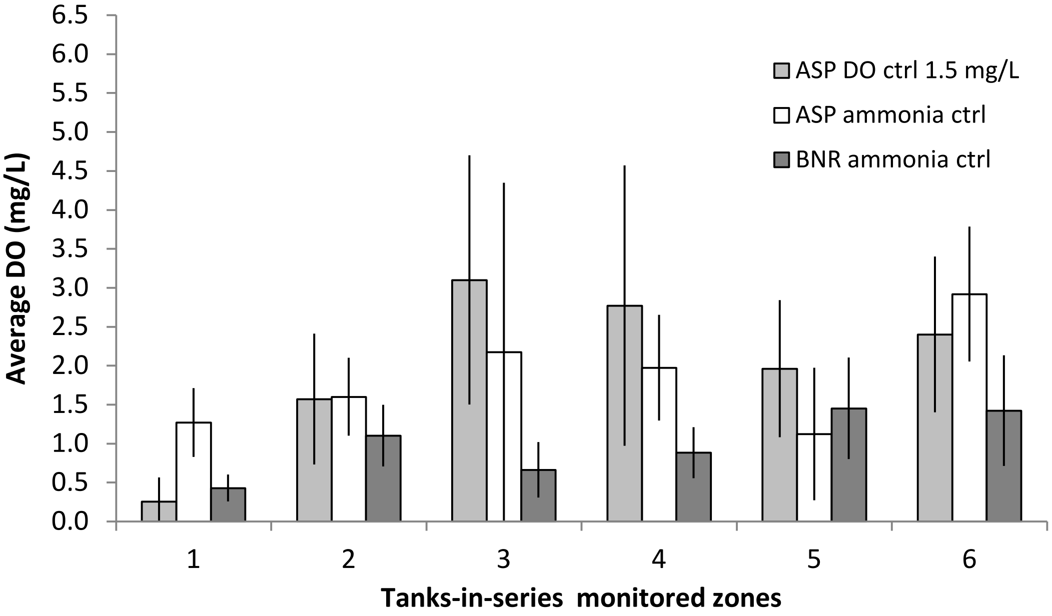


Figure 6.5: Comparison of spatial DO trends during different process controls within sites A and B (represented by A and B before each graph)

6.3.2. Nitrous oxide emissions under different control settings

Peaks in dissolved N_2O were observed in the middle of the aeration lanes, particularly in the NH_4^+ controlled ASP, where dissolved N_2O was lower in the first two zones, and peaked further downstream in zones 3 and then 5 at 0.99 and 1.97 kgN_2O-N/day per kgNH_4-N/day respectively (Fig. 6.6A). This therefore suggests that N_2O is being produced within the nitrifying lanes, rather than just transferred from previous non-aerated zones.

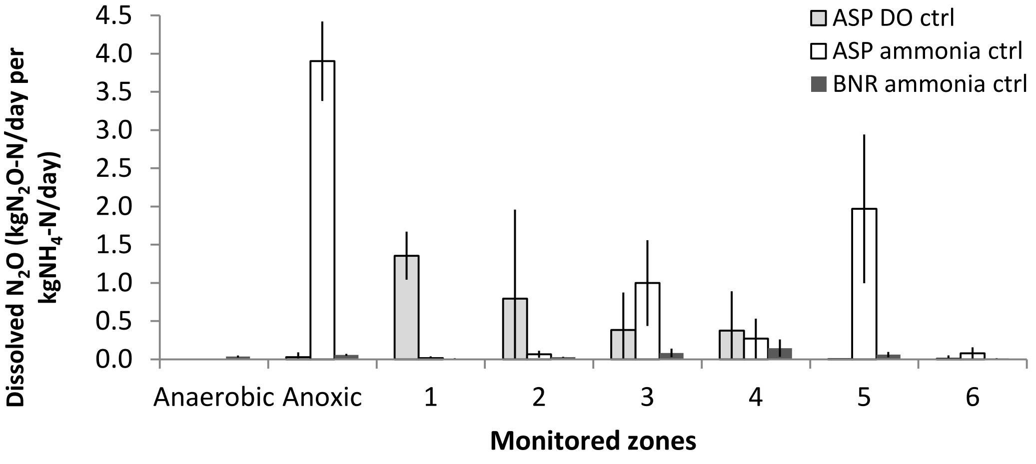
On the other hand, peaks in the N_2O off-gas were mostly see in the first two zones in all processes in site B (Fig. 6.6B), particularly in the ASP lane controlled under both DO (0.04 and 0.1 kgN_2O-N/day per kgNH_4-N/day for zones 1 and 2 respectively) and NH_4^+ (0.03 and 0.1 kgN_2O-N/day per kgNH_4-N/day for zones 1 and 2 respectively) set-points. These peaks were concurrent with higher aeration in the first two zones in the nitrifying ASP lane, as well as in zone 2 in the BNR lane (Fig. 6.4), thus suggesting that airflow is an influential parameter in controlling off-gas N_2O. Lower airflow therefore, will result in reduced off-gas emissions, such as seen in zone 1 in the BNR lane, where the lower airflow rate (883 m^3/day, Fig. 6.4B) in relation to zone 2 (4646 m^3/day, Fig. 6.4B), led to comparably lower off-gas N_2O (0.001 kgN_2O-N/day per kgNH_4-N/day) than in zone 2 (0.01 kgN_2O-N/day per kgNH_4-N/day).

In the non-aerated zones, the anoxic zone for the ASP under NH_4^+ control showed the highest value for dissolved N_2O (Fig. 6.6A), at 3.9 kgN_2O-N per kgNH_4-N/day, which was also the highest value seen in all monitored processes. The anoxic zones in the same ASP under DO set-point control and in the BNR, showed much lower dissolved N_2O, at

0.03 and 0.06 $kgN_2O-N/kgNH_4/N$ per day, respectively. The anaerobic zone in the BNR was also low at 0.04 $kgN_2O-N/kgNH_4/N$ per day. Average concentrations of off-gas N_2O in the non-aerated zones were as follows for all configurations: the anoxic zone in the nitrifying ASP showed an average range between 2.0–10 and 5.0–9.0 ppmv for DO and NH_4^+ set-point controls respectively, and in the BNR lane, 2.0–13 and 2.0–14 ppmv, for the anaerobic and anoxic zones respectively (Fig. 6.6B), with the limit of detection on the gas analyser (N-TOX®) at 2.0 ppmv.

Analysis of variance showed that the DO and NH_4^+ control settings impacted considerably ($p < 0.05$) on the diurnal trends of both N_2O and operational conditions (Table 6.1). Nitrous oxide (off-gas and dissolved) and DO were also affected by changes in the aeration passes ($p < 0.05$, Table 6.1), which therefore contributed to the variability seen in the tanks-in-series zones, across all the monitored processes. The variation in airflow, N_2O in the off-gas and DO trends, were all was affected by the changes in diurnal variation ($p < 0.05$. Dissolved N_2O on the other hand, showed no statistical significance with diurnal variability ($p = 0.97$). The most significant fluctuations in diurnal variability were seen in the off-gas N_2O emissions and DO trends, particularly so under the DO set-point control of 2.0 mg/L. By contrast, the BNR lane showed the most stable trends in both off-gas N_2O and DO, with the ASPs under DO set-point 1.5 mg/L and NH_4^+ controls showing DO variability trends halfway between DO set-point 2.0 mg/L ASP and BNR lanes.

A



B

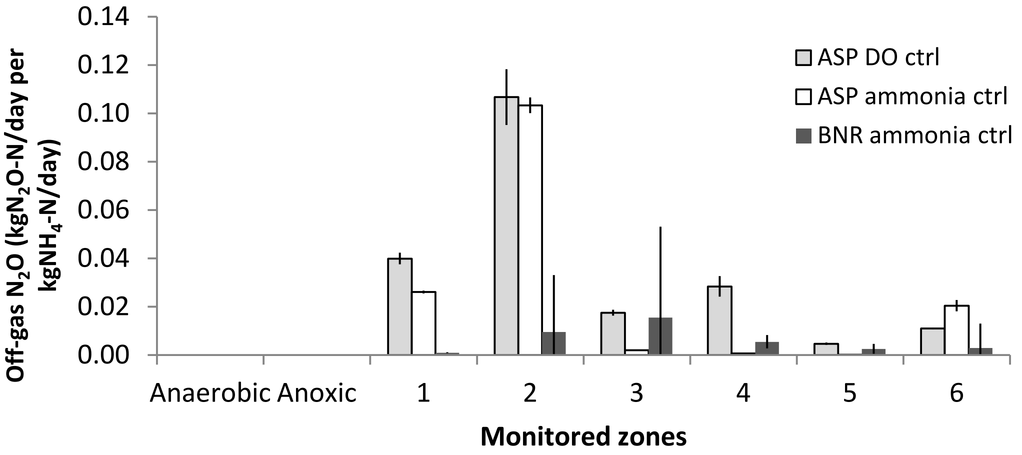


Figure 6.6: Comparison of normalised dissolved (A) and off-gas (B) N_2O per process control setting in site B. Nitrous oxide rates (KgN2O-N/day) are normalised per ammonia load (kgNH_4-N/day)

Table 6.1: Analysis of variance (ANOVA), using general linear model, with p values compared for: effects of the aeration pass, operational control settings and diurnal variation on N_2O (dissolved and off-gas), airflow and DO for each monitored processes. The data was based on the daily average values per zone, for each lane.

Variables	Control settings[a]	Aeration pass [b]	Diurnal variation
Dissolved N_2O	<0.05	<0.05	0.97
Off-gas N_2O	<0.05	<0.05	<0.05
Airflow	<0.05	0.82	<0.05
DO	<0.05	<0.05	<0.05

[a] *Refers to the process settings in each monitored lane: DO set-point controls of 1.5 and 2.0 mg/L for ASP at site A, DO set-point control 1.5 mg/L and* NH_4^+ *control for ASP and* NH_4^+ *controlled BNR in site B.*

[b] *The first, middle and last aeration passes, containing the theoretical tanks-in-series zones in each of the plug-flow lanes monitored. For site A: zones 1-2, 3-5 and 6-8 are in the first, middle and last aeration passes respectively. For site B: zones 1-2, 3-4 and 5-6 are in the first, middle and last aeration passes respectively.*

6.3.3. Emission factors

The highest combined emissions released from any process, at 1.55 kgN_2O-N/day, were seen for the nitrifying ASP in site A at set-point 2.0 mg/L, which also corresponded to the highest EFs across all nitrogen fractions: 0.58, 0.72, 1.59 and 3.9 % of the influent and removed TN and NH_4^+ respectively (Table 6.2). The second highest emissions came from the nitrifying ASP in site B under NH_4^+ control, where the combined emissions of 1.19 kgN_2O-N/day, resulted in EFs of 0.09, 0.14, 0.1 and 0.34 % of the influent and removed TN and NH_4^+ respectively. Although second highest, the EFs for the NH_4^+ controlled lane, were five to 11 times lower than those from the set-point 2.0 mg/L lane in site A. The lowest emissions were seen in the same process at site A, but for set-point 1.5 mg/L, at 0.05 % of both influent TN and NH_4^+. The values were very similar to the same 1.5 mg/L control setting in site B (0.07 and 0.08 % of influent TN and NH_4^+), identical for the NH_4^+ removed (both 0.2 %) and again similar for the TN removed (0.13 and 0.12 % for sites A and B respectively). Overall, the EFs increased from the influent to the removed nitrogen fractions, the exception being the BNR process, which showed the same EFs for both influent and removed NH_4^+ (0.1 %), and similar EFs for influent (0.08 %) and removed (0.09 %) TN.

Table 6.2: Nitrous oxide emission factors for sites A and B based on different nitrogen fractions and mass flows

Sites	**Emission factors (%)**				**Mass inflow (kgN/day)**				**Mass outflow (kgN/day)**				**Combined emissions (kgN/day)**[d]
Process configuration/ control settings	N_2O-N/TN load[a]	N_2O-N/NH_4-N load[a]	N_2O-N/TN removed[b]	N_2O-N/NH_4-N removed[c]	TN	NH_4-N	NO_3-N	NO_2-N	TN	NH_4-N	NO_3-N	NO_2-N	N_2O-N
Site A													
ASP set-point 1.5 mg/L	0.05	0.05	0.13	0.20	199	168	2.38	0.06	129	1.24	67.40	0.27	0.09
ASP set-point 2.0 mg/L	0.58	0.72	1.59	3.90	268	215	5.30	0.18	170	1.75	105	1.58	1.55
Site B													
ASP set-point 1.5 mg/L	0.07	0.08	0.12	0.20	830	711	6.14	0.46	338	3.86	120	0.28	0.59
ASP NH_4^+ control	0.09	0.14	0.15	0.34	1270	823	5.28	1.20	471	2.84	397	0.93	1.19
BNR NH_4^+ control	0.08	0.10	0.09	0.10	831	701	5.11	1.30	110	1.76	106	0.73	0.68

[a] *Refers to TN and NH_4^+ fractions measured in the settled sewage*

b Refers to TN fractions from settled sewage minus waste and final effluents

[c] *Refers to NH_4^+ removed from within the nitrifying tanks*

[d] *Total combined emissions for all monitored processes in sites A and B includes the sum of off-gas N_2O in all zones plus dissolved N_2O in the last zone, which is zone 8 for site A and zone 6 for site B. The emissions relate to quantified N_2O in the aerated zones only*

6.3.4. Carbon impact and process efficiency

Comparison between the carbon footprint added by N_2O emissions to that associated with the energy used to aerate each of the monitored lanes (Table 6.3), showed that site A had the lowest carbon footprint contribution from process emissions, at 11 and 13 %, for set-points 2.0 and 1.5 mg/L, respectively. Because of the disproportionally high energy use at 2.7 GWh/year, the DO set-point of 2.0 mg/L showed the lowest contribution to operational carbon from process emissions, despite having the highest actual N_2O footprint (Table 6.3), at 175,101 kg of CO_2 equivalents per year ($kgCO_2e$/year).

The highest contribution of process emissions to the overall operational carbon footprint was instead from the NH_4^+ controlled ASP at site B, where emissions contributed 28 %. This lane also showed a high N_2O footprint at 134,110 $kgCO_2e$/year, only second to the DO set-point 2.0 mg/L in site A. However, the N_2O emission footprint from the NH_4^+ controlled ASP contributed more to the overall carbon footprint because the energy requirements of this process were lower, and therefore had a comparably lower carbon footprint at 341,365 $kgCO_2e$/year, than the energy requirements of the DO set-point control of 2.0 mg/L, at 1,471,220 $kgCO_2e$/year. The same process under DO set-point control, as well as the NH_4^+ controlled BNR, contributed less to the overall carbon footprint of the lanes, at 19 and 20 % respectively.

However, when comparing process efficiency, both for the amount of energy input as well as airflow delivered to the process to treat 1.0 kg of NH_4-N (Table 6.3), the nitrifying ASP under NH_4^+ set-point control showed to be marginally more efficient (80 m^3 and 5.0 kWh per kg NH_4^+ treated) than the same process under DO set-point control of 1.5 mg/L (85 m^3 and 6.0 kWh per kg NH_4^+ removed). Overall, the nitrifying ASP lane at site A was less efficient than the ASP lane at site B, particularly for the DO set-point at 2.0 mg/L: 1,001 m^3 and 140 kWh per kg NH_4^+ removed respectively. Furthermore, when comparing the same control setting in the two sites (DO set-point control 1.5 mg/L), the nitrifying ASP at site B showed more to be over three times more efficent in airflow and four times in energy required respectively, per kg NH_4^+ removed. The BNR plant showed overall low airflow and energy requirements, at 23 m^3 and 2.0 kWh per kg NH_4^+ removed. However, in BNR systems, the NO_3^- generated during nitrification is used as an electron acceptor for denitrification during oxidation of organic matter (Grady et al., 1999; Wang et al., 2011c), therefore requiring less aeration by comparison to conventional nitrifying ASPs.

Table 6.3: Carbon impact and process efficiency from a range of monitored processes

Process	Energy input (kWh/ year)	Energy costs (£/year)[a]	Energy emissions ($kgCO_2e$/ year)[b]	Process emissions ($kgCO_2e$/ year)	Total emissions N_2O + energy ($kgCO_2e$/ year)	CO_2e N_2O emissions (%)[c]	Airflow (m^3/ day)[e]	NH_4^+ removed (kgN/ day)	Process efficiency (airflow/ kg NH_4-N removed)	Process efficiency (energy /kg NH_4-N removed)
Site A										
ASP at DO 1.5 mg/L	430,561	30,139	234,225	34,143	268,368	13	15,550	52	298	23
ASP at DO 2.0 mg/L	2,704,446	189,311	1,471,220	175,101	1,646,320	11	52,939	53	1,001	140
Site B										
ASP at DO 1.5 mg/L	498,481	34,894	278,180	67,306	345,490	19	19,933	235	85	6
ASP at NH_4^+ control	627,508	43,926	341,365	134,110	475,475	28	28,167	353	80	5
BNR at NH_4^+ control	531,586	37,211	293,870	77,396	371,266	20	15,893	697	23	2

[a] *Cost based on £0.07 per kWh*

[b] *1.0 kWh = 0.544 CO_2 equivalents (UKWIR, 2008)*

[c] *N_2O emissions kg of carbon equivalent emissions added to operational carbon*

[d] *Relates to electricity input required to run blowers (kWh/day)*

[e] *Average recorded airflow delivered to the process (m^3/day)*

6.4. Discussion

6.4.1. Nitrous oxide emissions from different process settings

Research linking process control settings (DO and NH_4^+ set-points) and configuration (nitrifying ASP versus BNR) is usually carried out under controlled laboratory conditions, whereas at full-scale, is very limited, and mostly it has been carried out outside of the United Kingdom (GWRC, 2011). This study enabled the direct comparison of both operational settings and process configuration at two large-scale WWTPs, for the first time, comparing the effect of each change on process emissions under field conditions (e.g., variable influent load, non-optimal aeration equipment and control, etc).

The data analysis revealed that the control settings of NH_4^+ and DO set-points have a significant effect on DO, which in turn impacts on N_2O production and release (Table 6.1). Therefore, the stability, or lack thereof, in DO trend was largely dependent on the control settings. Whilst the aeration requirements in the BNR process are different from the nitrifying lanes, the stability in DO profiles achieved by each process is independent of how it meets its oxygen demand and therefore, comparable. The BNR lane revealed the most stable operational profile, which was in turn accompanied by the lowest variability in emissions. This is significant, as it suggests stability in DO rather than a simple DO threshold is key in minimising process emissions. In addition, these findings support that of previous research (Ahn et al., 2010a; b; Foley et al., 2010a), which suggests that processes that achieve complete (or near-complete) nitrification and denitrification are more likely to prevent transient accumulation of N_2O in the bulk liquid, which could potentially lead to more emissions being released (Chandran et al., 2011; Wang et al., 2011c).

The general consensus is that N_2O is not only predominantly emitted from aeration tanks, (Ahn et al., 2010a; Czepiel et al., 1995; GWRC, 2011; Ren et al., 2013), but is also produced therein (Foley et al., 2010a; Rassamee et al., 2011; Ren et al., 2013; Shi et al., 2011; Xiuhong et al., 2008). This therefore, makes nitrification both a source of N_2O production, particularly during NH_4^+ oxidation by AOB (Kim et al., 2010; Tallec et al., 2006; Wunderlin et al., 2012; Yu et al., 2010), as well as of N_2O emissions due to the effects of air-stripping. This was also confirmed by the current research findings, whereby dissolved and off-gas N_2O were measured in all the aeration zones, across the monitored nitrification tanks in site A (Aboobakar et al., 2013a; b) and site B (Fig. 6.6). However, the large peak in dissolved N_2O in the anoxic zone of the NH_4^+ controlled ASP lane, was comparably higher than that seen in the nitrifying zones of the same process, thus showing that N_2O production from non-aerated zones can also be significant. Indeed, this agrees with previous full-scale studies, which have shown that, although atmospheric release was very limited due to the absence of active aeration, anoxic zones were nevertheless found to be responsible for a considerable proportion of N_2O generated therein (Foley et al., 2010a; Ren et al., 2013). This has been linked to incomplete denitrification due to sub-optimal conditions, such as the presence of transient low DO (Tallec et al., 2008), low C/N ratios (Aboobakar et al., 2014a; Hanaki et al., 1992; Itokawa et al., 2001) and NO_2^- accumulation (Aboobakar et al., 2014a; Kampschreur et al., 2008a; Rassamee et al., 2011; Wunderlin et al., 2012), further reinforcing the need for complete nitrification and denitrification in order to limit N_2O formation and subsequent release.

6.4.2. Balancing carbon impact with process efficiency

Generally, the results showed that N_2O emissions from biological wastewater treatment can contribute significantly to the overall carbon footprint, although the range seen in this study, 11 to 28 %, is not as wide by comparison to a previous full-scale study from the Netherlands, in which N_2O emissions contributed between 2 to 88 % of the overall carbon footprint (Daelman et al., 2013; GWRC, 2011).

The indirect emissions associated with generation of electricity required to aerate the nitrifying lanes, contribute the most to the total operational carbon footprint of the processes. Indeed, in processes with relatively low nitrogen load, particularly when over-aerated, the energy contribution becomes more relevant. This is seen in the ASP lane at site A, where under DO set-point control of 2.0 mg/L, which despite having the largest N_2O footprint in all monitored lanes (175,101 $kgCO_2e$/year), translated nevertheless into the lowest contribution from process emissions (11 %) to the overall carbon footprint, because of the considerably higher contribution from energy-related emissions. By contrast, the footprint contribution from process emissions becomes more significant with relatively efficient energy contribution. This is the case with the nitrifying ASP under NH_4^+ control at site B, where the N_2O emissions showed the highest contribution (28 %) to the overall carbon footprint of the lane, despite having a lower footprint (134,110 $kgCO_2e$/year) than the above lane at site A.

By comparing the two control settings, regardless of process configuration, it seems that, under NH_4^+ control, N_2O emissions contributed more to the overall carbon footprint of the relevant lanes than those under DO control. However, when comparing the energy and airflow inputs to treat 1.0 kg of NH_4^+, it becomes clear that site B is more efficient than site A (Table 6.3); therefore, in this case, more efficiency also means greater contribution from N_2O emissions to the overall carbon footprint. This highlights concerns with efficient NH_4^+ removal, whereby there is an increased risk of displacing the pollution issue from the water into the atmosphere. Therefore, an acceptable balance needs to be achieved between carbon footprint and process efficiency. Comparing the monitored processes, this balance is found in the BNR lane, whereby the highest efficiency is accompanied by relatively low EFs (0.08–0.1 % across all nitrogen fractions, Table 6.2) and footprint contribution from N_2O, at 77,396 $kgCO_2e$/year. These findings show that the significant benefits of the BNR come from the stability seen in DO profile, as well as significantly more efficient NH_4^+ removal.

Furthermore, as explained above, the BNR configuration requires less aeration because of the anoxic removal of organic matter via NO_3^- generated from nitrification, therefore leading to reduction in energy consumption. A comparison between conventional nitrifying ASP and BNR plants reported a 30 % reduction in aeration costs in the nitrification-denitrification BNR (Rosso and Strenstrom, 2007). In the current study, the BNR showed a reduction in aeration costs of 15 and 80 % in comparison to the ASPs in NH_4^+ and DO-set point 2.0 mg/L controls respectively. However, it also represented an increase in cost of 19 and 6 % from the nitrifying ASPs in DO set-point control 1.5 mg/L in sites A and B respectively. Nevertheless, in terms of airflow requirements, the BNR was still 92 and 73 % more efficient than for these two lanes (sites A and B respectively) at removing NH_4^+. For all these reasons, it can therefore be concluded that the best balance between carbon footprint and process efficiency is the one provided by the BNR lane, where this balance is achieved by keeping sustained stability in operational conditions.

However, the use of BNR processes is dependent on influent characteristics, based primarily on the amount of readily biodegradable material required to maintain both denitrification and enhanced phosphorus removal. Estimated minimum ratios of biochemical oxygen demand (BOD) to total Kjeldahl nitrogen (TKN) of 3:1 (BOD:TKN) and of BOD to phosphorus (P) of 25:1 (BOD:P) are recommended (WEF, 2005), in order for reliable denitrification and enhanced phosphorus removal respectively, to be achieved. Furthermore, these are approximate ratios, and the actual ratios will depend on operating conditions and substrate biodegradability, which in turn will affect nutrient removal capabilities (WEF, 2005). As such, whilst BNR was the best option in this study, it would only be feasible under those conditions and therefore, with a limited application across the industry. The second best option was the ASP at the same site B (Tables 6.2 and 6.3), operated at DO set-point control of 1.5 mg/L, which showed to have the lowest overall carbon footprint in site B (345,490 $kgCO_2e$/year), as well as the lowest emissions at 0.59 kgN/day (only second to the emissions under the same set-point at site A, at 0.09 kgN/day). However, this process had a less stable range of EFs when compared to the BNR (0.07–0.2 % across all nitrogen fractions) and was not as efficient (Table 6.3). It was nevertheless, still more efficient than the DO-controlled ASP lane at site A, under both set-points, and similar to the efficiency levels within the same process under NH_4^+ control. Furthermore, it produced less than half of the N_2O emissions seen in the ASP (0.59 kgN/day) than when operated under NH_4^+ control (1.19 kgN/day). These reasons therefore, make it a second option to the BNR lane, and better when compared to the other ASP options.

Finally, the analysis of the robustness and appropriateness of the ancillary equipment itself is also critical. Although more powerful than in the ASP at site B, the blowers in the BNR were more efficient and the plant required one blower on duty, instead of two as the ASP, which proved to be a more costly option under NH_4^+ controlled settings. The energy consumption – as well as performance – of the process is clearly dependent on blower efficiency and effective aeration control. The more efficient blowers will lead to reduction in carbon footprint because of a better airflow supply, which in turn, has a positive effect on the DO availability in terms of less fluctuations and adequate oxygen supply. Additionally, different aeration systems may also promote or minimise N_2O emissions from activated sludge processes. For example, the tapered distribution of the diffusers in the nitrifying lane may have a potentially negative contribution to the fluctuations in airflow and DO, since with tapered aeration, the diffusers arrangement differs between the front and back end of the aeration tank: at the front end (influent of aeration tank), the diffusers are arranged closely together because of the higher oxygen demand, whereas at the back end (effluent of the aeration tank), they are more spaciously distributed due to a lower oxygen demand. This may contribute to variability in DO and aeration and controlling that variability is key in mitigating N_2O production and emission.

Another type of method includes mechanical surface aerators, where oxygen is transferred to the bulk liquid by air-water contact in the atmosphere rather than through bubbling such as in the processes monitored in this study; through surface aeration therefore, more turbulence and a high oxygen transfer rate (k_La) are provided to the process (Ye et al., 2014), and, if dissolved N_2O is present, these conditions could facilitate the transfer to off-gas N_2O, therefore contributing to higher emissions (Ye et al., 2014).

In some aeration methods on the other hand, diffusers at the bottom of aeration tanks are combined with submerged mechanical paddles, whereby the paddles rotate in the opposite direction to the compressed diffused air. As the air rises up from the diffusers, the paddles shears the coarse bubbles whist also providing mixing. This combined system, potentially offers more efficiently distributed aeration, with less compressed air required in comparison to diffused aeration. These conditions in turn, may lead to less fluctuations in aeration and DO availability, therefore minimising N_2O production and emission.

Furthermore, the obtained data allows for a comparison of the relevance in using different nitrogen fractions to obtain a particular EF. For example, it can be argued that EFs based on influent data say very little about how effective the process is at removing nitrogen. By contrast, the EFs based on NH_4^+ removal (Table 6.2), highlight how much of that NH_4^+ is converted to N_2O, which is not visible when looking at the influent-based factors. Indeed, the highest EFs in this study come from those based on NH_4^+ removed. So it seems that factors based on influent load offer a “best case scenario”, as does the estimated UKWIR emission factor, obtained from the influent TN (UKWIR, 2009). Therefore, for the nitrifying processes in particular, an EF based on removed NH_4^+ may be more appropriate, although not so relevant for the BNR, judging by the little variability seen in the EFs for this process across all nitrogen fractions. Furthermore, there is evidence to show that greater nitrogen (rather than just NH_4^+) removal could result in lower emissions in WWTPs (Chandran et al., 2011; Foley et al., 2010a), and in this case, EFs which account for total removed nitrogen may be able to capture this better. These differences will become more relevant in a future where the reporting of process emissions is enforced by regulations.

The results in this study clearly show that a generic EF, based on estimations, is very limited, as it fails to take into account the influence played by operational variables and control settings in triggering, or controlling, N_2O production and emissions.

Instead, a range of quantifiable EFs which consider the operational impact, is more appropriate to classify WWTPs (Foley et al., 2010a), since it would help to distinguish between low and high risk of N_2O being generated and emitted.

It follows therefore, that there is value in measuring EFs across different nitrogen fractions, since it can show how stable – or not – a process may be. It also provides a good indication of the expected range of N_2O emissions in processes with the same control settings. However, this type of generalisation can only be made by using an inventory of quantifiable emissions, obtained from a comprehensive online monitoring of both N_2O and operating conditions, as in the approach adopted by this study. To our knowledge, the link between operating conditions, control settings and EFs had never shown in such detail before.

It should be noted however, that even though N_2O may have a significant impact on the total carbon footprint, any operational changes to mitigate for those emissions will result in expenditures for WWTPs. Furthermore, there is currently a lack of economical benefits and regulatory incentives to encourage such changes (Pijuan et al., 2014), although opportunities to mitigate emissions whilst improving biological wastewater treatment have been identified (Chandran et al., 2011; Corominas et al., 2010; 2012; Desloover et al., 2011; Ni et al., 2013; Flores-Alsina et al., 2011; Shahabadi et al., 2009; 2010; Wang et al., 2011c). Indeed, N_2O emissions credit has been recently proposed as an incentive to reward WWTPs which adopt an integrated approach of improved nitrogen removal and minimisation of N_2O emissions (Wang et al., 2011). This however, would require a thorough account of how emissions evolve in full-scale environments. As such, the comprehensive online methodology of this study, can provide a robust framework to quantifying process emissions and influencing operational factors.

6.5. Conclusion

The objective of this study was to quantify and characterise N_2O emissions across different full-scale processes, as well as investigating how those emissions are affected by changes in operational variables. It also aimed at identifying the best compromise between low process emissions, reduction in carbon footprint and efficiency in nitrogen removal. The main findings were:

- Stability in DO profiles within and across WWTPs resulted in lower N_2O production and emissions, irrespective of process configuration.

- Measuring EFs across all nitrogen fractions is a valuable approach, which can capture not only magnitude but also variability in N_2O emissions.

- Processes operated under the same control setting (DO set-point 1.5 mg/L in sites A and B), but under different loading rates were found to have similar, or identical, EF, suggesting that process control is more important that loading rates.

- The more efficient the carbon footprint associated with energy consumption, the larger the contribution from process emissions to the overall footprint.

- The BNR lane offered the best balance between carbon footprint and process efficiency, followed by the nitrifying ASP lane in the same site operated at DO set-point control of 1.5 mg/L.

- A comprehensive online methodology, such as adopted in this study, can provide a robust framework to quantifying process emissions and influencing operational factors.

CHAPTER 7

THESIS DISCUSSION

7. THESIS DISCUSSION

There is an increasing need to reduce greenhouse gas (GHG) emissions and to identify influencing factors (Kampschreur et al., 2009a) from wastewater treatment plants (WWTPs), particularly process emissions consisting of nitrous oxide (N_2O), and methane (CH_4) GHG, with global warming potentials (GWP) about 310 and 21 times higher than carbon dioxide (CO_2) respectively (IPCC, 2006). However, the challenges offered by a full-scale environment have, to date, restricted a real-time, comprehensive approach of monitoring emissions and influencing factors. As a result, the link between operational parameters and emissions, although believed to be a critical one, particularly where N_2O emissions versus dissolved oxygen (DO) variability are concerned, is only partially understood. This study addresses this knowledge gap, by reporting the findings of a long-term, online, continuous monitoring of GHG emissions and operational variables. A number of activated sludge systems operated at different control settings were measured, ranging from nitrifying activated sludge (ASP) lanes controlled under ammonia (NH_4^+) and DO (1.5 and 2.0 mg/L) set-points, as well as a biological nutrient removal (BNR) lane under NH_4^+ control. Through employing this robust methodology, a quantifiable inventory of emissions was obtained, as well as insights into the effect of operational changes on GHG emissions at full-scale. Finally, the operational conditions to achieve the appropriate balance between lower process emissions and carbon footprint as well as improved process efficiency, were recommended.

7.1. Profiling GHG emissions at full-scale

Currently, there is a lack of legislative and economical incentives to drive reporting and compliance of process emissions and quantification standards (Listowski et al., 2011; Pijuan et al., 2014). Therefore, measuring GHG emissions from WWTPs has relied on a variety of methods, from grab to online sampling, and short to long-term monitoring. The diversity in methodologies has been suggested as a contributing factor to the large variability in reported emissions (Law et al., 2012). Furthermore, comparison of the impact of different emission sampling strategies (Daelman et al., 2013), found that unlike long-term online monitoring, short-term grab sampling failed to capture the trend in diurnal and seasonal variations. The monitoring in this study consisted of a long-term (28 months) online approach, measuring diurnal and spatial (six to eight zones per monitored lane) off-gases (N_2O, CH_4 and CO_2) and dissolved N_2O within the same, as well as in different, activated sludge systems (sites A and B), consisting of two nitrifying ASP lanes (monitored under DO set-point controls of 1.5 and 2.0 mg/L as well as NH_4^+ set-point control) and a BNR lane (controlled under NH_4^+ set-point) designed to achieve enhanced phosphorus removal. For example, for off-gas N_2O in one lane, concentrations were captured every minute, resulting in 1,440 sampling periods over 24 hours, or 60 per minute. This is considerably higher than previous simulations for 24-hour online campaigns, which estimated 237 sampling periods over the course of one day, around 10 per hour (Daelman et al., 2013). When covering the spatial monitoring of an entire nitrifying lane (for example: six to eight zones, one week per zone), a large dataset for off-gas N_2O alone has been generated, which had not been carried out at this scale before. Analysis of variance showed that the variability in emissions was significantly affected ($p < 0.05$) by differences in operational settings and configurations (Aboobakar et al., 2014b), therefore making emission factors site and process specific (Kampschreur et al., 2009a).

Furthermore, measured CH_4 emissions in a nitrifying ASP also revealed considerable variability. The CH_4 factors were found to range from 0.04–0.1 % of influent soluble chemical oxygen demand (COD), at 0.07 % average, and 0.04–11 % of removed COD (Aboobakar et al., 2013b). This is comparable to a previously reported full-scale value of 0.08 % of influent COD (Wang et al., 2011a), but lower than other studies: 0.34 % (Czepiel et al., 1993) and 1.13 % (Daelman et al., 2012) probably due to the inclusion of an anaerobic digestion facility. Furthermore, in the United Kingdom, the Environment Agency (EA) has estimated an average of 0.0004 $kgCH_4$/day per cubic metre (m^3) of treated wastewater (George et al., 2009), which includes emissions from primary sedimentation. In the current study, for the nitrifying lane only, it was found to be 0.0003 $kgCH_4$/day per m^3 of treated wastewater. Unlike for N_2O, dissolved CH_4 in the nitrifying lane was not measured. However, online simultaneous measuring of off-gas N_2O, CH_4 and CO_2, showed a similar profile for all three GHG and for airflow rates: as airflow increased, so did GHG emissions, which was seen in diurnal as well as in spatial variability trends. Therefore, in aeration zones where average airflow rates were higher (133–139 m^3/h in the first and 88–95 m^3/h in the last aeration passes respectively), the same was observed for average CH_4 emissions (20–24 and 8.8–9.3 gCH_4/h for first and last aeration passes respectively), which dropped in the middle aeration pass (3.8–5.7 gCH_4/h), where equally, there was a drop in airflow rates (27–43 m^3/h). According to these observations, it was suggested that emissions increased with airflow due to the effects of air-stripping, whereby dissolved CH_4 present in the bulk liquid would therefore be stripped as off-gas emissions (Aboobakar et al., 2013b). Therefore, because of the aerobic conditions, as well as low biodegradable organic fraction, competition for carbon uptake (Andalib et al., 2011), and the presence of nitrogen oxides (Banihani et al.,2009; Klüber and Conrad, 1998), all of which prevail in the nitrifying lane and have been found to inhibit CH_4 production, it seems that CH_4 emitted from the nitrifying lane was most likely generated elsewhere. Nevertheless, once in contact with the aerated environment, CH_4 was released into the atmosphere, which makes aerated tanks an emission hotspot. Therefore, the likely locations where CH_4 is formed, i.e., non-aerated zones, are not necessarily the ones where it is emitted, i.e., aerated tanks, shown in the current research (Aboobakar et al., 2013b) by the release of 667 $kgCH_4C$/year from a nitrifying ASP lane.

Furthermore, the findings (Aboobakar et al., 2013a; 2014a; b) also showed variability in the N_2O emission factors (EF), ranging from 0.05 to 0.58 % of the total nitrogen (TN) load. This falls within previously reported full-scale values of zero up to 25 % of TN load (Ahn et al., 2010; Benckiser et al., 1996; Czepiel et al., 1995; Desloover et al., 2011; Joss et al., 2009; Kampschreur et al., 2008; Kimochi et al., 1998; Sümer et al., 1995). Additionally, N_2O EFs were found to be dependent on the nitrogen fraction, i.e., amount of N_2O emitted relative to influent or removed (TN or NH_4^+) nitrogen. By linking EFs with operating conditions across all monitored processes, it was shown that the process with most fluctuating DO trend also shower wider, and higher, EFs across the nitrogen fractions: the ASP in site A under set-point control of 2.0 mg/L, whereby EFs consisted of 0.58 to 0.72 % (of TN and NH_4^+ load respectively) and 1.59 up to 3.9 % (of TN and NH_4^+ removed respectively). By comparison, the EFs for the same process under the set-point of 1.5 mg/L, ranged from 0.05 % (of TN and NH_4^+ loads) to 0.13 and 0.2 % (of TN and NH_4^+ removed respectively). Additionally, the BNR lane, achieved a better consistency across all EFs (ranging between 0.08–0.1 % of TN and NH_4^+ load respectively, to 0.09–0.1 % of TN and NH_4^+ removed respectively). The findings also showed that two ASP lanes operated under the same setting at different sites (DO set-point control of 1.5 mg/L at sites A and B), showed similar EFs (0.05 and 0.07–0.08 % of TN and NH_4^+ load, 0.13 and 0.12 % of TN removed, for sites A and B respectively) and even the same EF (0.2 % of NH_4^+ removed for both sites). Furthermore, the obtained data allowed an assessment of the relevance of using different nitrogen fractions to obtain a particular EF. For example, it can be argued that factors based on influent data say very little about how effective the process is at removing nitrogen. By contrast, those based on NH_4^+ removal highlight how much of that NH_4^+ was converted to N_2O during wastewater treatment, which was not visible when looking at the influent-based EF. Indeed, the highest EFs in this study came from those based on NH_4^+ removed (ranging from 0.1–3.9 % across all processes). So it seems that factors based on influent load offered a best-case scenario (ranging from 0.05–0.08 % across all processes), as does the UKWIR emission factor, estimated at 0.2 % (UWKIR, 2009) and the IPCC emission factor, estimated at 0.035% (IPPC, 2006), both based on the influent TN.

Therefore, the observed variability in N_2O emissions cannot be defined by a "one-size-fits-all" estimated EF, especially a low value with large uncertainty, which seems to be the case with the existing guidelines, with the UKWIR's EF carrying a large uncertainty of 30–300 % (UKWIR, 2009) and the IPCC's of 0.05–25 % (IPCC, 2006). Indeed, care must also be taken when choosing the right nitrogen fraction so that process EFs are adequately represented. Based on the current findings, for the ASP processes, an EF based on removed NH_4^+ may therefore be more appropriate, although not so relevant for the BNR, judging by how little variability there was in the EFs for this lane across all nitrogen fractions. Furthermore, there is evidence to show that greater nitrogen (rather than just NH_4^+) removal could result in lower emissions in WWTPs (Chandran et al., 2011; Foley et al., 2010a), and in this case, EFs which account for total removed nitrogen (found in this study to range from 0.09–1.59 % across all measured processes) may be able to capture this better. These differences will become more relevant in a future where the reporting of process emissions is enforced by regulations. Nevertheless, the results in this study clearly show that a single generic EF, based on estimations, is inappropriate, as it carries a magnitude of uncertainty and fails to take into account the influence played by operational variables. Instead, a range of quantifiable EFs which consider the operational impact, the specific processes (ASP versus BNR) and respective nitrogen removal targets (NH_4^+ for ASPs and TN for BNRs for example), is more appropriate to classify WWTPs, since it would help to distinguish between low and high risk of N_2O being emitted (Foley et al., 2010a). It follows therefore, that there is value in measuring EFs across different nitrogen fractions, since it showed how stable (in the case of the BNR lane) – or not (in the case of the ASP operated at DO set-point control of 2.0 mg/L) – a process may be. It also provided a good indication of the expected range of N_2O emissions in processes with the same control settings (shown by the similar emission factors in the ASP lanes at sites A and B operated under the same DO set-point control of 1.5 mg/L).

However, this type of generalisation can only be made by using an inventory of quantifiable emissions, obtained from a comprehensive online monitoring of both GHG and operating conditions, as the approach adopted by this research.

7.2. The effect of operational variables on N_2O

Nitrous oxide production has been shown to occur in nitrifying lanes, with reported EFs ranging from 0.1–0.4 % (Tallec et al., 2006), to 0.2–3.9 % (Aboobakar et al., 2014a; b) of removed NH_4^+, despite not being a direct intermediate in the nitrification pathways. This production has been linked with low DO conditions, with the highest emissions recorded at DO concentrations below 1.0 mg/L, both from findings at full-scale (Aboobakar et al., 2013a), and laboratory-scale (Aboobakar et al., 2014a; Tallec et la., 2006).

Indeed, laboratory experiments (Aboobakar et al., 2013a), where nitrification tests were carried out under low DO conditions (~0.5 mg/L), saw an increase in dissolved N_2O concentrations (up to 0.28 mgN/L), as NO_2^- began to accumulate (from zero up to 0.11 mgN/L). This agrees with the hypothesis that low DO conditions may trigger a biological stress response in AOB (Kampschreur et al., 2008a), in which accumulated NO_2^- is reduced to N_2O, through a nitrifier denitrification pathway (Colliver and Stephenson, 2000; Tallec et al., 2006). Furthermore, the findings in this study have shown that even at optimised DO conditions (~6.0 mg/L), a sudden drop in DO (to ~4.5 mg/L) triggered a peak in NO_2^- (up to 0.11 mgN/L), followed by a peak in dissolved N_2O (up to 0.03 mgN/L) concentrations. What this suggests is that, sudden changes in DO conditions, i.e. a dynamic profile, rather than just low concentrations, may also trigger a transient response in AOB to produce N_2O through nitrifier denitrification, which had also been reported by previous research (Burgess et al., 2002a; Kampschreur et al., 2008a; 2009; Tallec et al., 2006; Vanrolleghem et al., 2004).

However, the current study has gone further, by also confirming these findings at full-scale (Aboobakar et al., 2013a; 2014a): N_2O emissions in a nitrifying lane at a DO set-point control of 2.0 mg/L, were unexpectedly higher (1.55 kgN_2O-N/day) than at a lower set-point of 1.5 mg/L (0.09 kgN_2O-N/day); despite the fewer occasions during the higher set-point when DO concentrations dropped below 1.0 mg/L, which has been suggested as a threshold for increased emissions (Aboobakar et al., 2013a; Cébron et al., 2005; Goreau et al., 1980; Tallec et al., 2006). However, the DO conditions at DO set-point 2.0 mg/L fluctuated more (0.3–4.5 mg/L) than at set-point 1.5 mg/L (0.16–2.0 mg/L), implying that the increase seen in DO variability was strongly related to an increase in N_2O production. Therefore, the findings here (both at laboratory and full-scale), show that although N_2O is indeed produced under low DO conditions, fluctuating conditions can trigger increased N_2O production, even at higher DO concentrations. Furthermore, in the lab-scale tests, the falls in DO followed by peaks in NO_2^- and N_2O, were always observed upon addition of NH_4^+ (0.5–20 mg/L), which agrees with the findings by Kim et al. (2010) and Rassamee et al., (2011), whereby it was suggested that N_2O production is linked with NH_4^+ oxidation.

Release of N_2O to the gas phase during nitrification however, is mostly attributed to air-stripping. Indeed, off-gas emissions are part of a physical process dictated by the liquid-gas mass transfer from turbulence in wastewater, caused by active or passive aeration and mixing (Law et al., 2012; Ren et al., 2013). In that sense, emissions are not synonymous with N_2O biosynthesis, which is instead governed by biochemical pathways. However, the interaction between the two was seen in the ASP lane controlled under the two DO set-points of 1.5 and 2.0 mg/L, through aeration stress events (Aboobakar et al., 2014a), during which air supply to the nitrifying lane was interrupted for a period of time (ranging from 15 minutes up to three-hour periods, Fig. 5.4). During these events, off-gas N_2O dropped dramatically (to nearly zero), whereas dissolved N_2O began to accumulate in the bulk liquid (from 0.002 up to 0.09 mgN/L), within less than 10 minutes after aeration had stopped. Furthermore, DO depleted very quickly during these periods (<0.2 mg/L). With aeration restored, dissolved N_2O dropped to zero, but off-gas N_2O increased immediately (up to 0.05 mg/L), at concentrations higher than prior to interrupted aeration periods. A similar interaction between N_2O off-gas emissions and production was seen during normal operation, in the NH_4^+ controlled ASP: the dramatic reduction in aeration from zone 4 (average airflow: 728 m^3/day) to zone 5 (average airflow: 31 m^3/day), triggered by the NH_4^+ control set-up (Fig. 6.4B), resulted in a dip in DO from 2.0 mg/L (zone 4) to 1.1 mg/L (zone 5), which meant that the DO concentration in zone 5 was below the average (1.8 mg/L) and indeed the lowest seen in the ASP lane (Fig. 6.5B). The lower airflow rates in this zone, albeit resulting in lower off-gas emissions (0.0001 kgN_2O/day per $kgNH_4$/day, Fig. 6.6B), led nevertheless to a peak in dissolved N_2O (increasing from 0.27 to 1.97 kgN_2O/day per $kgNH_4$/day, from zones 4 to 5 respectively, Fig. 6.6A), because of the transient changes in DO conditions from zones 4 to 5 (Fig. 6.5B). This generated N_2O was eventually air-stripped in zone 6 (off-gas N_2O in this zone: 0.02 kgN_2O-N/day per $kgNH_4$/day, Fig. 6.6B), where there was an increase in aeration (average airflow: 2,255 m^3/day, Fig. 6.4B), therefore impacting on the overall N_2O emissions within that lane (Fig. 6.6). From these observations three conclusions can be drawn: firstly, that N_2O produced in the bulk liquid is triggered by the sudden changes in DO, particularly by a drop or depletion in concentrations; this in turn, is brought about by changes in airflow supply, leading to low aeration or failure. Secondly, produced N_2O is mostly air-stripped due to increased aeration, therefore releasing the accumulated dissolved N_2O into the atmosphere. Similarly, Foley et al. (2010) and Ren et al. (2013) reported a low emission flux from processing units with high concentrations of dissolved N_2O, such as in anoxic compartments, primary settling and sludge tanks, as these were shown to have limited wastewater turbulence and mechanical agitation; in aeration tanks however, N_2O in the off-gas was air-stripped, therefore increasing emissions from therein.

Furthermore, excessive aeration was seen to contribute to high and fluctuating DO, as well as to off-gas N_2O emissions. Indeed, at the DO set-point 2.0 mg/L, the average airflow (3,340–11,870 m^3/day) represented an increase of 340 %, from the average airflow in the same lane, at DO set-point of 1.5 mg/L (770–3,330 m^3/day). This in turn led to higher variability in off-gas N_2O emissions at 2.0 mg/L DO set-point (0.02–0.27 kgN_2O-N/day), compared to the lower DO set-point (0.01–0.06 kgN_2O-N/day). Moreover, excessively aerated nitrifying lanes, particularly in the transition between aerated and non-aerated compartments, could introduce oxygen to denitrification zones, leading to incomplete denitrification due to the metabolic effects of DO on both synthesis and activity of denitrifying enzymes (Kampschreur et al., 2009a), resulting in the accumulation of N_2O (Kampschreur et al., 2009a; Otte et al., 1996). The findings from this study therefore suggest that controlled aeration may also control off-gas N_2O emissions, and, if achieved through a consistent airflow, which can both reduce fluctuations without limiting DO availability, it may also minimise transient N_2O production.

The effect of dynamic conditions on N_2O is further extended to NH_4^+, of which high concentrations, reported from 90–350 mg/L (Kim et al., 2010), 50–500 mg/L (Law et al., 2012), 15–49 mg/L (Tallec et al., 2006) to 25 mg/L (Wunderlin et al., 2012), are a determining factor in N_2O production from nitrification and denitrification (Kampschreur et al., 2008a; Kim et al., 2010). Indeed, as observed in the nitrification lab-scale tests (Aboobakar et al., 2014a), sudden addition of NH_4^+ triggered significant peaks in dissolved N_2O, accompanied by a drop in DO and nitrite (NO_2^-) accumulation, which has also been previously reported (Burgess et al., 2002a; Kampschreur et al., 2008a; Kim et al., 2010; Wunderlin et al., 2012). Additionally, intermediates of NH_4^+ oxidation, such as hydroxylamine (NH_2OH), are also known to trigger N_2O production pathway (Wunderlin et al., 2012). However, it should be noted that relatively high concentrations of NH_2OH, around 10 mg/L, are needed to drive that N_2O production (Wunderlin et al., 2012). This is unlikely to occur in full-scale activated sludge systems, because the oxidation of NH_2OH is the energy-generating step during NH_4^+ oxidation by AOB, thus making accumulation of this intermediate biochemically unfavourable (Casciotti et al., 2001; Wunderlin et al., 2012).

Finally, this research has shown that N_2O production is inherently linked to NH_4^+ oxidation, not only at high (20 mg/L) but also at very low NH_4^+ concentrations, <0.1–5.0 mg/L (Aboobakar et al., 2014a). This is more relevant however, during peak loads, when sudden changes in NH_4^+ concentrations, lead to an increase in oxygen demand, therefore triggering a drop in DO availability. During these events, a strong positive correlation ($r^2 = 0.82$) was seen between NH_4^+ loading and N_2O emissions (Aboobakar et al., 2013a), whereas at the same time, there was a strong negative correlation between NH_4^+ load and DO ($r^2 = 0.77$). Additionally, these low DO periods (<1.0 mg/L) produced the highest N_2O emissions (3.5 gN_2O-N/h). Therefore, these observations agree with the assumption that N_2O emissions are more likely to occur during higher nitrification rates (Kampschreur et al., 2008b; Kim et al., 2010), as a biological stress response, due to competition for available oxygen in the water, triggered by the sudden increase in NH_4^+ concentrations.

The lab-scale study was set up to mimic the final stages (last aeration pass of the lane), of a full-scale nitrifying ASP lane operated at DO set-point control; where, as expected, NH_4^+ concentrations (discharge averages at 1.0–1.1 mg/L) and C/N ratios (averages 2.4–2.8) were typically low, since at this stage, nitrification has mostly taken place (15–16 mg/L average nitrate (NO_3^-) and there is low organic carbon availability (soluble COD average 18.5 mg/L). However, N_2O was still produced (ranging from 0.0001–0.001 and 0.05–0.17 kgN_2O-N per load, for set-points 1.5 and 2.0 mg/L respectively) and emitted (0.02–0.03 and 0.02–0.09 kgN_2O-N per load for 1.5 and 2.0 mg/L respectively), in that final aeration pass, with measured DO ranging from 0.3–1.8 (set-point 1.5 mg/L) and 1.8–2.5 mg/L (set-point 2.0 mg/L). Denitrification batch tests with intermittent aeration (Aboobakar et al., 2014a), showed that, under the low C/N ratios of 2.4 and 2.8, N_2O was produced (up to 0.03 and 0.02 mg for C/N 2.4 and 2.8 respectively) concurrently to NO_2^- accumulation (3.9 and 3.2 mg for 2.4 and 2.8 C/N ratios respectively), and mostly as conditions became anoxic (once aeration stopped and DO depleted). By comparison, under optimal C/N ratio of 4.5, with conditions kept consistently anoxic (DO <0.5 mg/L), NO_3^- was fully reduced, with no accumulation of NO_2^- or N_2O. However, the introduction of intermittent aeration to the batch tests under optimal C/N of 4.5, also led to some NO_2^- accumulation (0.6 mg) as well as N_2O production (0.007 mg).

Furthermore, comparison between denitrification (low C/N ratios) and nitrification (low NH_4^+ concentrations of 0.5–5.0 mg/L) batch tests, using the same nitrifying sludge, showed that more N_2O was produced under denitrifying (0.003–0.004 mgN/gVss /h) than nitrifying (0.001–0.003 mgN/gVss /h) conditions, irrespective of whether nitrification was carried under low (~0.5 mg/L) or optimised (>6.0 mg/L) DO conditions. Indeed, when converted to emission factors (N_2O produced based on percentage of removed nitrogen), low NH_4^+ nitrification tests resulted in a range of 0.1–0.25 %, by contrast to the low C/N denitrification tests, where N_2O emission factors were determined as 2.4 and 4.1 % (for C/N ratios of 2.8 and 2.4 respectively).

Therefore, based on the lab and full-scale findings, the link between denitrification and N_2O emissions in the final stages of nitrification, can be explained as follows: firstly, that incomplete heterotrophic denitrification is taking place in the final stages of a nitrifying lane; secondly, N_2O production from incomplete denitrification may be significant, most likely due to sub-optimal conditions such as low C/N ratios and transient low DO periods, which have also been observed by other studies (Tallec et al., 2008; Wunderlin et al.,2012), and in the full-scale nitrifying ASP (Aboobakar et al., 2013a; 2014a); thirdly, the lower the C/N ratio, the more NO_2^- accumulates and consequently, the more N_2O is produced under anoxic conditions. Indeed, accumulation of NO_2^- during denitrification has been linked to high N_2O production by previous research, both due to DO presence (Kampschreur et al., 2009a) and C/N ratios below 3.5, which were found to trigger high N_2O emission, ranging from 10–64 % of nitrogen load (Hanaki et al., 1992; Itokawa et al., 2001; Schalk-Otte et al., 2000). The emission factors for denitrification seen in the current study fall below this range, although they agree with the theory that low C/N ratios (<3.5) will indeed increase heterotrophic N_2O production and that this is dependent upon NO_2^- accumulation and DO presence. As a result, transient low DO conditions in the final aeration pass of the full-scale nitrifying lane (shown by the lower average of the measured DO at 0.3 mg/L), combined with the low C/N ratios, further promoted incomplete heterotrophic denitrification, thus contributing to the emissions rates therein (found to be 0.25 % and 1.38 % of NH_4^+ removed in the final aeration pass for set-points 1.5 and 2.0 mg/L respectively).

Therefore, production and release of N_2O was determined to be largely affected by dynamic fluctuations in physio-chemical operational parameters, implying that process emissions can be mitigated by minimising operational variability and promoting complete nitrification and denitrification. Some of these measures are discussed in the next section.

7.3. Minimising N_2O emissions

Stability, rather than a threshold in DO, is key to minimising process emissions. This was shown by the current findings (Aboobakar et al, 2014b), whereby an analysis of variance showed the BNR lane to have a more stable ($p<0.05$) DO profile than the ASP lanes. This stability was seen specifically in the more narrow range of measured DO concentrations (0.4–1.5 mg/L, $\pm$0.4), compared to the next most stable DO profile, from the ASP lane at site A, controlled at DO set-point 1.5 mg/L (0.16–2.0 mg/L, $\pm$0.8). Not surprisingly, EFs in the BNR were also the most stable of all measured processes, shown to change very little across all nitrogen fractions (0.08–0.1 %), when compared to the ASP lanes (0.05–3.9 % across all nitrogen fractions). The BNR also operated at a stable airflow rate (883–4,646 m^3/day), compared to the more vigorous and wider airflow rates seen in the ASP lanes operated at DO set-point control 2.0 mg/L (3,340–11,870 m^3/day) and under NH_4^+ control (31–9,536 m^3/day).

It should be noted however, that in BNR plants, the NO_3^- generated during nitrification is used as an electron acceptor for denitrification during oxidation of organic matter (Grady et al., 1999; Wang et al., 2011c); therefore, less aeration and oxygen are needed by comparison to conventional nitrifying ASPs. As such, DO and airflow requirements in the two types of configurations are not comparable. Nevertheless, the stability achieved by each process configuration is additional to the differences in DO and airflow requirements and, therefore, provides valid grounds for the above comparisons.

Furthermore, because BNR plants require less aeration, and therefore less energy, the carbon footprint associated with energy could potentially be reduced by more widespread adoption of BNR (Rosso and Stenstrom, 2007; Wang et al., 2011c). In a previous study, a comparison between conventional nitrifying ASP and BNR plants reported a 30 % reduction in aeration costs in a nitrification-denitrification BNR (Rosso and Stenstrom, 2007). In the current study, the BNR showed a reduction in aeration costs of 15 and 80 % in comparison to the ASPs in NH_4^+ and DO-set point 2.0 mg/L controls respectively. However, it also represented an increase in cost of 19 and 6 % from the nitrifying ASPs at DO set-point control 1.5 mg/L in sites A and B respectively. Nevertheless, the BNR was still 92 and 73 % more efficient than these two lanes at removing NH_4^+. This translated as 23 m^3 and 2.0 kWh of airflow and energy inputs respectively, per kg NH_4^+ treated. By comparison, the second most efficient lane, the ASP in the same site, under NH_4^+ and DO control settings, required 80 and 85 m^3 in airflow as well as 5.0 and 6.0 kWh of energy respectively, to treat 1.0 kg of NH_4^+. Reduction in aeration and energy consumption therefore, had a positive impact on process efficiency, because significantly less airflow and energy was needed for NH_4^+ removal in the BNR when compared with the ASP lanes, making the BNR 60–73 and 92–99 % more efficient than the ASPs in the same site (site B) and at site A, respectively.

There are also other energy-saving advantages: for example, retrofitting nitrifying ASPs to comply with tighter nitrogen and phosphorus removal consents has become common practice in many WWTPs. In many cases, this means that anaerobic zones are added to the ASPs which replace part of the volume of the nitrifying lanes, therefore reducing aeration – and hence energy – requirements (Wang et al., 2011c). Such upgrades are usually done without affecting the nitrification process, since most plants are designed to over-treat NH_4^+ (Rosso and Stenstrom, 2007; Wang et al., 2011c). Indeed, this was the case with the monitored BNR, which was upgraded from an ASP, to comply with phosphorus removal consent of 1.0 mg/L or 80 % removal (Pitt et al., 2008).

At the same time, care must be taken to avoid airflow fluctuations: aeration must not be so low that it compromises oxygen availability leading to N_2O production, such as the average airflow rate of 31 m^3/day seen in zone 5 of the ASP lane under NH_4^+ control, which represented a drop in aeration of 96 % from preceding zone 4, leading to low DO and increased N_2O production (detailed in section 7.2 above). Or, it must not be so intensive, that it triggers release from dissolved to gaseous phase, which was again seen in the same process, in the following zone 6, where the average airflow of 2,255 m^3/day represented an almost 99 % increase in airflow, thereby leading to higher N_2O emissions. By comparison, in the same zone 5 operated under DO set-point of 1.5 mg/L, the airflow rate was an average of 1,672 m^3/day, with airflow dropping only by 34 % from the previous zone 4. This in turn had a positive effect on the DO, which was higher (2.0 mg/L) in this zone than when operated under NH_4^+ control (1.1 mg/L). More importantly, less N_2O was produced therein, as shown by the very low dissolved N_2O average (0.0004 compared to the 1.96 kgN_2O/day per load seen for the same zone under NH_4^+ control). Consequently, less N_2O was air-stripped in the following zone 6 (0.01 compared to 0.02 kgN_2O/day per load observed for the same zone under NH_4^+ control). Therefore, sufficiently stable, rather than intensive aeration can reduce N_2O production and emissions in ASPs. At the same time, it can offer considerable offsets in carbon emissions from energy consumption by avoiding over-aeration, as clearly exemplified by the process in site A controlled under two different DO set-points: at set-point 2.0 mg/L, the operational carbon emissions associated with electric energy consumption for aeration corresponded to 1,471,220 tonnes of CO_2e/year, whereas at set-point 1.5 mg/L, that dropped to 234 tonnes of CO_2e/year, therefore representing an offset of 84 % in operational carbon footprint.

It should be noted however, that any operational changes to mitigate for N_2O emissions will result in expenditures for WWTPs. Currently, there is a lack of economical and regulatory incentives to encourage such changes (Pijuan et al., 2014), although opportunities to mitigate emissions whilst improving biological wastewater treatment have been identified (Chandran et al., 2013; Corominas et al., 2010; 2012; Desloover et al., 2011; Ni et al., 2011; Flores-Alsina et al., 2011; Shahabadi et al., 2009; 2010; Wang et al., 2011c).

7.4. Research impact: implementing changes

As evidenced by the findings reported in the previous sections, sudden process disturbances in DO and aeration should be avoided, since controlling variability is key to mitigate N_2O production and emissions (Ahn et al., 2010a; b; Chandran et al., 2011; Kampschreur et al., 2008a). From a practical operational perspective, this means applying time-dependent methods to detect fluctuation patterns in operational variables. Monitoring of aeration and DO is already employed by most WWTPs with activated sludge systems, through DO probes and airflow meters. Therefore, by integrating this monitoring approach with supervisory control and data acquisition systems (SCADA) for example, reliable detection and control of fluctuations could potentially be achieved. However, this research also showed that reliability of the monitoring in this case, particularly considering the online nature of the method, was strongly dependent on the effectiveness of the equipment employed. In order to keep that equipment running efficiently, consistent calibration and servicing of DO and airflow meters was required (according to manufacturer's manuals for DO probes from Hach Lange Ltd., UK, and airflow meters from Omni Instruments Ltd., UK).

Moreover, the robustness of ancillary equipment is paramount to a more stable process. Indeed, although more powerful than in the ASPs (800 kW compared to the 400 kW power of the ASPs), the blowers in the BNR were more efficient, (average airflow rates ranging from 30–240 m^3/h, compared to the 0.7–760 m^3/h airflow rates of the monitored ASP), and therefore, the BNR plant required one blower on duty, rather than two, as per the ASP in the same site. As a result, the BNR plant required 2.0 kWh and 23 m^3 of energy and aeration input to treat 1.0 kg of NH_4^+, compared to the ASP in the same site, which required 5.0–6.0 kWh and 80–85 m^3 (under set-points of

NH_4^+ and DO 1.5 mg/L respectively), to treat the same amount of NH_4^+. Therefore, energy use and process performance, clearly depended on blower efficiency delivering better aeration control, which in turn provided a more stable DO distribution (range of measured DO in the BNR: 0.4–1.5 mg/L, $\underline{+}0.4$), as well as more efficient NH_4^+ removal. Overall, this is beneficial to the biological process, since it reduces transient stress responses, therefore minimising formation of N_2O during nitrification. Additionally, the tapered distribution of the diffusers in the nitrifying lane may have a potentially negative contribution to the fluctuations in airflow and DO, since in a tapered aeration system, the diffusers arrangement differs between the front and back end of the aeration tank: at the front end (influent of aeration tank), the diffusers are arranged closely together because of the higher oxygen demand, whereas at the back end (effluent of the aeration tank), they are more spaciously distributed due to a lower oxygen demand. This in turn may contribute to variability in DO and aeration.

Therefore, the recommended operational conditions to deliver the appropriate balance between minimising energy usage, improving treatment efficiency and reducing GHG emissions, were achieved by the BNR plant (Aboobakar et al., 2014b) monitored in this study. Indeed, the significant benefits of the BNR came from the stability seen in operational variables and blower efficiency. On aeration alone, it meant a reduction of 15–80 % in costs compared to the ASP lanes in NH_4^+ control and DO set-point control of 2.0 mg/L (Aboobakar et al., 2014b). It was also 60–99 % more efficient than the ASPs at NH_4^+ removal. It showed the most stable, as well as relatively low, EFs across all nitrogen fractions (<0.2 % estimated guideline, UKWIR, 2009). Therefore, based on the findings, as discharge consents become stricter by targeting TN discharge, upgrading to BNR plants seems to be beneficial.

It should be noted however, that BNR plants are limited to the availability of readily biodegradable carbon required for denitrification as well enhanced phosphorus removal. Thus, in order for reliable removal of TN (measured as Kjeldahl nitrogen, TKN) and phosphorus to be achieved, a minimum ratio of biochemical oxygen demand (BOD) to TKN of 3:1 and of BOD to phosphorus of 25:1 respectively are recommended (WEF, 2005). And although shown to be the best option in this study, BNR plants however, can only be beneficial under the above conditions. Where these conditions are not met, ASPs remain a less limited alternative. In this study, the nitrifying ASPs under DO control settings, operating at a set-point of 1.5 mg/L (sites A and B) proved to be more efficient than operating at DO set-point 2.0 mg/L, with 70–84 % (site A) and 92–96 % (site B) less aeration and energy required to remove 1.0 kg NH_4^+, and over 80 % more economical (in terms of energy for aeration costs). The differences between DO set-points were evident in terms of airflow: the higher set-point (2.0 mg/L) showed excessive and fluctuating aeration, which translated as an increase of up to 340 % in average airflow from set-point 1.5 mg/L, with higher N_2O emission factors (up to 3.9 % of removed NH_4^+, compared to the 0.2 % at 1.5 mg/L).

Furthermore, processes operated under the same control setting (DO set-point 1.5 mg/L in sites A and B), were found to have similar, or identical EF, suggesting that operational process control is more important for controlling emissions than loading rates. Additionally, the quantifiable data obtained in this research could help predict the range of EFs for processes operated within the same control settings. The EFs obtained from the lanes controlled under DO set-point 1.5 mg/L, were also lower than at NH_4^+ set-point control, at 0.34 % of removed NH_4^+. Under the NH_4^+ control setting however, the ASP lane was generally more efficient than under DO set-point control, although this efficiency varied, depending on the DO set-point and site monitored. The most significant difference in efficiency was seen in comparison to the DO set-point of 2.0 mg/L (site A), which required 1001 m^3 of airflow and 140 kWh of energy per kg of treated NH_4^+, compared to the NH_4^+ controlled ASP lane, which required 80 m^3 of airflow and 5.0 kWh of energy per kg of treated NH_4^+. Nevertheless, as explained above (section 7.3), under the NH_4^+ control setting, the changes in airflow and DO in the last two aeration zones (zones 5 and 6) of the nitrifying ASP at site A, triggered significant N_2O production and emission. However, a more stable DO and aeration profile under DO set-point of 1.5 mg/L in the same lane, saw an improved reduction in N_2O produced and emitted from the same two zones. Indeed, in zone 5, over 99 % less N_2O was produced from NH_4^+ to DO set-point controls. Equally in zone 6 (more aerated than zone 5 in both settings but with better airflow control in DO set-point 1.5 mg/L), that meant a reduction in off-gas N_2O emissions of 50 % (from NH_4^+ to DO control settings). Therefore, when operating the ASP under NH_4^+ control, which was the baseline mode of operation in site B, better aeration and DO control is required, similarly to the control seen under DO set-point; particularly towards the end of the nitrifying lane, which, judging by the comparison data from zones 5 and 6 under the two different settings, could see a potential reduction in overall N_2O production and emissions. Under the NH_4^+ control setting, stability in the last two zones could be achieved by monitoring DO and airflow adjacently to the feedback NH_4^+ control monitor two-thirds down the lane, thus preventing dynamic changes (low to high) to airflow and DO trends.

Therefore, based on the above discussion, a stable operational control could have a three-fold benefit for WWTPs:

- a more stable DO profile leading to lower N_2O production (seen in the BNR lane and in the ASP at set-point 1.5 mg/L in site B, whereby less N_2O was produced because of more stable DO profiles; compared to the same ASP under NH_4^+ control, where due to a sudden fall in DO in zone 5 significant N_2O was synthesised; and in the ASP in site A operated at DO set-point 2.0 mg/L, which due to a very fluctuating DO profile N_2O synthesised was over 17 times higher than in the same ASP operated under the more stable DO set-point of 1.5 mg/L);
- optimised aeration and energy consumption (as evidenced by the operational efficiency achieved by the BNR lane) therefore minimising operational carbon footprint (seen again in the BNR lane and ASPs operated under DO set-point control of 1.5 mg/L, which offered the lowest carbon emissions from energy consumption);

- and finally, reduced off-gas process emissions (shown to be lower in the lanes where excessive aeration was prevented).

Furthermore, N_2O emissions credit has been recently proposed as an incentive to reward WWTPs which adopt an integrated approach of improved nitrogen removal and minimisation of N_2O emissions (Wang et al., 2011c). This would require a detailed profiling of N_2O emissions at full-scale environments and how they are influenced by operational variables. This relationship can only be correlated by high frequency, online sampling of both operating conditions and N_2O (Daelman et al., 2013), as achieved by this study.

Approaches to achieve the objectives set by this research as well as potential outcomes are summarised in Fig. 7.1: spatial and diurnal online monitoring of GHG emissions and operating conditions is advised, in order to obtain a reliable inventory. This in turn allows for better understanding of how to minimise emissions by achieving operational stability (reducing variability in DO, aeration and NH_4^+, promoting complete nitrification and denitrification). Finally, operational stability has a positive knock-on effect on the balance between low emissions, reduced carbon footprint and efficiency, particularly with BNR plants, shown to be 60–99% more efficient than ASPs. However, where BNR is not feasible, ASP control under DO set-point of 1.5 mg/L is preferable to 2.0 mg/L, since this could result in lower EF, more stable operational conditions and reduction in aeration requirements (up to 340 %). Operating ASPs under NH_4^+ control, can lead to 6–96 % more efficiency than operating under DO set-point; however, because of the control set-up, there is less control over DO availability at the back-end of the process, under NH_4^+ than DO set-point controls, therefore leading to higher variability therein. A way to avoid this is by improving monitoring of both DO and airflow, two-thirds down the lane (next to the NH_4^+ monitor), when controlling the process under NH_4^+ set-point.

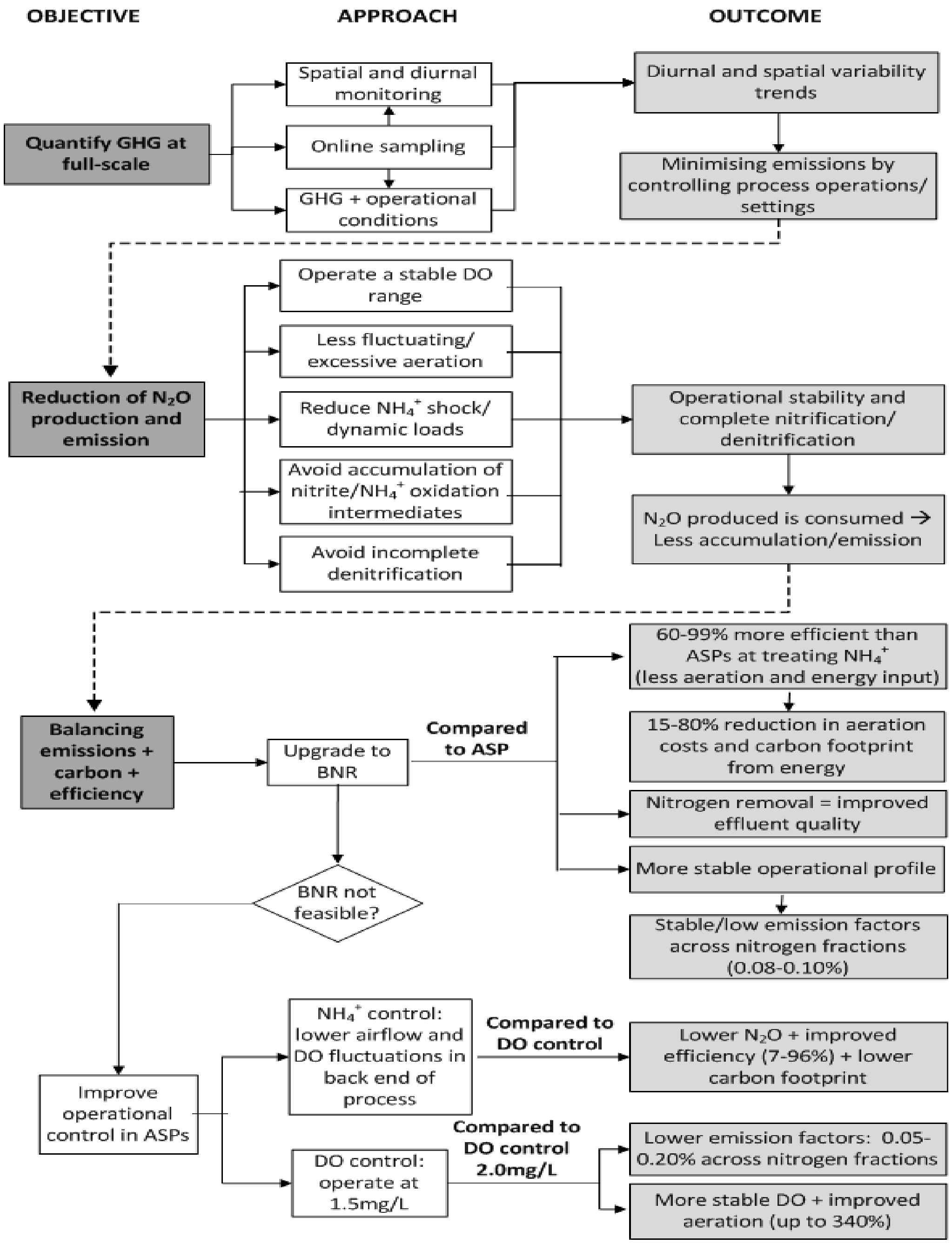


Figure 7.1: Flow chart addressing the main objectives of the research and recommended options and outcomes of managing emissions, carbon footprint and improved effluent quality in activated sludge systems. Recommendations are based on current findings as well as published by others.

7.5. Recommendations for future research

The methodology approached adopted by this study, an online, long-term, monitoring of GHG process emissions as well as operational variables, integrating spatial and diurnal variability, has offered insight into how emissions vary at full-scale and how operational changes affect those emissions. This methodology has produced an inventory of GHG that is robust enough to challenge current guidelines, such as the UK's estimated N_2O EF of 0.2 % of TN load (UKWIR, 2009), which based on the findings, was shown to be a best-case scenario. Therefore, in order to avoid under or over-estimating process emissions, a robust monitoring framework is strongly advised. When considering the impact of GHG across WWTPs, this framework could be integrated into a life cycle approach, to provide a quantifiable inventory of overall GHG emissions from biological wastewater treatment. This type of inventory may become increasingly relevant as the water industry moves towards a "carbon neutral" future, driven by changes in environmental legislation and organisational commitments to reduce carbon footprint (Foley et al., 2010b).

One of the shortcomings in the current study however, was the lack of online monitoring of dissolved CH_4 due to time restrictions. This made it unable to determine whether or not methanogenesis (CH_4 production) is taking place in nitrifying ASPs. Therefore, future monitoring should include online dissolved CH_4, in order for a correlation to be established between produced and emitted CH_4.

Through the intensive monitoring campaign, key conclusions were drawn: namely, that an operationally stable process will emit less N_2O, reduce operational carbon and improve efficiency. This balance was found to be mostly achieved by the BNR plant, followed by the ASP monitored at the same site (site B). Based on this, further mitigating strategies to achieve this balance have been proposed (Fig. 7.1). However, it is advisable that, before implementing these measures, further monitoring of other BNR plants is carried out, in order to compare with the findings from the plant monitored in this study. Additional monitoring of ASP plants controlled at DO set-points below 1.5 mg/L should also be considered; this could potentially determine whether ASPs can be controlled at lower DO set-point thresholds while at the same time, achieving operational stability and reduced process and carbon emissions, without compromising effluent quality. Finally, a risk assessment and feasibility study should also be undertaken, in order to measure the operational impact of proposed mitigating strategies (Fig. 7.1).

Finally, further lab-scale work is needed, to unravel the mechanistic contributions of different activated sludge microbial pathways to N_2O production. Although a genomic inventory of metabolic pathways of N_2O production by AOB has recently been developed (Chandran et al., 2011), further work is required to build on that, so that the contribution of biochemical pathways to N_2O production can be combined with the contributions of environmental factors to N_2O emissions at full-scale. By doing so, a complete N_2O inventory can be constructed. And given the parallels between low emissions and improved nitrogen treatment (Chandran et al., 2011; Foley et al., 2010a; Wang et al., 2011c), there is opportunity to simultaneously minimise emissions and increase effluent quality, therefore providing a sustainable framework to wastewater treatment.

CHAPTER 8

CONCLUSIONS

8. CONCLUSIONS

- Methane (CH_4), although potentially formed in non-aerated compartments, was nevertheless emitted in aerobic zones, at an average emission factor (EF) of 0.07 % of both influent and removed chemical oxygen demand (COD), up to 667 kgCH_4/year emitted, therefore making the monitored aeration tank an emission hotspot.

- Nitrous oxide (N_2O) EFs depended on relative nitrogen fractions, with influent-based EFs showing a best-case scenario, at 0.05–0.72 % of both influent total nitrogen (TN) and ammonia (NH_4^+), compared to the higher EFs based on removed nitrogen at 0.13–3.9 % of both TN and NH_4^+ removed.

- The nitrifying activated sludge plant (ASP) lanes controlled under the same DO set-point of 1.5 mg/L, had similar, or identical, EF, suggesting that control settings could help predict the range of EF. Therefore, a range of quantifiable EF, taking into account process operational variability and control settings, is more appropriate than a single, estimated factor.

- Dissolved oxygen (DO) was key in controlling N_2O production both from aerated and non-aerated zones, with higher fluctuations in DO leading to higher N_2O production. Therefore, a stable DO profile was more important than a DO threshold in minimising N_2O production, irrespective of process configuration. Based on these conclusions, the proposed research hypothesis, stated as: "N_2O production can be directly linked to oxygen availability in biological treatment processes and therefore, minimised by influencing oxygen presence in the bioreactors", can thus be amended, since changes or fluctuations in DO were more important than absolute levels in influencing N_2O production.

- The variability in DO in turn, was significantly dependent on process control settings ($p < 0.05$). Consequently, control settings which introduced higher DO fluctuations led to increased N_2O production, which in turn was air-stripped under intensive aeration.

- N_2O was always produced in the presence of NH_4^+, even at low concentrations (=<0.5 mg/L). This was always followed by a peak in nitrite (NO_2^-) and more significant under low DO conditions, therefore linking N_2O production with NH_4^+oxidation, particularly with nitrifier nitrification.

- Incomplete denitrification under low carbon to nitrogen (C/N) ratios was also found to significantly trigger N_2O production (EFs of 2.4 and 4.1 % of reduced TN at C/N ratios of 2.8 and 2.4 respectively), particularly during intermittent aeration.

- Therefore, nitrifier denitrification and incomplete denitrification were found to simultaneously trigger N_2O production in the final stages of nitrification.

- The biological nutrient removal (BNR) lane was the most operationally stable process (DO range 0.4–1.5 mg/L ±0.4; airflow range 23–200 m^3/h ±50), therefore offering the best balance between efficiency (60–99 % less aeration and energy per kg of treated NH_4^+ than ASP lanes), low carbon footprint and reduced process emissions (EF: 0.08–0.1 % across all nitrogen fractions).

- The second best operational configuration was the ASP lane under DO set-point control of 1.5 mg/L, with low EFs (0.05–0.2 %), more stable operational conditions and reduction in aeration requirements (up to 340 % less than DO set-point 2.0 mg/L).

- Operating the ASP under NH_4^+ control settings however, led to 6–96 % more efficiency than under DO set-points, although more DO and aeration control in the back end of process was required under this setting.

- Only an online, long-term methodology such as adopted in this study, can offer detailed insights into emission variability and the effect of operational variables on promoting or reducing emissions.

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APPENDICES

Appendix 1: Tanks-in-series calculations and Tank Schematics

Tanks-in-series calculations

Flow (Q) information obtained from Process Design Group (PDG), Severn Trent Water

Date range	Between 1/6/06 - 31/12/10
Total days recorded	1590 days
Readings	Daily Q (FFT) recorded from SCADA
Assumptions	1) Assume 20% of FFT to ASP as determined during recorded days (1590 days) 2) Assume half of 20% of FFT (~10%) per each ASP lane
Average Q for ASP4 (m^3/s)	0.121
Average daily Q for ASP4, per lane (m^3/s)	**0.060**

Tanks in Series Formula

Formula:	$\dfrac{\mathbf{7.4 \times Q \times (1 + R) \times L}}{\mathbf{W \times H}}$
Where:	
Q	Average daily sewage flow (m^3/s)
R	Recycle Ratio (RAS as a proportion of Q)
L	Length of flow path in tank (m)
W	Width of flow path in tank (m)
H	Depth of liquid in tank (m)

Coleshill TIS calculations

Flow (Q, m^3/s) - data sent by PDG - see above	0.06 m3/s
R	0.8
L (m) - from Tank Schematics	188.4 m
W (m) - from Tank Schematics	6.1
H (m) - from asset database STAR	2.98
Calculation for TIS for ASP, 1 lane only =	**(7.4*0.06*(1+0.8)*188.4)/(6.1*2.98)**
TIS for ASP, 1 lane only =	**8**
Length per zone (m)	*23.6*

Trial Plan(s)

Plan A	
Conditions	5
Zones (as per above)	8
days in zone	7
days per condition	56
total days for all conditions	280
No of months required for trials*	**9.23**

Plan B	
Conditions	5
Zones (as per above)	8
days in zone	3.5
days per condition	28
total days for all conditions	140
No of months required for trials*	**4.62**

**Calculations for months required for trials:*

4.333333333	average no. of weeks per month
30.33333333	average no. Of days per month

Tank Schematics

Tank Schematics for ASP 4, Coleshill Sewage Treatment Works (site A) – *attached document.*

Aeration tank Al-9 and AL-10

Electronic
16.9.99
Conversion

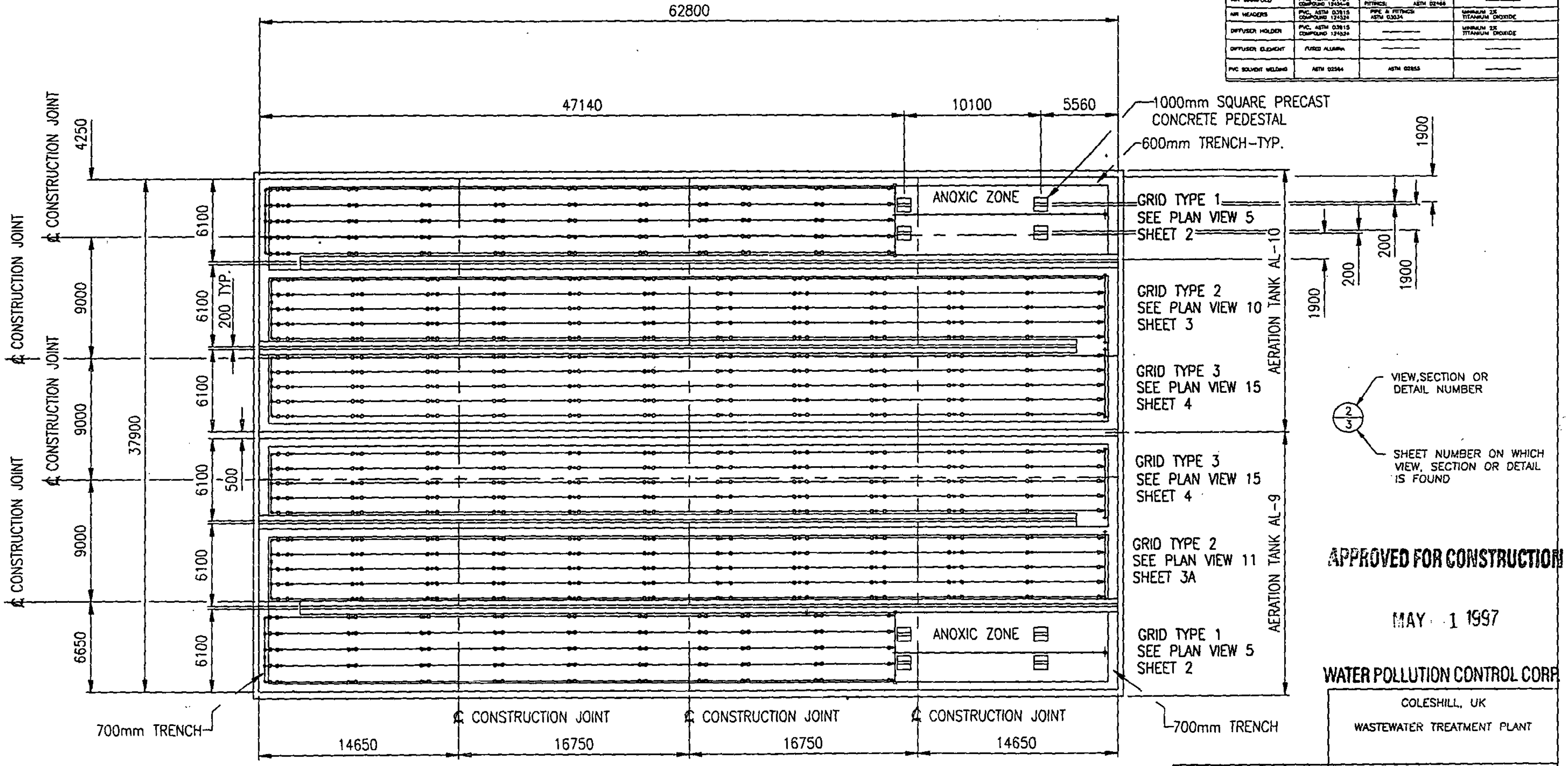
- **General arrangement**
  - 97-3737 E1 – Key plan of aeration tanks AL-9 and AL-10
  - 97-3737 E2 – Plan view and section of grid type 1 aeration tank AL-9 and AL-10
  - 97-3737 E3 – Plan view and section of grid type 2 aeration tank AL-10
  - 97-3737 E4 – Plan view and section of grid type 2 aeration tank AL-9
  - 97-3737 E5– Plan view and section of grid type 3 aeration tank AL-9 and AL-10
  - 97-3737 E6 – Details
  - 97-3737 E7– Pressure mounting assemblies and details (3 - valve connecting box)

97-3737/A

10/89

CERAMIC AERATION MATERIAL AND MANUFACTURING SPECIFICATIONS

ITEM	MATERIAL SPECIFICATION	MANUFACTURING SPECIFICATION	NOTES
SUPPORTS	304L STAINLESS STL	———	"L" GRADE NOT REQUIRED FOR NON-WELDED PARTS
BOLTS, NUTS, WASHERS	18-8 STAINLESS STL	———	———
FIXED JOINT O-RING	NATURAL RUBBER/SBR	———	45 ± 5 DUROMETER SHORE A COMPRESSION SET 5% MAX
EXPANSION JOINT O-RING	NATURAL RUBBER/SBR	———	40 ± 5 DUROMETER SHORE A 0.45 COEFFICIENT OF FRICTION MAX
DIFFUSER HOLDER O-RING	POLYISOPRENE	———	40 ± 5 DUROMETER SHORE A 500% ELONGATION
AIR MANIFOLD	PVC, ASTM D1784 COMPOUND 12454-B	PIPE: ASTM D1785 FITTINGS: ASTM D2466	———
AIR HEADERS	PVC, ASTM D3915 COMPOUND 124524	PIPE & FITTINGS: ASTM D3034	MINIMUM 2% TITANIUM DIOXIDE
DIFFUSER HOLDER	PVC, ASTM D3915 COMPOUND 124524	———	MINIMUM 2% TITANIUM DIOXIDE
DIFFUSER ELEMENT	FUSED ALUMINA	———	———
PVC SOLVENT WELDING	ASTM D2564	ASTM D2855	———



KEY PLAN ①

APPROVED FOR CONSTRUCTION

MAY 1 1997

WATER POLLUTION CONTROL CORP

COLESHILL, UK

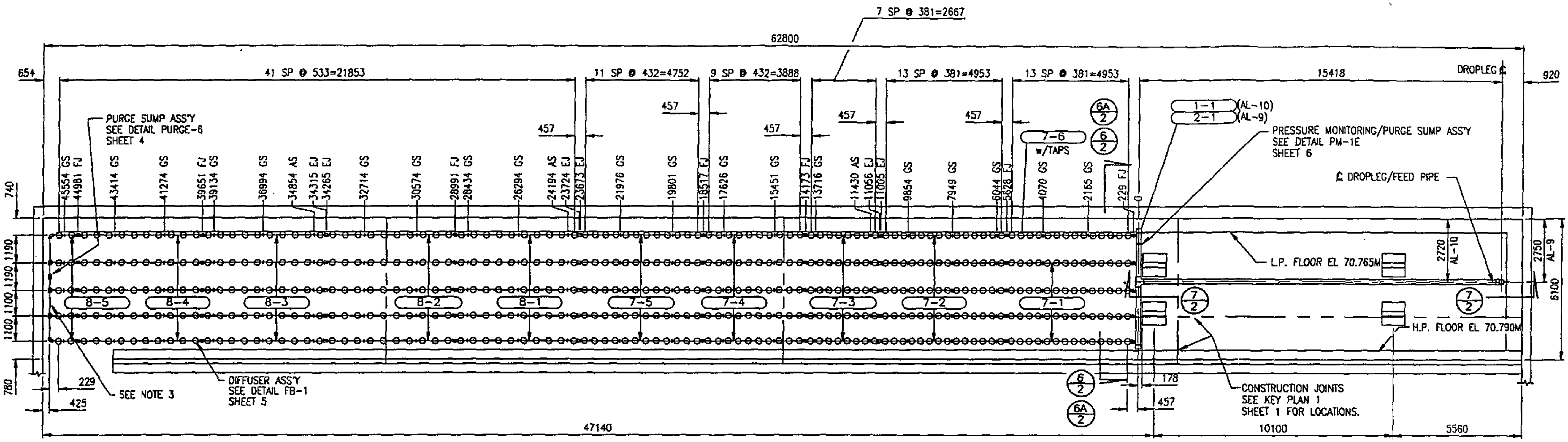
WASTEWATER TREATMENT PLANT

THIS DRAWING IS THE PROPERTY OF WATER POLLUTION CONTROL CORP AND IS SUBMITTED IN CONFIDENCE. IT IS NOT TO BE DISCLOSED, USED OR DUPLICATED WITHOUT PERMISSION OF WATER POLLUTION CONTROL CORP.

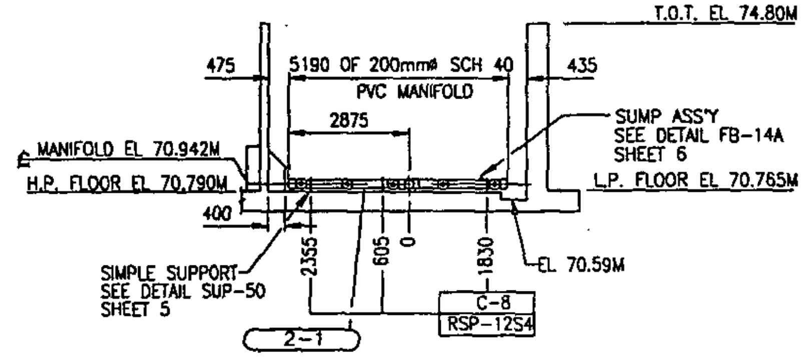
KEY PLAN
AERATION TANKS AL-9 & AL-10

SANITAIRE®
WATER POLLUTION CONTROL CORP
MILWAUKEE, WISCONSIN

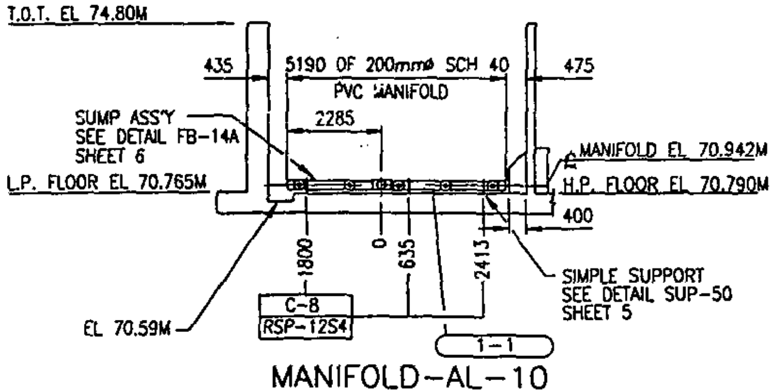
CUST NO. N10706/001				DRWN BY RH DATE 4-25-97	MODEL CER	JOB 97-3737
DWG NO.	NO.	DATE	REVISION	BY	CHKD BY JC DATE 4-28-97 APPVD BY DAK DATE 4-30	SHT E-1



GRID TYPE 1
AERATION TANK AL-10-(SHOWN) & AL-9-(MIRROR IMAGE)
PLAN VIEW ⑤



MANIFOLD-AL-9
SECTION (6A)
(1) REQ'D-AS SHOWN

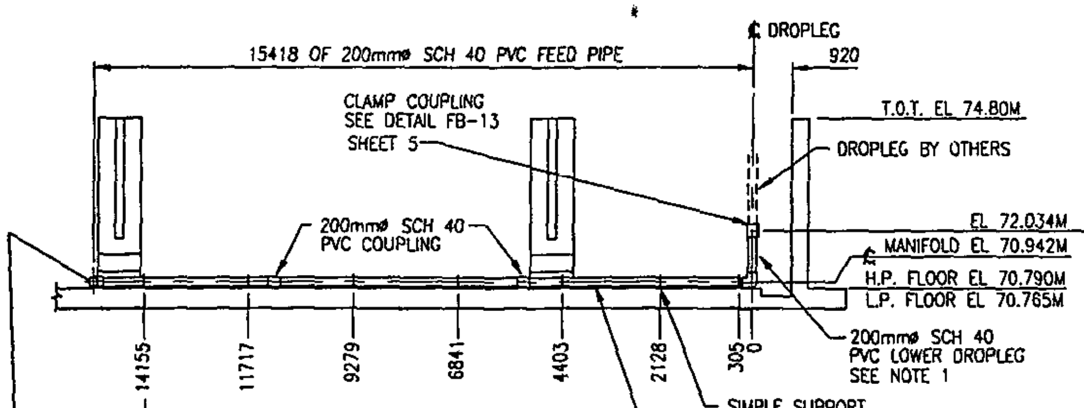


MANIFOLD-AL-10
SECTION (6)
(1) REQ'D-AS SHOWN

NOTE: SUPPORT SPACING

Every attempt has been made to insure locational dimensions of the supports are correct. However, after one line of air distributor anchors for any grid type have been installed, the locations must be checked for proper clearances by installing the supplied air headers. Spacing between lines must be checked for fit with the cross manifold and drain line. Any discrepancies or interferences must be brought to the attention of SANITAIRE prior to further installation.

The actual support anchor locations must be indexed from the centerline of the manifold. The actual accumulative dimensional error from the manifold to the anchor bolt must not exceed ± 3/4".



FEED PIPE
SECTION (7)
(2) REQ'D-AS SHOWN

LEGEND

GS	GUIDE SUPPORT SEE DETAIL SUP-1 SHEET 5
AS	ANCHOR SUPPORT SEE DETAIL SUP-12 SHEET 5
FJ	FIXED JOINT SEE DETAIL FB-10A SHEET 5
EJ	EXPANSION JOINT SEE DETAIL FB-11 SHEET 5

FOR TYPICAL AIR DISTRIBUTOR SECTION SEE DETAIL FB-20 SHEET 3

NOTES:

1. PVC DROPLEG WILL BE SHIPPED TO JOBSITE 152mm LONGER THAN REQUIRED, TO ACCOUNT FOR TANK VARIANCES. CONTRACTOR TO CUT TO SUIT AND SOLVENT WELD INTO MANIFOLD TO MAINTAIN 3mm MAXIMUM GAP BETWEEN STAINLESS STEEL AND PVC DROPLEGS.
2. C-8 / RSP-12S4 —REFERS TO THE MANIFOLD SUPPORT SIZE AND CORRESPONDS TO THE TABLE SHOWN WITH THE SUPPORT DETAIL.
   INDICATES THE SUPPORT STAND PART NUMBER.
3. SANITAIRE WILL PROVIDE THE LAST AIR DISTRIBUTOR WITH 1 (ONE) OPEN END WITH 152mm OF EXTRA PIPE. CONTRACTOR IS TO CUT THE OPEN END OF THE PIPE AND SOLVENT WELD ON TEES AND ELBOWS TO MAKE SURE THE DRAINLINE LINES UP.

GRID TYPE '1'

2 -TANK(S)
1 -GRID(S) PER TANK
5 -AIR DISTRIBUTORS PER GRID
100 -DIFFUSERS PER AIR DISTRIBUTOR
500 -DIFFUSERS PER GRID
1000 -TOTAL DIFFUSERS INSTALLED FOR THIS GRID TYPE

APPROVED FOR CONSTRUCTION

MAY 1 1997

WATER POLLUTION CONTROL CORP

SANITAIRE TO HERE

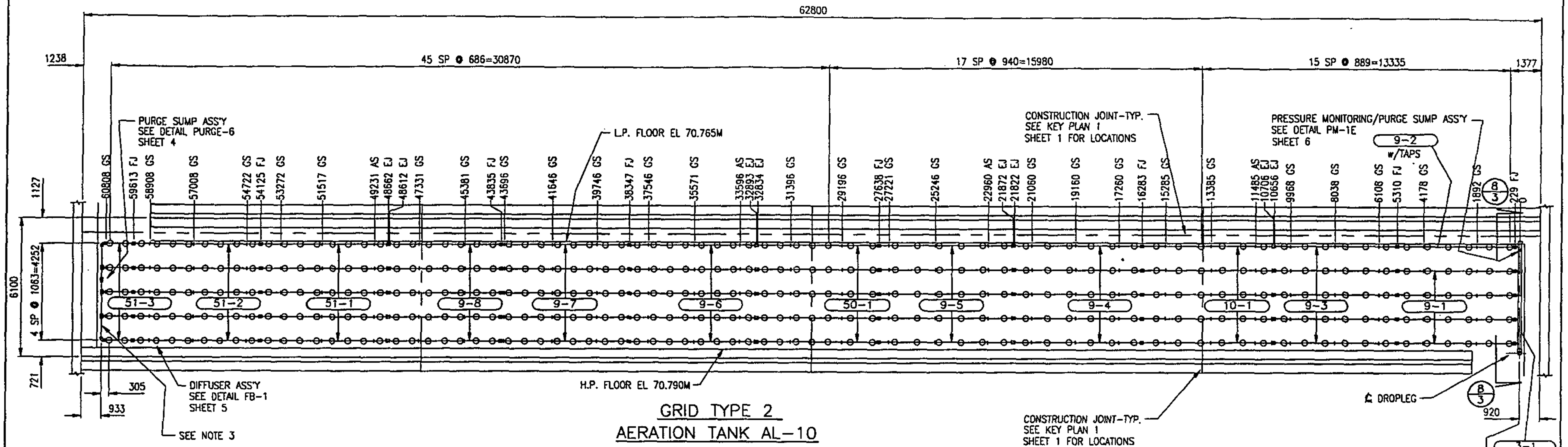
COLESHILL, UK
WASTEWATER TREATMENT PLANT

PLAN VIEW & SECTION
GRID TYPE 1
AERATION TANK AL-9 & AL-10

SANITAIRE
WATER POLLUTION CONTROL CORP
MILWAUKEE, WISCONSIN

CUST NO. H10706/001	NO.	DATE	REVISION	BY
DWG NO.				

DRWN BY RH DATE 4-25-97
CHKD BY JC DATE 4-28-97
APPVD BY DATE 4-30
MODEL CER
JOB 97-3737
SH E-2



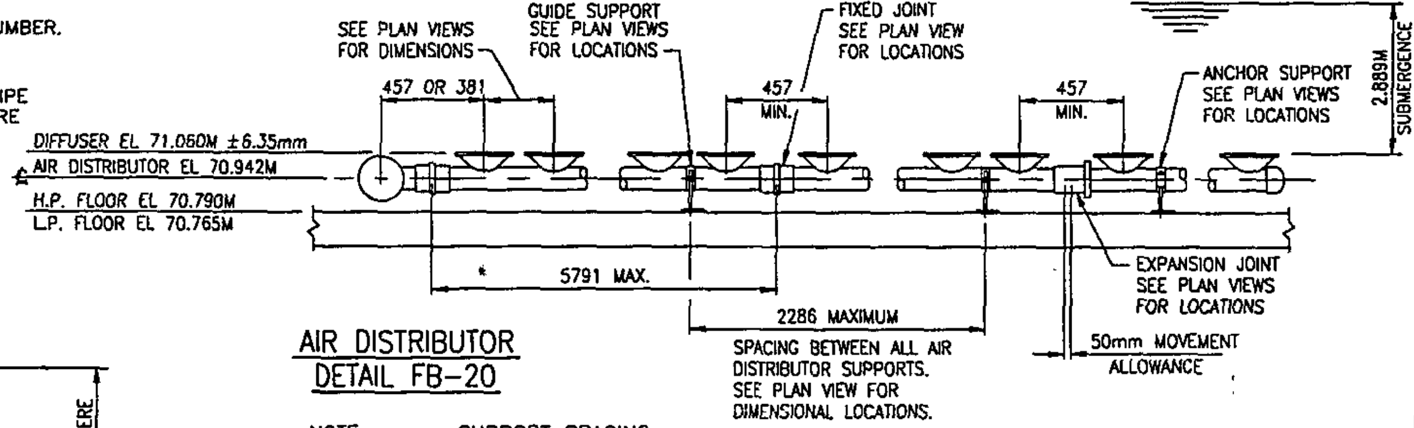
GRID TYPE 2
AERATION TANK AL-10
PLAN VIEW ⑩

GRID TYPE '2'

2 -TANK(S)
1 -*GRID(S) PER TANK*
5 -AIR DISTRIBUTORS PER GRID
78 -DIFFUSERS PER AIR DISTRIBUTOR
390 -DIFFUSERS PER GRID
780 -TOTAL DIFFUSERS INSTALLED
FOR THIS GRID TYPE

NOTES:

1. PVC DROPLEG WILL BE SHIPPED TO JOBSITE 152mm LONGER *THAN REQUIRED, TO ACCOUNT FOR TANK VARIANCES.* CONTRACTOR TO CUT TO SUIT AND SOLVENT WELD INTO MANIFOLD TO MAINTAIN 3mm MAXIMUM GAP BETWEEN *STAINLESS STEEL AND PVC DROPLEGS.*
2. C-6 / RSP-12S4 —REFERS TO THE MANIFOLD SUPPORT SIZE AND *CORRESPONDS TO THE TABLE SHOWN WITH THE* SUPPORT DETAIL. —INDICATES THE SUPPORT STAND PART NUMBER.
3. SANITAIRE WILL PROVIDE THE LAST AIR DISTRIBUTOR WITH 1 (ONE) OPEN END WITH 152mm OF EXTRA PIPE. CONTRACTOR IS TO CUT THE OPEN END OF THE PIPE AND SOLVENT WELD ON TEES AND ELBOWS TO MAKE SURE THE DRAINLINE LINES UP.



AIR DISTRIBUTOR
DETAIL FB-20

LEGEND

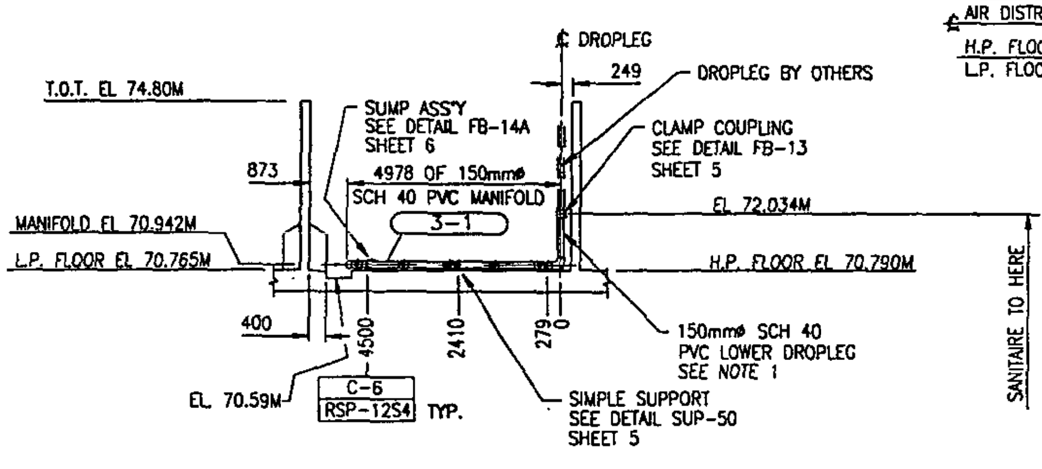
GS - *GUIDE SUPPORT* SEE DETAIL SUP-1 SHEET 5

AS - ANCHOR SUPPORT SEE DETAIL SUP-12 SHEET 5

EJ - EXPANSION JOINT SEE DETAIL FB-11 SHEET 5

FJ - *FIXED JOINT* SEE DETAIL FB-10A SHEET 5

FOR TYPICAL AIR DISTRIBUTOR SECTION SEE *DETAIL* FB-20 SHEET 3



MANIFOLD-AL-10
SECTION ⑧
(1) REQ'D-AS SHOWN

NOTE: SUPPORT SPACING

Every attempt has been made to insure locational dimensions of the supports are correct. However, after one line of air distributor anchors for any grid type have been installed, the locations must be checked for proper clearances by installing the supplied air headers. Spacing between lines must be checked for fit with the cross manifold and drain line. Any discrepancies or interferences must be brought to the attention of SANITAIRE prior to further installation.

The actual support anchor locations must be indexed from the centerline of the manifold. The actual accumulative dimensional error from the manifold to the anchor bolt must not exceed ± 3/4".

APPROVED FOR CONSTRUCTION

MAY 1 1997

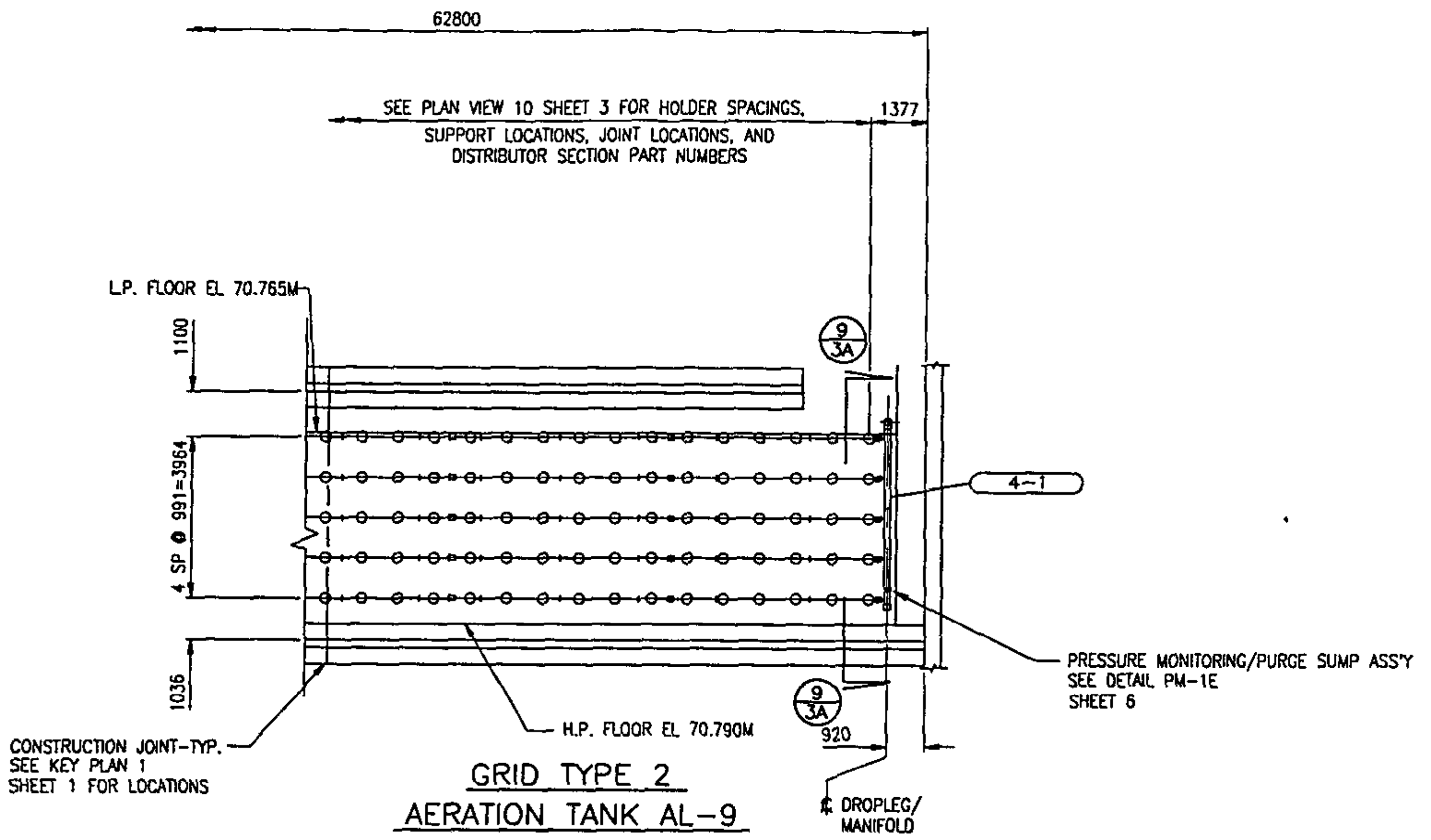
WATER POLLUTION CONTROL CORP.

COLESHILL, UK
WASTEWATER TREATMENT PLANT

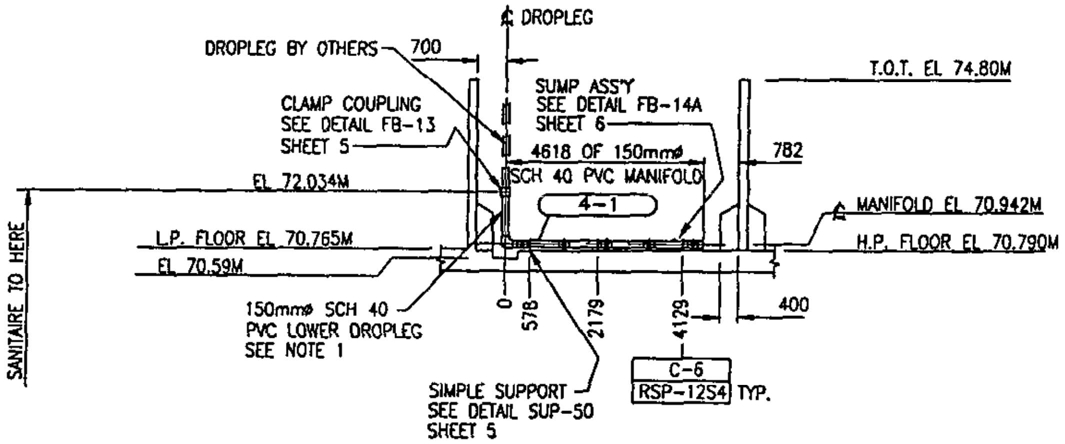
PLAN VIEW & SECTION
GRID TYPE 2
AERATION TANK AL-10

SANITAIRE
WATER POLLUTION CONTROL CORP
MILWAUKEE, WISCONSIN

CUST NO.	H18708/001	NO.	DATE	REVISION	BY	DRWN BY RH	DATE 4-25-97	MODEL CER	JOB 97-3737
DWG NO.						CHKD BY JC	DATE 4-28-97		SH E-3
						APPRD BY AAE	DATE 4-30		



GRID TYPE 2
AERATION TANK AL-9
PLAN VIEW ⑪



MANIFOLD-AL-9
SECTION ⑨
(1) REQ'D-AS SHOWN

NOTES:

1. PVC DROPLEG WILL BE SHIPPED TO JOBSITE 152mm LONGER THAN REQUIRED, TO ACCOUNT FOR TANK VARIANCES. CONTRACTOR TO CUT TO SUIT AND SOLVENT WELD INTO MANIFOLD TO MAINTAIN 3mm MAXIMUM GAP BETWEEN STAINLESS STEEL AND PVC DROPLEGS.
2. C-6 / RSP-12S4 —REFERS TO THE MANIFOLD SUPPORT SIZE AND CORRESPONDS TO THE TABLE SHOWN WITH THE SUPPORT DETAIL.
   └INDICATES THE SUPPORT STAND PART NUMBER.
3. SANITAIRE WILL PROVIDE THE LAST AIR DISTRIBUTOR WITH 1 (ONE) OPEN END WITH 152mm OF EXTRA PIPE. CONTRACTOR IS TO CUT THE OPEN END OF THE PIPE AND SOLVENT WELD ON TEES AND ELBOWS TO MAKE SURE THE DRAINLINE LINES UP.

LEGEND

GS – GUIDE SUPPORT
SEE DETAIL SUP-1
SHEET 5

AS – ANCHOR SUPPORT
SEE DETAIL SUP-12
SHEET 5

EJ – EXPANSION JOINT
SEE DETAIL FB-11
SHEET 5

FJ – FIXED JOINT
SEE DETAIL FB-10A
SHEET 5

FOR TYPICAL AIR DISTRIBUTOR
SECTION SEE DETAIL FB-20
SHEET 3 -

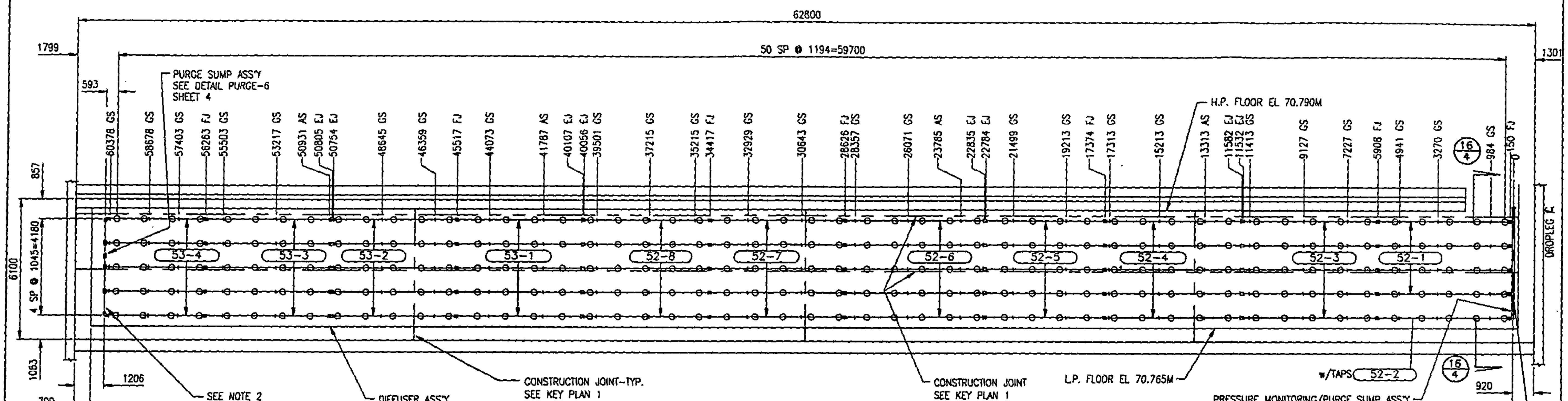
APPROVED FOR CONSTRUCTION
MAY 1 1997
WATER POLLUTION CONTROL CORP.

COLESHILL, UK
WASTEWATER TREATMENT PLANT

PLAN VIEW & SECTION
GRID TYPE 2
AERATION TANK AL-9

SANITAIRE®
WATER POLLUTION CONTROL CORP
MILWAUKEE, WISCONSIN

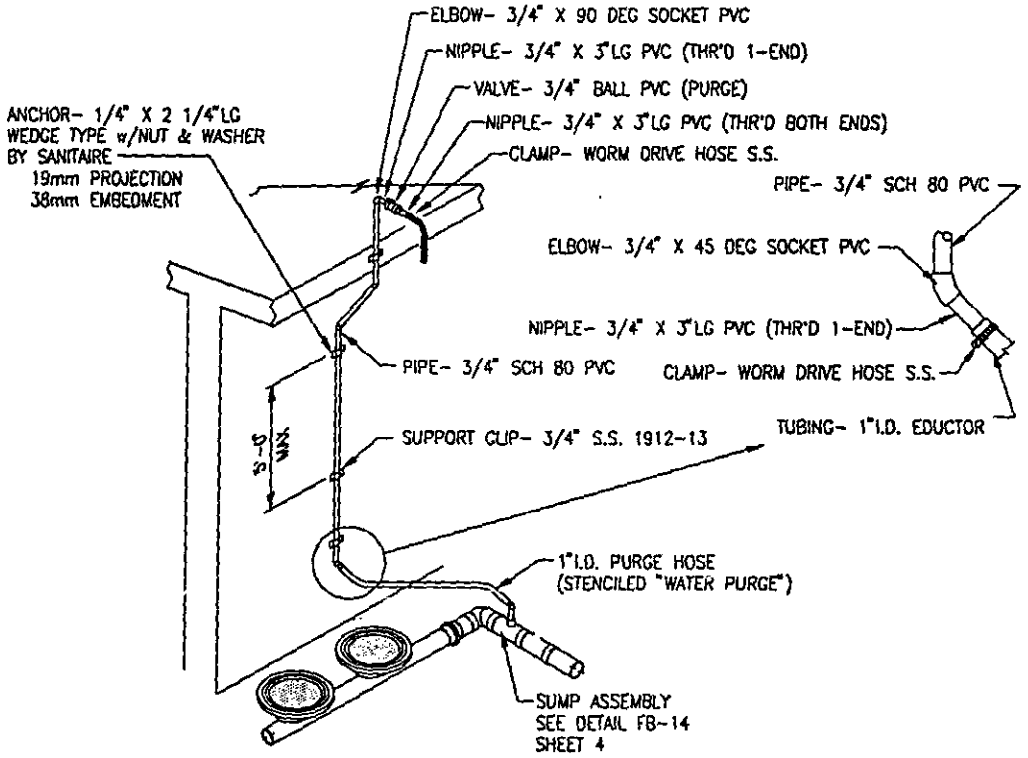
CUST NO. H10706/001	NO.	DATE	REVISION	BY	DRWN BY RH DATE 4-25-97	MODEL CER	JOB 97-3737
DWG NO.					CHKD BY JC DATE 4-28-97 APPD BY DATE 4-30		SHT E-3A



GRID TYPE 3

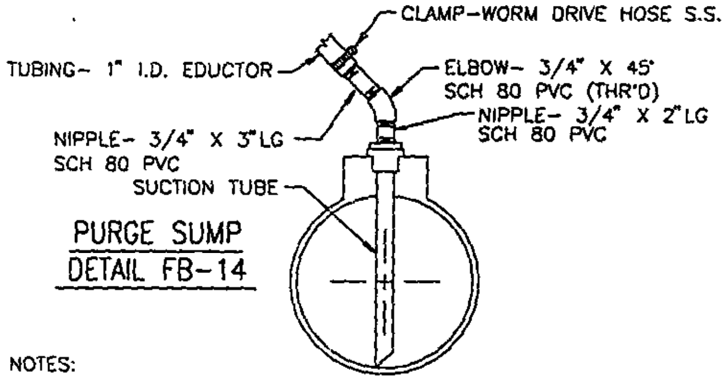
AERATION TANK AL-10-(SHOWN) & AL-9-(MIRROR IMAGE)

PLAN VIEW ⑮



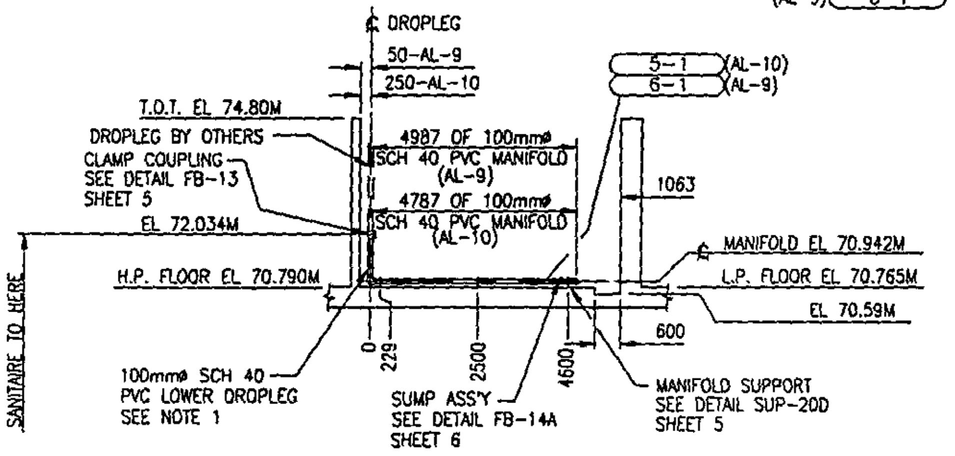
PURGE SUMP ASSEMBLY

DETAIL PURGE-6



PURGE SUMP

DETAIL FB-14



SECTION ⑯

(1) REQ'D-AS SHOWN (AL-10)
(1) REQ'D-MIRROR IMAGE (AL-9)

NOTES:

1. PVC DROPLEG WILL BE SHIPPED TO JOBSITE 152mm LONGER THAN REQUIRED, TO ACCOUNT FOR TANK VARIANCES. CONTRACTOR TO CUT TO SUIT AND SOLVENT WELD INTO MANIFOLD TO MAINTAIN 3mm MAXIMUM GAP BETWEEN STAINLESS STEEL AND PVC DROPLEGS.
2. SANITAIRE WILL PROVIDE THE LAST AIR DISTRIBUTOR WITH 1 (ONE) OPEN END WITH 152mm OF EXTRA PIPE. CONTRACTOR IS TO CUT THE OPEN END OF THE PIPE AND SOLVENT WELD ON TEES AND ELBOWS TO MAKE SURE THE DRAINLINE LINES UP.

NOTE: SUPPORT SPACING

Every attempt has been made to insure locational dimensions of the supports are correct. However, after one line of air distributor anchors for any grid type have been installed, the locations must be checked for proper clearances by installing the supplied air headers. Spacing between lines must be checked for fit with the cross manifold and drain line. Any discrepancies or interferences must be brought to the attention of SANITAIRE prior to further installation.

The actual support anchor locations must be indexed from the centerline of the manifold. The actual accumulative dimensional error from the manifold to the anchor bolt must not exceed ± 3/4".

GRID TYPE '3'

2 -TANK(S)
1 -GRID(S) PER TANK
5 -AIR DISTRIBUTORS PER GRID
51 -DIFFUSERS PER AIR DISTRIBUTOR
255 -DIFFUSERS PER GRID
510 -TOTAL DIFFUSERS INSTALLED FOR THIS GRID TYPE

LEGEND

GS - GUIDE SUPPORT
SEE DETAIL SUP-1
SHEET 5

AS - ANCHOR JOINT
SEE DETAIL SUP-12
SHEET 5

FJ - FIXED JOINT
SEE DETAIL FB-10A
SHEET 5

EJ - EXPANSION JOINT
SEE DETAIL FB-11
SHEET 5

FOR TYPICAL AIR DISTRIBUTOR
SECTION SEE DETAIL FB-20
SHEET 3

APPROVED FOR CONSTRUCTION

MAY 1 1997

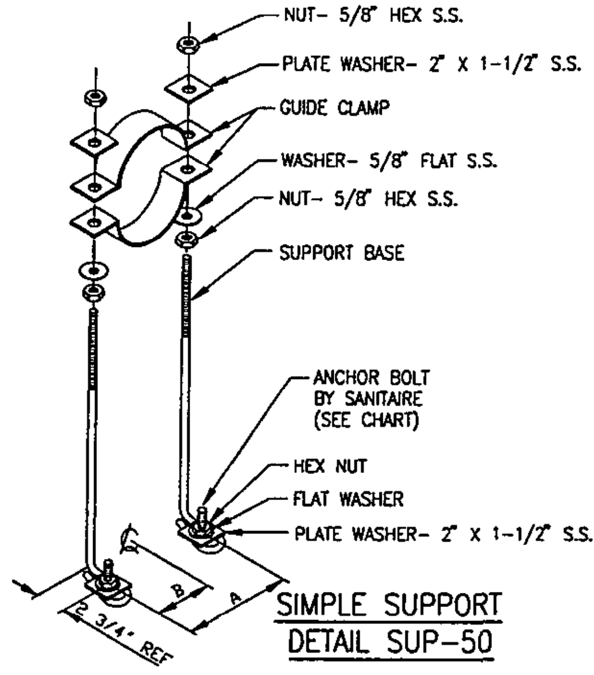
WATER POLLUTION CONTROL CORP

COLESHILL, UK
WASTEWATER TREATMENT PLANT

PLAN VIEW & SECTION
GRID TYPE 3
AERATION TANK AL-9 & AL-10

SANITAIRE®
WATER POLLUTION CONTROL CORP
MILWAUKEE, WISCONSIN

CUST NO. H10708/001	NO.	DATE	REVISION	BY	DRWN BY RH DATE 4-25-97	MODEL CER	JOB 97-3737
DWG NO.					CHKD BY JC DATE 4-28-97 APPVD BY DOE DATE 4-30		SH E-4

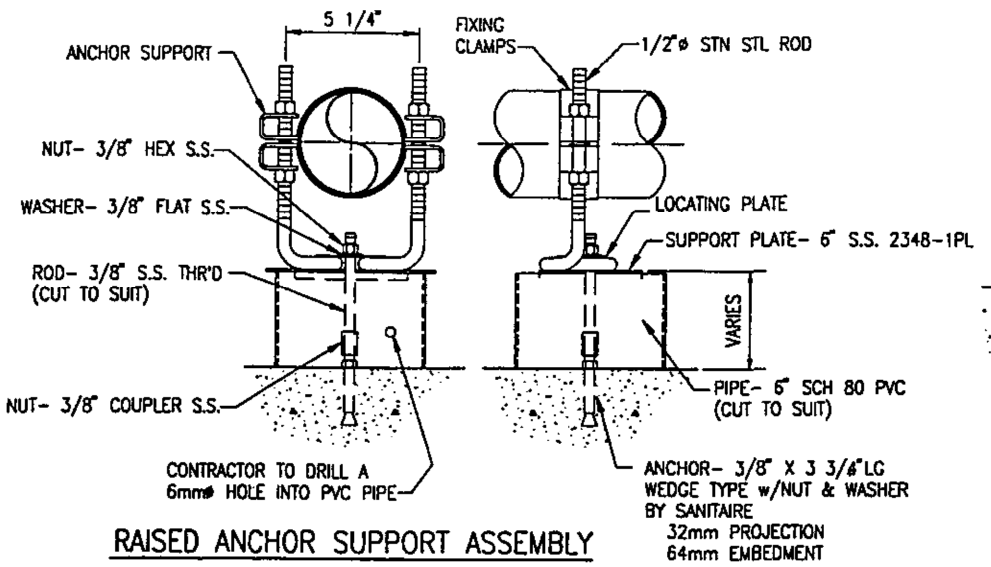


SIMPLE SUPPORT
DETAIL SUP-50

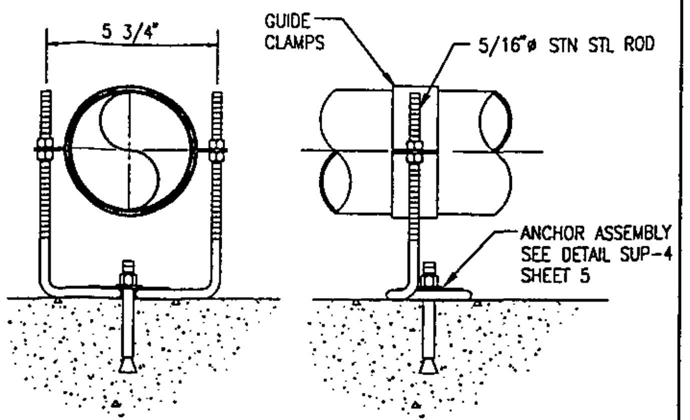
ANCHOR SPACING		
HDR. DIA.	A	B
~~4"ø~~	~~6 5/8"~~	~~3 5/16"~~
6"ø	222mm	111mm
8"ø	274mm	137mm
~~10"ø~~	~~12 7/8"~~	~~6 7/16"~~
~~12"ø~~	~~14 7/8"~~	~~7 7/16"~~

SIMPLE SUPPORT EXPANSION ANCHOR CHART			
HEADER DIA.	ANCHOR BOLT	PROJECTION HOLD	EMBEDMENT
6"ø 8"ø	1/2"ø X 4 1/2"	44mm	70mm
~~10"ø~~ ~~12"ø~~	~~5/8"ø X 4 3/4"~~	~~2"~~	~~2 3/4"~~

MAN. IDENT	HDR. DIA.	SUPPORT BASE	GUIDE STRAP		PLATE WASHER	
			304	~~316~~	304	~~316~~
~~C-4~~	~~4"~~	SEE DRAWINGS	~~CG4500-4~~	~~CG4500-6~~	~~2278-1W4~~	~~2278-1W6~~
C-6	6"		CG6625-4	~~CG6625-6~~	2278-1W4	~~2278-1W6~~
C-8	8"		CG8625-4	~~CG8625-6~~	2278-1W4	~~2278-1W6~~
~~C-10~~	~~10"~~		~~CG1075-4~~	~~CG1075-6~~	~~2278-1W4~~	~~2278-1W6~~
~~C-12~~	~~12"~~		~~CG1275-4~~	~~CG1275-6~~	~~2278-1W4~~	~~2278-1W6~~

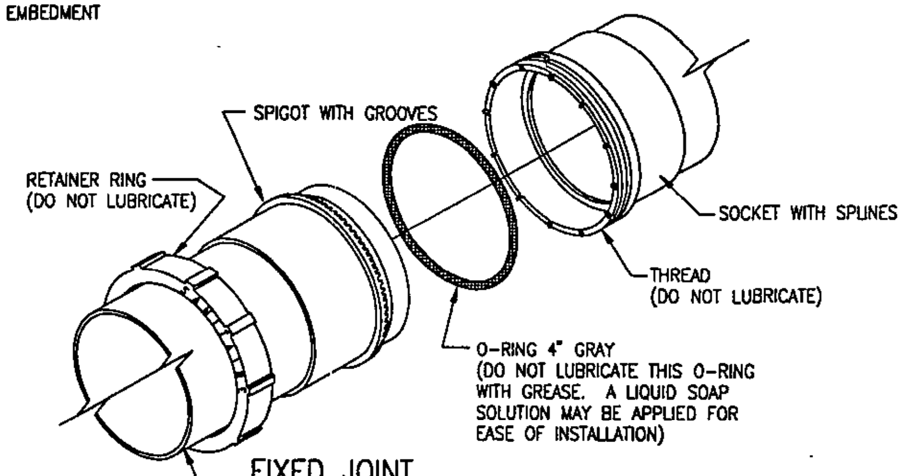


RAISED ANCHOR SUPPORT ASSEMBLY
DETAIL SUP-12

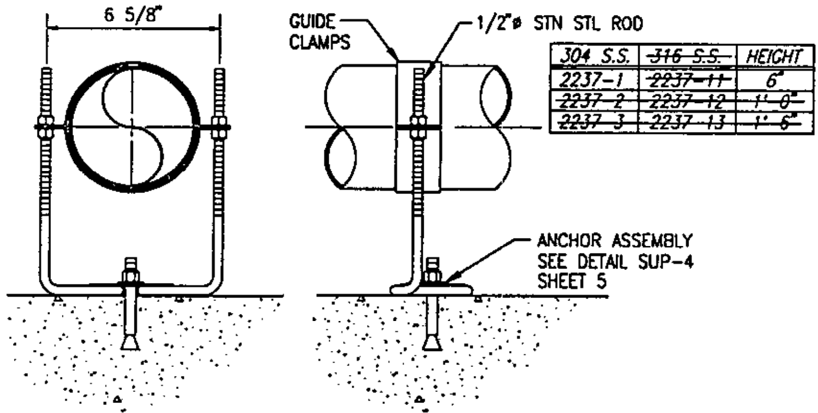


GUIDE SUPPORT
DETAIL SUP-1

304 S.S.	316 S.S.	HEIGHT
~~2346-1SP~~	~~2346-11S~~	~~5"~~
2346-2SP	~~2346-12S~~	8"
~~2346-3SP~~	~~2346-13S~~	~~11"~~

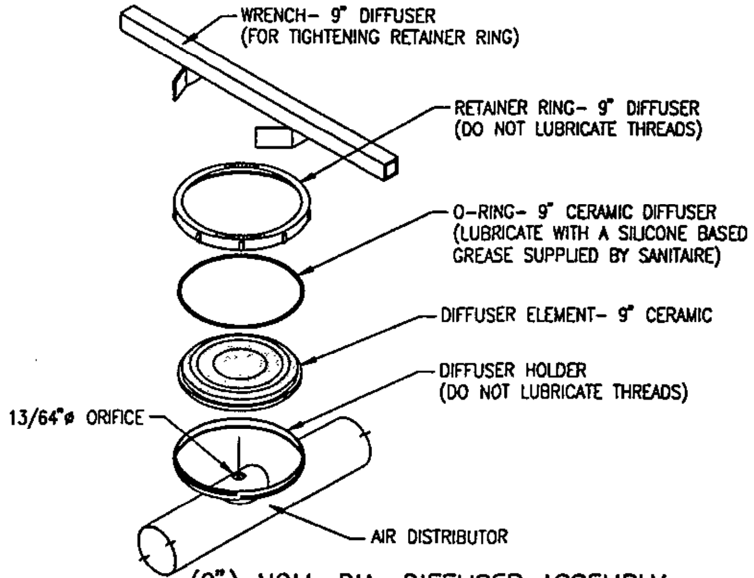


FIXED JOINT
DETAIL FB-10A

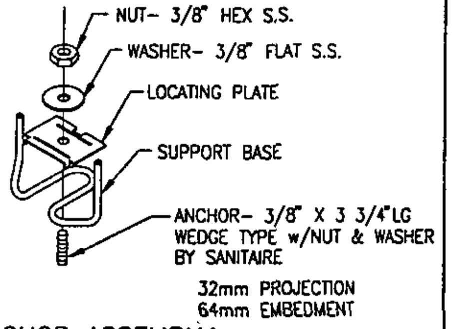


304 S.S.	~~316 S.S.~~	HEIGHT
2237-1	~~2237-11~~	6"
~~2237-2~~	~~2237-12~~	~~1'-0"~~
~~2237-3~~	~~2237-13~~	~~1'-6"~~

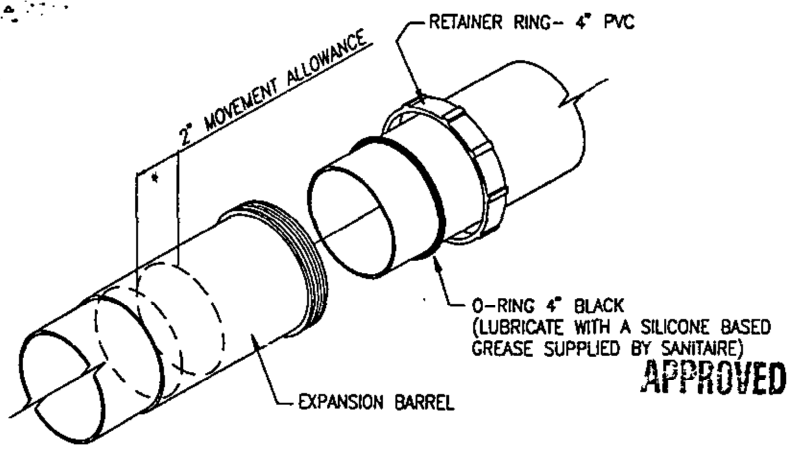
MANIFOLD SUPPORT
DETAIL SUP-20D



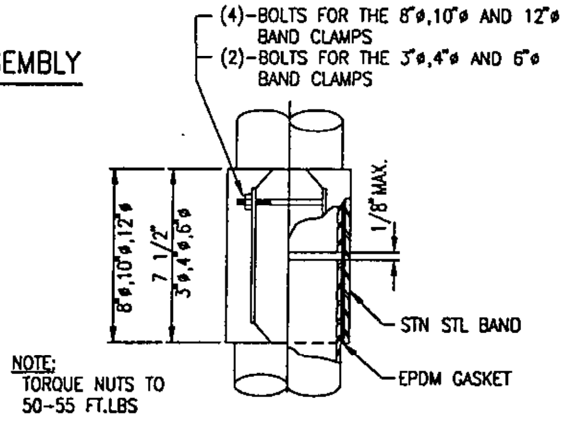
(9") NOM. DIA. DIFFUSER ASSEMBLY
DETAIL FB-1



ANCHOR ASSEMBLY
DETAIL SUP-4



EXPANSION JOINT
DETAIL FB-11



NOTE:
TORQUE NUTS TO 50-55 FT.LBS

CLAMP COUPLING
DETAIL FB-13

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WATER POLLUTION CONTROL CORP.

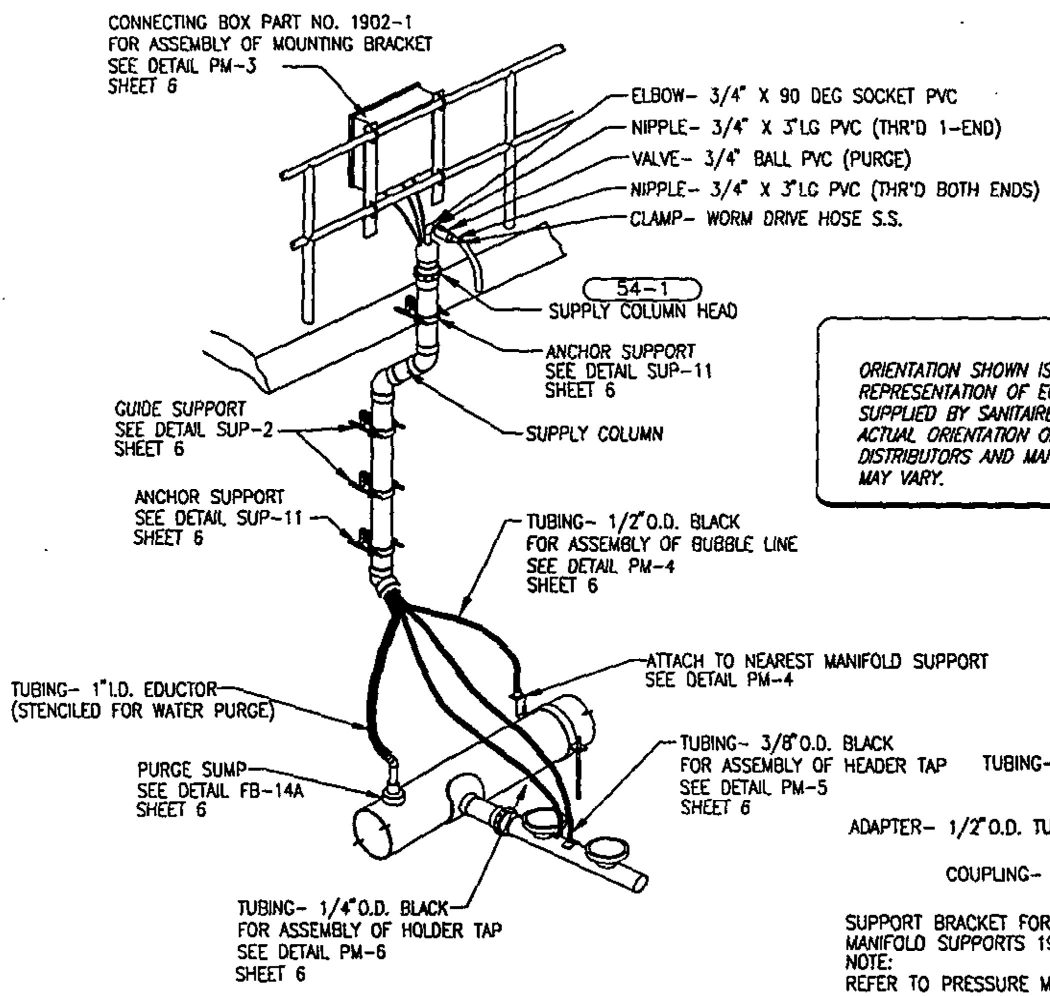
COLESHILL, UK
WASTEWATER TREATMENT PLANT

DETAILS

SANITAIRE®
WATER POLLUTION CONTROL CORP
MILWAUKEE, WISCONSIN

CUST NO. H10706/001				
DWG NO.	NO.	DATE	REVISION	BY

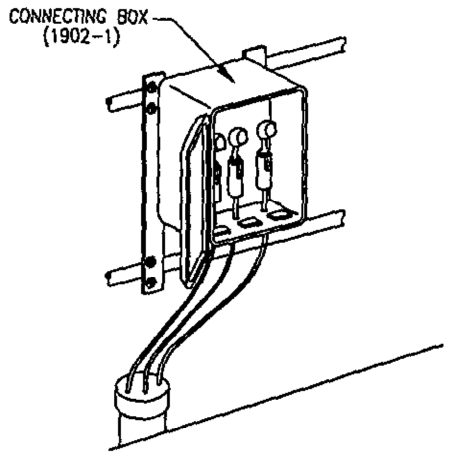
DRWN BY RH	DATE 4-25-97	MODEL	JOB 97-3737
CHKD BY JC	DATE 4-28-97	CER	
APPVD BY ΔΔE	DATE 4-30		SHT E-5



PURGE SUMP/PRESSURE MONITORING ASSY

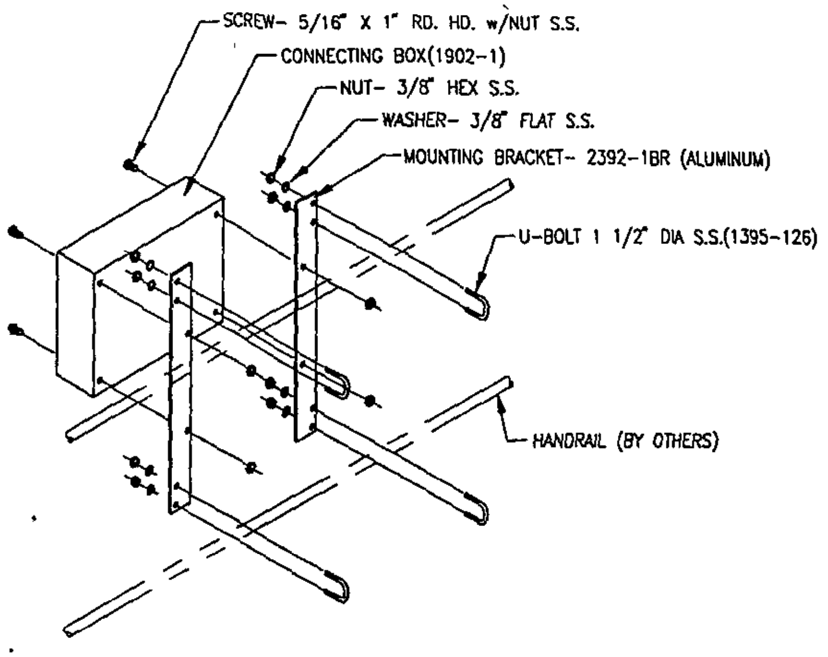
DETAIL PM-1E

ORIENTATION SHOWN IS A GENERAL REPRESENTATION OF EQUIPMENT SUPPLIED BY SANITAIRE. ACTUAL ORIENTATION OF AIR DISTRIBUTORS AND MANIFOLDS MAY VARY.



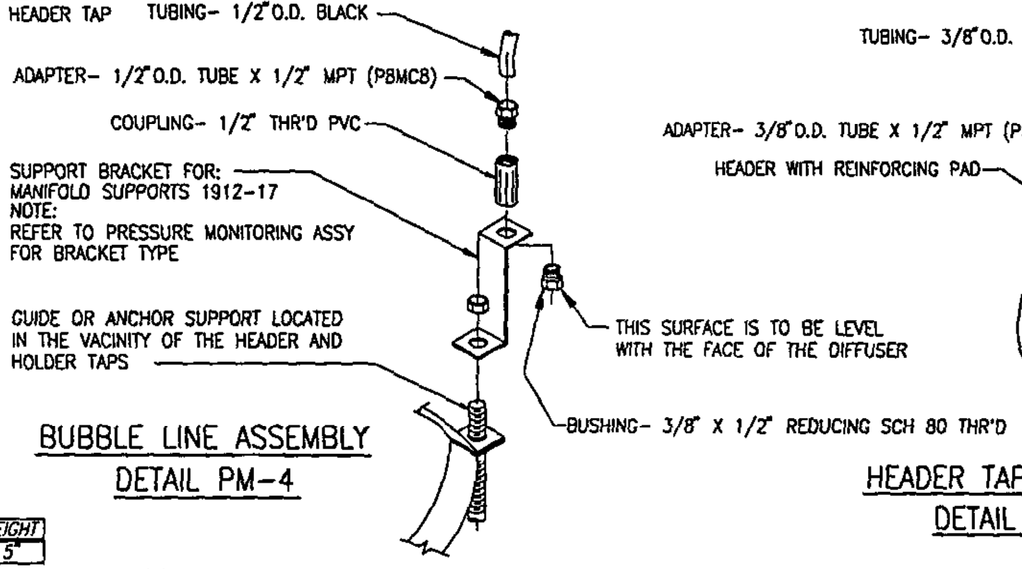
PRESSURE MONITORING PANEL CONNECTION

DETAIL PM-2



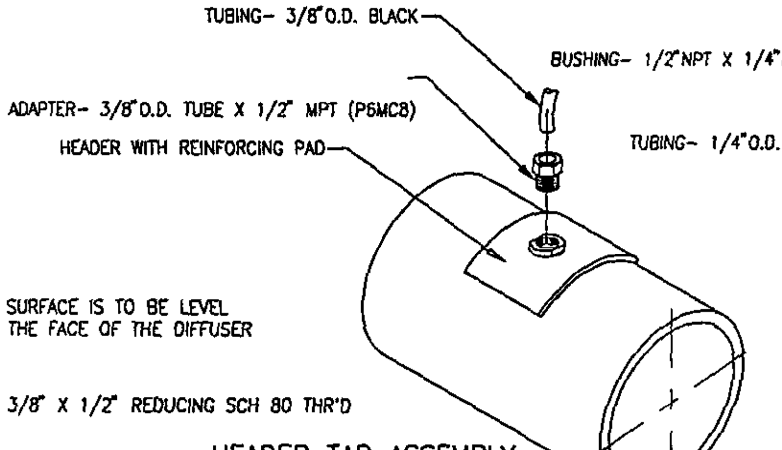
CONNECTING BOX ASSEMBLY

DETAIL PM-3



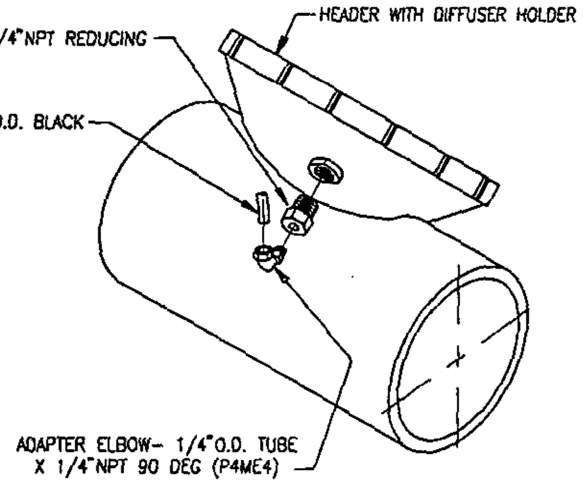
BUBBLE LINE ASSEMBLY

DETAIL PM-4



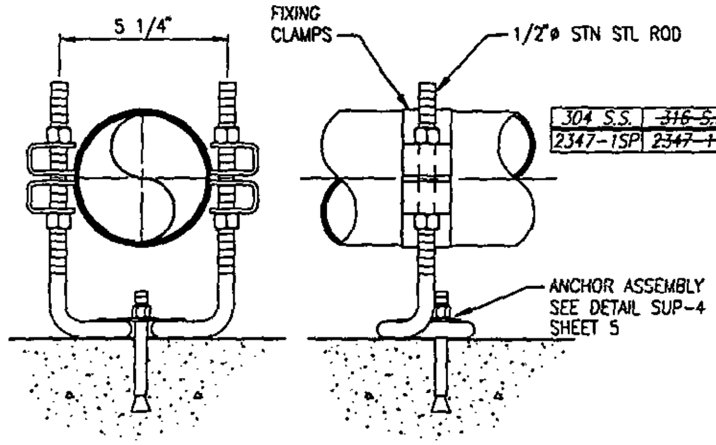
HEADER TAP ASSEMBLY

DETAIL PM-5



HOLDER TAP ASSEMBLY

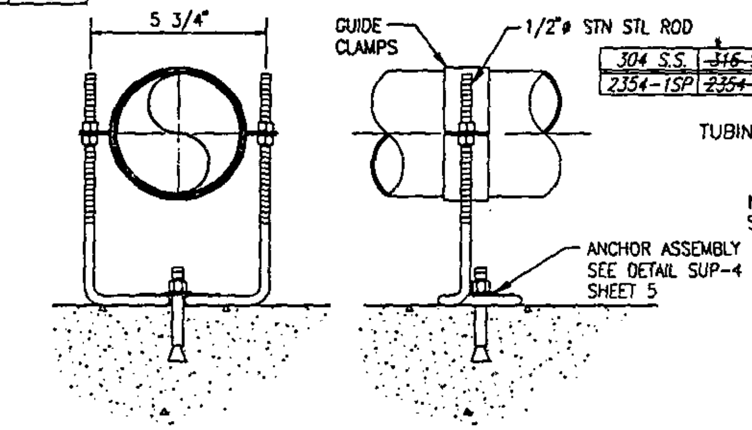
DETAIL PM-6



304 S.S.	~~316 S.S.~~	HEIGHT
2347-1SP	~~2347-11S~~	5"

ANCHOR SUPPORT

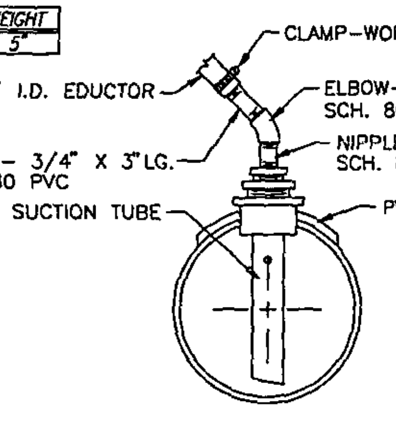
DETAIL SUP-11



304 S.S.	~~316 S.S.~~	HEIGHT
2354-1SP	~~2354-11S~~	5"

GUIDE SUPPORT

DETAIL SUP-2



PURGE SUMP

DETAIL FB-14A

APPROVED FOR CONSTRUCTION

MAY 1 1997

WATER POLLUTION CONTROL CORP.

COLESHILL, UK

WASTEWATER TREATMENT PLANT

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PRESSURE MONITORING
ASSEMBLIES & DETAILS
(3-VALVE CONNECTING BOX)

SANITAIRE®
WATER POLLUTION CONTROL CORP
MILWAUKEE, WISCONSIN

CUST NO.	H10706/001	NO.	DATE	REVISION	BY	DRAWN BY RH DATE 4-25-97 CHKD BY JC DATE 4-28-97 APPVD BY DGE DATE 4-30	MODEL CER	JOB 97-3737 SHT E-6
DWG NO.	PM-0							