Contribution of nitrous oxide emissions from wastewater treatment to carbon accounting

P. Winter, P. Pearce and K. Colquhoun

ABSTRACT

This paper describes research that investigated the contribution of nitrous oxide (N_2O) emissions from wastewater treatment to the greenhouse gas emissions of a wastewater treatment plant (WWTP). The research provided several months of robust data from a large-scale WWTP serving a population equivalent of 284,000. N_2O emissions were monitored online at the ventilation system of a covered activated sludge (AS) plant, therefore capturing the complete off-gas stream. This methodology eliminated errors incurred through sampling of small percentages of emission areas and allowed representative continuous measurements. Nitrogen load and dissolved oxygen (DO) were also monitored. To address seasonal variation, data were recorded in two extensive phases. In addition, three separate 24-hour surveys were conducted. Emissions of CO_2, CH_4 and N_2O associated with treatment were calculated using the UK Water Industry Research carbon accounting workbook. This study measured N_2O emissions from the AS process (nitrification and denitrification) equivalent to 17.5% of the annual GHG emissions (tonnes CO_2e) from processes at the WWTP. The emissions were within the range of published N_2O emissions. The diurnal profiles confirmed literature findings of a trend of increased N_2O emissions when the DO decreased. The DO in the high rate zone of the aeration lanes should be kept above 1 mg l^{-1} to avoid favourable conditions for N_2O emissions during nitrification.

Key words | activated sludge, carbon, greenhouse gas, nitrous oxide, wastewater treatment

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INTRODUCTION

Nitrous oxide (N_2O) is a greenhouse gas (GHG) that occurs naturally as a by-product of biological activity of bacteria living in certain types of plant roots. N_2O is formed in soils (Lopez-Fernandez *et al.* 2007), rivers and estuaries during biological denitrification and nitrification (Dong *et al.* 2004). Agricultural activities such as fertilizer applications and land spreading of manure contribute significantly to N_2O emissions (Scott *et al.* 2000). Combustion of fossil fuel is also an anthropogenic source of N_2O (Barton & Atwater 2002). In 2007, total emissions of N_2O from anthropogenic sources in the UK were 34.3 Mt CO_2e with the agriculture sector contributing 73% of the emissions (UK GHG Inventory National System 2009).

N_2O is a long-lived greenhouse gas with a greenhouse gas potential of 310 times that of carbon dioxide over a period of 100 years. The N_2O concentration in 2005 was 319 ppb, about 18% higher than its pre-industrial value and it has increased by about 0.8 ppb year^{-1} over the past few decades (IPCC 2007).

The UK water industry has to comply with standards derived from EU directives that may impact on N_2O emissions from wastewater treatment. The Urban Wastewater Treatment Directive (Council Directive 91/271/EEC) requires secondary (biological) wastewater treatment and even more stringent treatment where necessary (European Commission 2009). The Water Framework Directive may drive the requirement for ammonium (NH_4-N) removal according to the ecological status of the receiving water. In the UK, the Environment Agency sets and monitors maximum allowable concentrations of NH_4-N in the final

effluent. These discharge consents are site specific. At Reading Wastewater Treatment Plant (WWTP), the site where the research was conducted, the NH_4-N consent is 2 mg l^{-1} as a 95%ile.

Nitrogen removal can be achieved through biological processes that allow nitrification and denitrification to occur under controlled conditions and at a faster rate than would occur in nature. As N_2O is mainly produced during nitrification and denitrification, the production of N_2O occurs in biological nitrogen removal processes of a WWTP. These are biological processes where bacteria metabolise inorganic and organic carbonaceous material from the wastewater to oxidise NH_4-N to NO_3-N and reduce NO_3-N to N_2 gas, respectively. The oxygen required for nitrification is supplied by forced aeration. The wastewater treatment process which is employed at Reading WWTP is depicted in Figure 1. It consists of preliminary treatment (screenings and grit removal); primary treatment (removal of settleable organic solids); secondary treatment by activated sludge process (configured for the removal of nitrogen, phosphorus and soluble organic carbon;

settlement for separation of activated sludge from the final effluent); and tertiary treatment (sand filters for further removal of suspended organic material). Figure 1 also shows the sludge treatment stream of the works.

Reading WWTP is designed for biological removal of nitrogen and phosphorus (BNR process). This process was implemented to meet effluent quality standards for phosphorus, which aim to avoid eutrophication of the receiving water. Nitrogen removal, which is also part of the process, is achieved through nitrification followed by denitrification. The result is a typical total nitrogen concentration in the final effluent of less than 10 mg l^{-1}, which is lower than in most WWTPs. Because of the high degree of removal of total nitrogen the potential for N_2O emissions from the process is therefore higher compared with most plants.

Historically, the water industry did not focus on emissions of GHG; the priority has been to meet regulatory requirements for river quality standards. Recently, the financial regulator Ofwat recommended that each company should audit and quantify the GHG impact of its proposed business plan (Ofwat 2007) and so UK Water Industry Research Limited
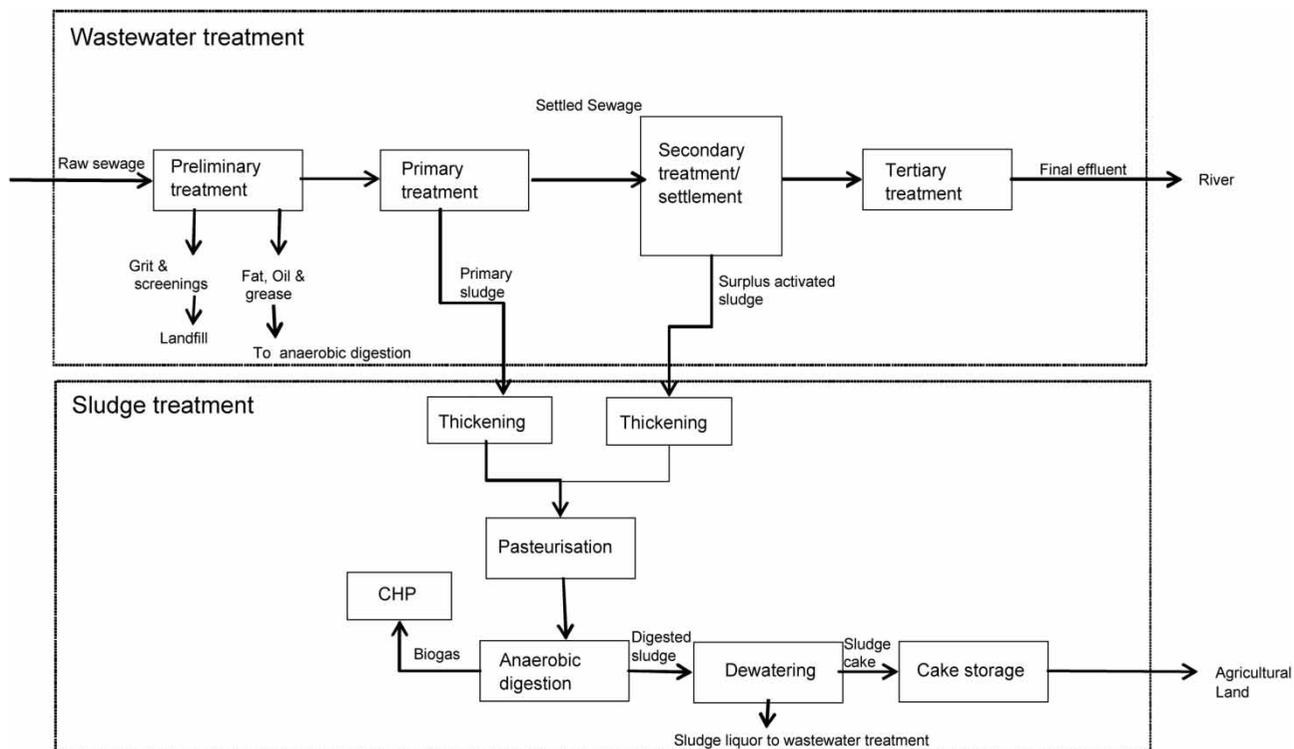

Figure 1 | Wastewater and sludge processes at Reading WWTP.

(UKWIR) developed a methodology for estimating greenhouse gas emissions. However it has been recognised that emissions of nitrous oxides remain difficult to estimate with reasonable accuracy (IPCC 2006; UKWIR 2008).

The methodology suggests the following formula to calculate N_2O emissions from treatment (UKWIR 2008):

$$N_2O \text{ emitted during treatment} = 0.002 \times N \text{ load on secondary treatment} \times 44/28 \tag{1}$$

where $0.002 =$ proposed emission factor for N_2O emissions from secondary treatment; $44/28 =$ conversion of kg N_2O-N into kg N_2O.

The above emission factor has been adjusted to relate only to N_2O from nitrification. It also has a high level of uncertainty, in the range of 30–300%. This means that, for example, for an estimate of 100, 95% of values would be in the range of 30–300 (UKWIR 2009a).

AIM AND OBJECTIVES

The aim of the research was to quantify N_2O emissions from an activated sludge (AS) process and to understand their contribution to GHG emissions from a wastewater treatment plant.

1. Measure N_2O emissions of an AS plant and calculate the mass of N_2O that is emitted during a specified operational period.
2. Calculate the GHG emissions of the WWTP through use of the UKWIR carbon accounting rules and identify the contribution of N_2O emissions.
3. Determine factors influencing N_2O emissions through monitoring of process parameters and wastewater characteristics.
4. Provide recommendations for process improvements to minimise N_2O emissions from the activated sludge process.

The formation of N_2O during wastewater treatment

Figure 2 shows the principal biochemical pathways of nitrification and denitrification that take place during secondary
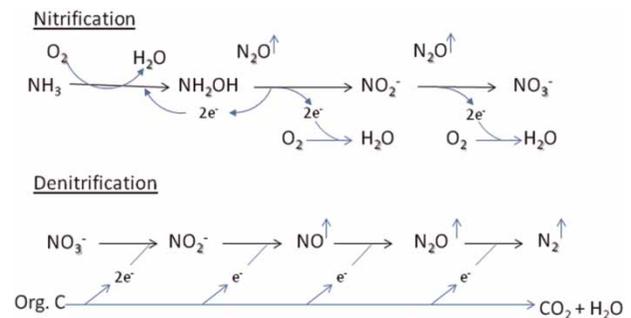
Figure 2 | Nitrification and denitrification in biological wastewater treatment (adapted from Wicht & Beier 1995 and Foley & Lant 2007).

treatment. Nitrification is an oxidation process, where ammonium (NH_4-N) is oxidised to nitrite (NO_2^-) and then to nitrate (NO_3^-). Denitrification is a reduction process where nitrate is reduced via nitrite to elemental nitrogen. Organic carbon acts as the reducing agent.

During nitrification, N_2O may be formed as a by-product at two stages as shown in Figure 2. The N_2O here would be readily stripped out of the wastewater into the gas phase under aerobic conditions owing to aeration of the wastewater to achieve oxygen transfer (Wicht & Beier 1995; Itokawa *et al.* 1996). N_2O production is closely related to nitrite accumulation. Incomplete nitrification with nitrite as an end product results in N_2O accumulation (Wicht & Beier 1995). Tests adding nitrite to the AS process resulted in an increase in N_2O production (Krauth 1993; Tallec *et al.* 2006). N_2O is formed during nitrification if microorganisms use nitrite rather than oxygen as electron acceptor (Krauth 1993).

A low but positive DO supply to the AS plant can result in N_2O emissions during nitrification. Highest N_2O emissions in lab-scale batch experiments were measured at DO concentrations of around $1 \text{ mg } O_2 \text{ l}^{-1}$ (Tallec *et al.* 2006). N_2O emissions were dependent on the DO level of an intermittently aerated reactor treating high strength wastewater. When the DO level was less than $1 \text{ mg } l^{-1}$, up to 40% of removed nitrogen was released as N_2O, whereas N_2O emissions were negligibly small when the oxygen supply was sufficient (Okayasu *et al.* 1997). Krauth (1993) specifies a DO range of 0.5 to $1 \text{ mg } l^{-1}$ at which N_2O concentrations increase. N_2O under low DO conditions was most likely produced by nitrifier denitrification where the oxidation of ammonia into nitrite is followed by the reduction of nitrite

to N_2O and N_2. This sequence is carried out by autotrophic ammonium oxidizers (Tallec *et al.* 2006; Kampschreur *et al.* 2009).

During denitrification, N_2O is an intermediate that may be emitted into the atmosphere if the N_2O reduction is slower than the N_2O production (Krauth 1993). Incomplete denitrification can lead to N_2O emissions. During nitrification, N_2O emissions are associated with increased nitrite concentrations but also with low DO levels as oxygen inhibits denitrification enzymes (Kampschreur *et al.* 2009). In low DO concentrations, N_2O can be the final product of denitrification instead of elemental nitrogen. Tallec *et al.* (2008) measured highest N_2O emissions from denitrifying activated sludge when the oxygen concentration was around $0.3 \, mg \, l^{-1}$. These N_2O emissions from denitrification were 4.4 times higher than the emissions from nitrification at around $1–2 \, mg \, O_2 \, l^{-1}$. Limited availability of organic carbon can increase the N_2O emissions during denitrification and the addition of methanol as an extra carbon source is reported to keep N_2O emissions low (Itokawa *et al.* 1996). However, this is debated, as Krauth (1993) shows that a readily available substrate would result in N_2O emissions because the N_2O reduction rate is slower than the nitrite reduction rate. Peak loads of highly degradable carbon such as industrial effluent could therefore result in increased N_2O emissions.

The impact of temperature on N_2O emissions from wastewater systems is not agreed in the literature. Gejlsbjerg *et al.* (1998) showed increased nitrous oxide production with increasing temperature. Temperature had a larger effect on ammonium oxidation than on nitrite oxidation, which led to high nitrite levels and increased N_2O production. Czepiel *et al.* (1995) found no significant correlation between nitrous oxide emissions and temperature in wastewater systems. Tallec *et al.* (2008) explains that oxygen levels during denitrification (non-covered anoxic tanks) range between 0.4 and $2 \, mg \, l^{-1}$ in winter, which represents favourable conditions for maximum N_2O emissions. Foley & Lant (2007) explain that N_2O is a highly soluble gas in water but, given its low atmospheric concentration, the solubility of N_2O in water is effectively zero in the temperature range $0–40 \, °C$. In a well-mixed aerated system, the mass transfer coefficient is likely to be quite high in comparison with quiescent conditions, and N_2O would be readily stripped out by the aeration of the wastewater in the first aerobic zone.

N_2O emissions from wastewater treatment plants

Conversion factors of wastewater nitrogen to N_2O emitted from biological treatment processes highlight the wide range of reported N_2O emission factors (Foley & Lant 2007; Kampschreur *et al.* 2009). Stephenson (2008) demonstrates that N_2O emissions rates not only vary greatly with type of wastewater treated and process type, they are also highly variable over time at any one site. Table 1 shows some emission factors reported in the literature.

METHODOLOGY

Monitoring of N_2O emissions was carried out from 17 November 2008 to 26 January 2009 (phase 1) and from 20 April to 30 June 2009 (phase 2). In addition, 24-hour surveys were carried out in January (survey 1), May (survey 2) and June (survey 3). Input data required for the carbon accounting spreadsheets were based on 12 months of data covering an annual reporting period for carbon accounting. Monthly calculations were matched with months when N_2O emissions were measured. Figure 3 depicts the scope of the research, its boundary and the main parameters of this work.

The AS plant at Reading WWTP comprises a reactor that is divided into several lanes. The reactor is covered and the process air is vented through a stack. Figure 4

Table 1 | N_2O emission factors reported in the literature

Conditions	Emission factor	Reference
Lab-scale batch tests with sludge from one full-scale nitrifying activated sludge plant (Paris conurbation)	$0.001–0.004 \, kg \, N_2O$-N/kg N treated during nitrification	Tallec *et al.* (2006)
Lab-scale test with sludge from 25 domestic WWTP in Germany	$0–0.146 \, kg \, N_2O$-N/kg N inlet (average of 0.006)	Wicht & Beier (1995)
Based on a single field test (Czepiel *et al.* 1995)	$3.2 \, g \, N_2O$/person/year (range of 2–8)	IPCC (2006)
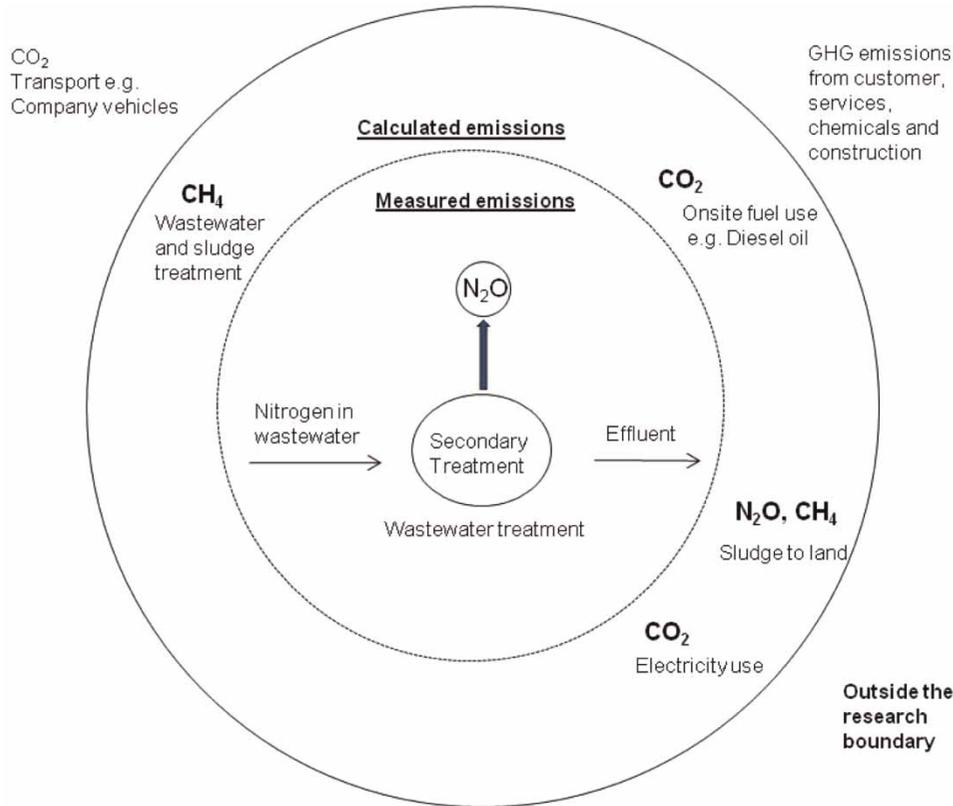
Figure 3 | Scope of the research, its boundary and the main parameters. *Note*: UK guidance notes for the boundary of reportable GHG emissions have changed subsequently and a direct comparison of future emissions may not be possible.
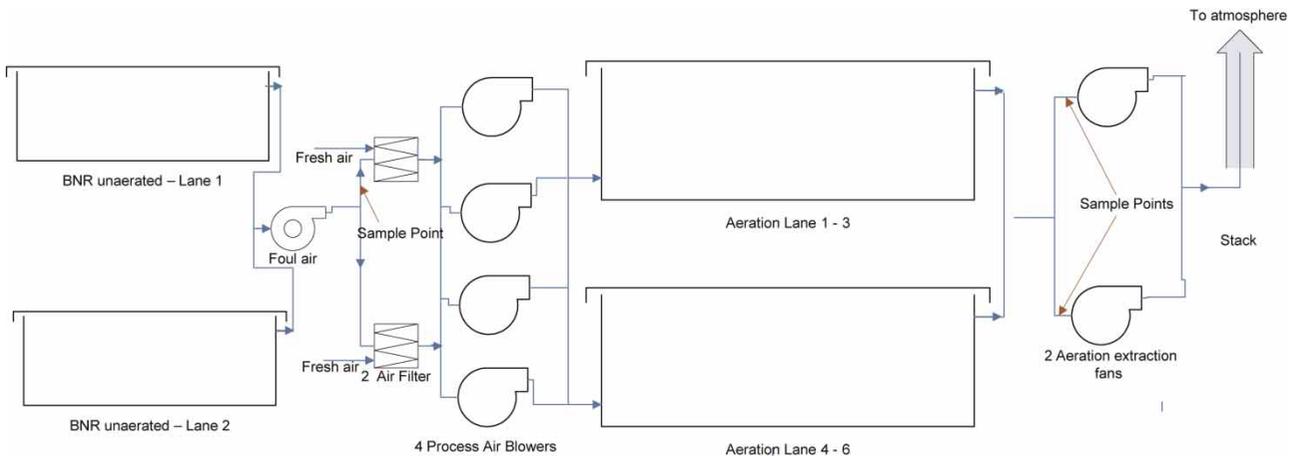
Figure 4 | Process air flow of the activated sludge plant.

shows the process air flow of the AS plant and the sample points for N_2O monitoring.

The two unaerated lanes comprise covered concrete tanks that are internally baffled. The unaerated zones use submersible high speed mixers to prevent settlement. The headspace gas from both lanes is exhausted via a common fan to the inlet of the air filters. There are four centrifugal blowers, which draw a mixture of air from the unaerated

lanes and fresh air through the air filters. The aeration air (process air) supply is regulated in response to the dissolved oxygen in the aerated reactor. Two extraction fans ventilate the headspace of the aeration lanes. The ventilation air flow was typically at least twice the process air flow. The mass of N_2O reported in this paper is based on velocity measurements at the ventilation stack as this was more representative for the emitted air volume (Equations (9) and (10)).

The methodology design was chosen because the AS plant at Reading WWTP is covered and the process air is vented through a stack. This scenario offered the opportunity to measure emissions from a full-scale plant at a single point. Alternative methods such as the use of a sample hood floating on an open aeration tank would have required extrapolating values from a small surface and other uncertainties associated with hood measurements. Gas sampling hoods typically cover less than 0.1% of the emission surface, therefore requiring measurement at many sample locations which have to be predetermined to be representative based on gas flux. At Reading WWTP, if hood measurement had been possible, a typical 1.5 m² sampling hood would cover 0.02% of the emission area. The practicalities of hood sampling would have made representative on-line monitoring over prolonged sampling periods impossible.

Instrumentation for monitoring

A N-Tox® monitoring system for N_2O measurement was used. The instrument comprises an integral sample pump, gas conditioning device, non-dispersive infrared (IR) gas analyser, auto-calibration system and data logging unit. The measurement range of the instrument was 2 ppm N_2O (4 mg/m³)–2,000 ppm N_2O (4,000 mg/m³). The instrument was placed close to the sample points. Data were downloaded via the data logging software. The response time of the instrument was 8–30 s. Readings were taken every minute during a 24-h sampling period.

To identify the nitrogen load to the activated sludge plant, 24-h composite samplers were operated during the monitoring period. The samplers were also used for hourly sampling. Three automatic samplers were operated to sample raw sewage, settled sewage and final effluent.

Calculations of N_2O emissions and CO_2 equivalent emissions

Using the ideal gas law, it can be shown that one mole of a gas occupies 22.41 l under standard conditions.

$$pV = nRT \tag{2}$$

where p = absolute pressure (101.3 kPa); V = volume (litre); n = number of moles. R = gas constant (8.314 l kPa mol^{-1} K^{-1}); T = temperature (273.15 K).

For the calculations from November to February a gas temperature of 283.15 K (10 °C) was assumed. For calculations from April to June, measurements showed that the gas temperatures were around 293.15 K (20 °C).

Therefore:

$$VN_2O_{10\,°C} = \frac{nRT}{p} = \frac{1 \times 8.314 \times 283.15 \text{ mol l kPa K}}{101.3 \text{ kPa mol K}} = 23.24\,l \tag{3}$$

$$VN_2O_{20\,°C} = \frac{nRT}{p} = \frac{1 \times 8.314 \times 293.15 \text{ mol l kPa K}}{101.3 \text{ kPa mol K}} = 24.06\,l \tag{4}$$

The density of N_2O was then calculated taking into account the molar mass:

$$\rho N_2O_{10\,°C} = \frac{m}{V} = \frac{44.02 \text{ g mol}}{23.24 \text{ l mol}} = 1.89 \text{ g l}^{-1} \tag{5}$$

$$\rho N_2O_{20\,°C} = \frac{m}{V} = \frac{44.02 \text{ g mol}}{24.06 \text{ l mol}} = 1.83 \text{ g l}^{-1} \tag{6}$$

Measurements of ppm were then converted into mass of N_2O per m³ of air:

$$1 \text{ ppm}_{N_2O_{10\,°C}} = \frac{1.89 \text{ g}}{10^6 \text{ l}} = 1.89 \text{ mg m}^{-3} \tag{7}$$

$$1 \text{ ppm}_{N_2O_{20\,°C}} = \frac{1.83 \text{ g}}{10^6 \text{ l}} = 1.83 \text{ mg m}^{-3} \tag{8}$$

Based on average velocity measurements (one extraction fan or two fans in operation) and stack diameter, the mass of N_2O per day was calculated based on the volumetric

air flow through the discharge stack (Figure 4).

$$\text{Volumetric air flow}_{1 \text{ fan}} = \text{velocity} \times \varnothing \text{ stack} = 10.2 \text{ m s}^{-1}$$
$$\times \pi (0.59 \text{ m})^2 \times 3,600 \text{ s} \times 24 \text{ h}$$
$$= 964 \times 10^3 \text{ m}^3 \text{ day} \qquad (9)$$

$$\text{Volumetric air flow}_{2 \text{ fans}} = \text{velocity} \times \varnothing \text{ stack} = 15 \text{ m s}^{-1}$$
$$\times \pi (0.59 \text{ m})^2 \times 3,600 \text{ s} \times 24 \text{ h}$$
$$= 1,417 \times 10^3 \text{ m}^3 \text{ day}$$
$$(10)$$

The ventilation air flow was calculated via air velocity measurements taken at the stack. A total of 27 measurements were taken during the second monitoring period and an average ventilation volume for operation with one fan and two fans respectively was used (Equation (9) and (10)). Air flow variations across the stack were within 10% of the average. The calculated volumetric air flow for one fan of 40,200 $\text{m}^3 \text{h}^{-1}$ corresponded well with the process design flow rate of 41,600 $\text{m}^3 \text{h}^{-1}$.

Calculation of N_2O-N emission factors

The emission factor for N_2O is expressed as the fraction of the nitrogen load to the plant that is emitted as N_2O nitrogen. The calculation of emission factors was based on UKWIR guidelines (UKWIR 2008).

$$\text{Emission factor (EF)} = \frac{\text{mass } N_2O\text{-N}}{\text{mass N load}} = \frac{N_2O \text{ mg d}}{\text{N load mg d}} \times \frac{28}{44}$$
$$(11)$$

Calculations of CO_2 equivalent emissions

The UKWIR (2009a) GHG Reporting Workbook was used for calculating generic GHG emissions from Reading WWTP as CO_2e. In addition indirect emissions contributing to the CO_2e are CO_2 from electricity imports and CH_4 from landfilled grit and screenings. Process emissions of CO_2 are excluded because they are considered to be short cycle (i.e. derived from recent biological activity).

RESULTS AND DISCUSSION

Tables 2 and 3 give a summary of the average results of phase 1 and phase 2, respectively.

Table 2 data shows that the AS plant emitted on average 10.6 ppm N_2O during phase 1. The average daily mass of N_2O derived from this measurement and the ventilation air volume was 21.9 kg. Taking into account the nitrogen load to the activated sludge plant, an emission factor of 0.0053 kg N_2O-N kg N^{-1} was calculated. That is 0.53% of the nitrogen load to the AS plant was emitted as N_2O-N during phase 1.

It can be seen from the Table 2 data that the gaseous N_2O emissions from the anoxic zone were insignificant for the assessment. These emissions were therefore not monitored during phase 2.

Table 3 summarises phase 2 of the research. In general, the emissions during this phase were higher than during phase 1. On average 12.3 ppm N_2O was emitted, which was equivalent to a mass of 24.8 kg N_2O. During phase 2, 0.58% of the nitrogen load to the AS plant was emitted as N_2O-N. The DO in the aeration lanes was on average 1.93 mg l^{-1}, about 0.9 mg l^{-1} lower than during phase 1. The nitrogen load to the AS plant was about 2.7 tonnes of nitrogen, which was 5% higher than in phase 1.

Analysis of N_2O data

Figures 5 and 6 give an overview of the daily average, peak and minimum N_2O concentrations for both phases. The average during phase 1 was 10.6 ppm N_2O. Peak concentrations were in general between 15 and 20 ppm. Figure 6 clearly highlights the low gaseous emissions found when monitoring the anoxic zone. The mass of gaseous N_2O emitted from the anoxic zone contributed less than 1% to the mass of N_2O from the aeration lanes and was not considered to be significant. However, dissolved N_2O that is formed in the anoxic zone would be carried over to the aerobic zone and stripped out by the intense aeration.

Figure 6 shows the N_2O concentrations during phase 2. The average concentration during this phase of monitoring was 12.3 ppm. There was a general trend of increasing daily average concentrations during May. There were two

Table 2 | Summary of the results of monitoring phase 1

		Average	St Dev	Max	Min
N$_2$O aerobic zone November 2008–January 2009					
N$_2$O	ppm	10.6	1.0	26.1	2.1
N$_2$O	mg m^{-3}	20.1	2.0	24.6	16.7
N$_2$O	g h^{-1}	913.8	114.6	1,152.1	669.3
N$_2$O	kg day^{-1}	21.9	2.8	27.7	16.1
N$_2$O-N/kg N to activated sludge plant	kg kg N^{-1}	0.0053	0.0010	0.0075	0.0037
N$_2$O-N/kg N inlet	kg kg N^{-1}	0.0051	0.0009	0.0065	0.0033
Ventilation air flow (calculated from velocity measurements)	m^3 h^{-1}	45,829	6,998	59,054	40,157
N$_2$O anoxic zone 16 Jan 2009–26 Jan 2009					
N$_2$O	ppm	0.9	0.2	10.3	0.0
N$_2$O	mg m^{-3}	1.7	0.3	2.3	1.1
N$_2$O	g h^{-1}	3.0	0.6	4.0	2.0
N$_2$O	kg day^{-1}	0.07	0.01	0.10	0.05
N$_2$O-N/kg N to activated sludge plant	kg kg N^{-1}	0.00003			
N$_2$O-N/kg N inlet	kg kg N^{-1}	0.00004			
Air flow anoxic zone (calculated)	m^3 h^{-1}	1,747			
Final effluent flow	m^3 day^{-1}	59,066	4,680	72,294	48,637
Dissolved oxygen aerobic zone	mg l^{-1}	2.81	1.74	8.86	0.29
Wastewater (14 composite samples 6 December 2008–27 January 2009)					
Total nitrogen inlet	kg day^{-1}	2,607	688	4,106	1,115
Total nitrogen settled sewage	kg day^{-1}	2,562	446	3,396	1,886
Total nitrogen primary liquor	kg day^{-1}	30	19	84	7
Total nitrogen to activated sludge	kg day^{-1}	2,592			
Total nitrogen in final effluent	kg day^{-1}	576	114	817	428

short periods when data was not collected. The daily average concentrations in June (13.6 ppm) remained relatively high compared with the previous months with a trend to decrease at the end of the monitoring period. In general, higher N$_2$O concentrations were measured in this phase than during phase 1.

Analysis of dissolved oxygen data

Dissolved oxygen (DO) figures in Tables 4 and 5 represent daily spot readings from SCADA. However, this would be insufficient detail for the assessment of diurnal profiles of N$_2$O. Literature clearly indicates the importance of DO levels for N$_2$O emissions (Okayasu *et al.* 1997; Tallec *et al.* 2006). To assess the relation, N$_2$O profiles of the 24-hour surveys were plotted together with the corresponding DO as 15-minute averages.
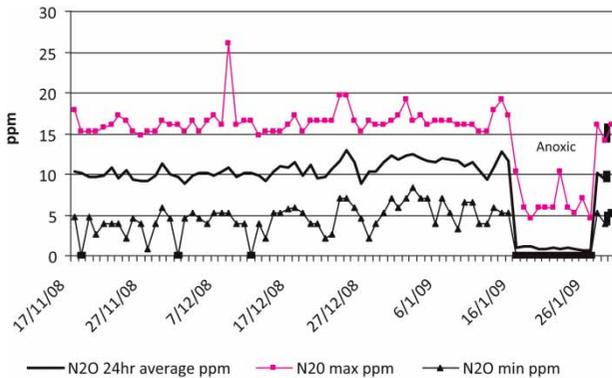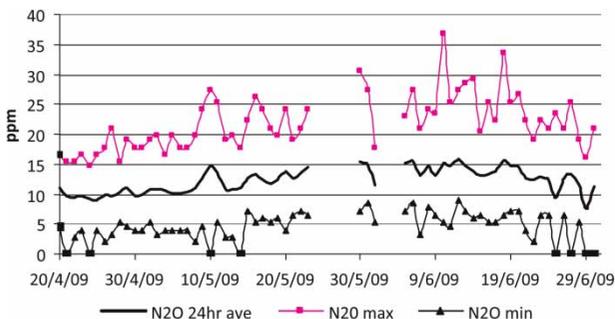
Figures 7 to 9 show the DO concentrations in the aeration lanes and N$_2$O emissions, respectively. The DO levels are shown in the high rate zone, which is the beginning of the aerobic zone and in the low rate zone, the end of the aerobic zone. The figures show a trend that was apparent for many days in particular during phase 2 where elevated N$_2$O emissions were noted in the afternoon. The DO levels, in general, tended to be low in the afternoon after initially increasing during the morning period.

It can be seen that the DO concentrations in the high rate zone were frequently less than 1 mg l^{-1}; such a low positive DO provides favourable conditions for N$_2$O formation. This is not untypical as most of the BOD is

Table 3 | Summary of the results of monitoring phase 2

		Average	St Dev	Max	Min
N$_2$O aerobic zone April 2009–June 2009					
N$_2$O	ppm	12.3	2.0	36.8	2.1
N$_2$O	mg m^{-3}	22.1	4.6	29.1	0.0
N$_2$O	g h^{-1}	1,035.2	196.7	1,496.7	0.0
N$_2$O	kg day^{-1}	24.8	4.7	35.9	0.0
N$_2$O-N/kg N to activated sludge plant	kg kg N^{-1}	0.0058	0.0011	0.0086	0.0038
N$_2$O-N/kg N inlet	kg kg N^{-1}	0.0068	0.0014	0.0095	0.0041
Ventilation air flow (calculated from velocity measurements)	m^3 h^{-1}	46,786	6,347	58,298	30,921
Final effluent flow	m^3 day^{-1}	54,986	3,310	68,029	49,358
Dissolved oxygen aerobic zone	mg l^{-1}	1.93	0.47	6.61	0.04
Wastewater (25 daily composite samples May 2009–June 2009)					
Total nitrogen inlet	kg day^{-1}	2,396	289	3,272	1,910
Total nitrogen settled sewage	kg day^{-1}	2,611	301	3,521	2,189
Total nitrogen primary liquor	kg day^{-1}	126	44	253	42
Total nitrogen to activated sludge	kg day^{-1}	2,737			
Total nitrogen in final effluent	kg day^{-1}	876	132	1,263	634

Figure 5 | Daily average, minimum and peak N$_2$O concentrations during phase 1.

Figure 6 | Daily average, minimum and peak N$_2$O concentrations during phase 2.

oxidised in this zone resulting in a high oxygen demand. The DO concentrations in the low rate zone were, in general, between 1.5 and 2.5 mg l^{-1} in the afternoon.

Figure 10 illustrates the correlation between N$_2$O emissions and the average DO (survey 1). It shows a negative relationship between these two parameters, where higher DO levels correspond with lower N$_2$O emissions, although the correlation is not strong ($R^2 = 0.49$). The weak correlation is probably a result of the large scatter in the data set.

Analysis of wastewater nitrogen

Figure 11 shows the daily average nitrogen load to the AS plant and the N$_2$O-N emissions during phase 2. A definitive interpretation is difficult, as the nitrogen load was not monitored continuously. However, it can be seen that the curves of N$_2$O-N emissions and N-load have a similar shape, which may indicate that an increase in N$_2$O-N emissions was influenced by an increase in N-load to the AS plant.

Analysis of 24-h surveys

Three 24-hour surveys were carried out. Table 4 gives an overview of the data.

Table 4 | Overview of 24-hour surveys

	Unit	Survey 1	Survey 2	Survey 3
N_2O	ppm	9.4	11.7	13.3
N load to AS plant	kg N	2945	3021	2862
N_2O-N emission	kg N_2O-N	10.97	13.08	17.98
Emission factor	kg N_2O-N/kg N	0.0037	0.0043	0.0063
DO	mg l^{-1}	1.47	1.61	1.28
Temperature				
Ambient max.	°C	9.9	15.2	22.4
Ambient min.	°C	4.4	14.8	8.9
Wastewater	°C	Not recorded	15.2	18.0
Ventilation air	°C	Not recorded	Not recorded	24.3
pH wastewater		8.1	7.8	7.5

Table 5 | Calculated CO_2e and measured N_2O emissions

	Unit	Month 12	Month 1	Month 5	Month 6	Annual
Measured N_2O emissions and associated CO_2e						
N_2O	ppm	10.5	11.3	12.1	13.3	11.5
N_2O	kg	666	637	789	755	8,523
CO_2e	kg	206,460	197,470	244,466	234,050	2,642,130
Calculated CO_2e from the WWTP through UKWIR workbook						
CO_2e WWTP	kg	1,203,679	1,176,575	1,089,896	1,053,435	13,286,160
N_2O (sewage treatment)	kg	217	217	217	217	2,608
CO_2e (from N2O)	kg	67,270	67,270	67,270	67,270	808,480
Calculated CO_2e from the WWTP including the measured proportion of N_2O						
CO_2e WWTP	kg	1,342,869	1,306,775	1,267,092	1,220,215	15,119,810
CO_2e (from N_2O)	%	15.4	15.1	19.3	19.2	17.5

Table 4 shows the highest N_2O emissions during survey 3. The nitrogen load to the AS plant was comparatively low, resulting in a high emission factor of 0.63%. This survey was carried out on a warm summer day with a maximum temperature of 22.4 °C and relatively warm sewage. The average DO on that day was low compared with the other surveys. In contrast the lowest emissions in this overview were recorded during survey 1 with 10.97 kg N_2O-N emitted on that day resulting in an emission factor of 0.37%.

Figures 12 to 14 depict the hourly averages of nitrogen load to the AS plant, N_2O-N emissions and DO in the aeration lanes (averages of high and low rate zones) for the three 24-hour surveys.

Analysis of CO_2 equivalent emissions

Table 5 gives an overview of the calculated CO_2e emissions from Reading WWTP. The UKWIR GHG workbook for estimating operational GHG emissions (UKWIR 2009a) calculates a theoretical mass of N_2O for sewage treatment and pumping. In order to derive the contribution of the N_2O emissions from this research, this calculated mass of N_2O emissions was replaced by the mass derived from the measured N_2O emission. Overall this investigation resulted in a higher 'carbon footprint' than the one calculated from the workbook.

Table 5 shows that the combined output of the sewage and sewage sludge workbook was 13,286,160 kg CO_2e per
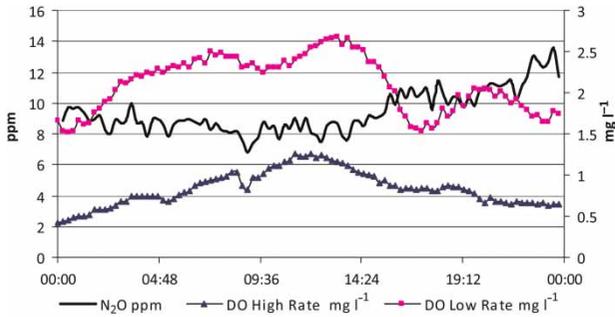
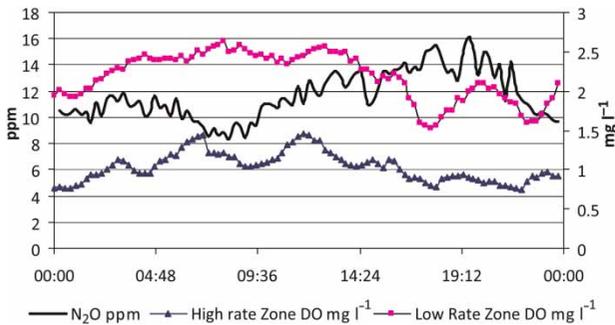**Figure 7** │ DO in aeration lanes and N_2O emissions (survey 1).

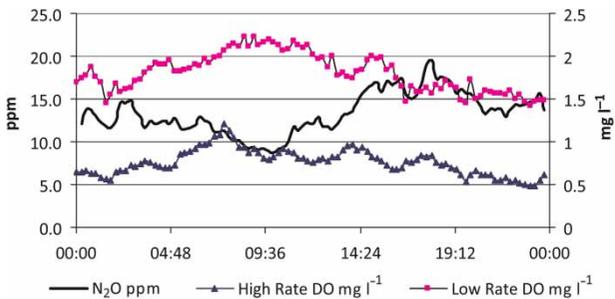**Figure 8** │ DO in aeration lanes and N_2O emissions (survey 2).

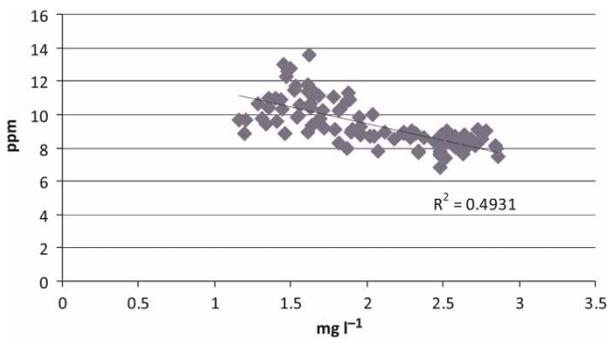**Figure 9** │ DO in aeration lanes and N_2O emissions (survey 3).

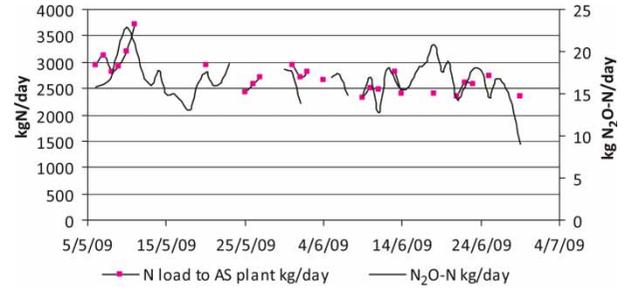**Figure 10** │ Correlation between N_2O emissions (ppm) and DO in aeration lanes (survey 1).

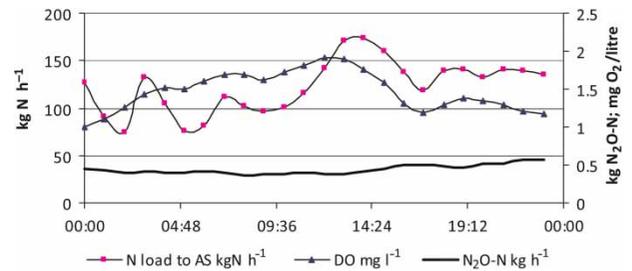**Figure 11** │ Nitrogen load and N_2O-N emissions (kg/d) vs. time (phase 2).

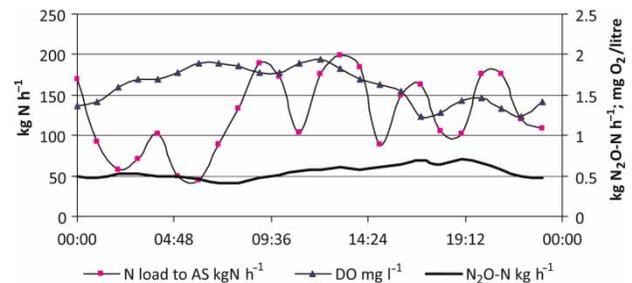**Figure 12** │ Hourly averages of N load, N_2O-N emissions and DO (survey 1).

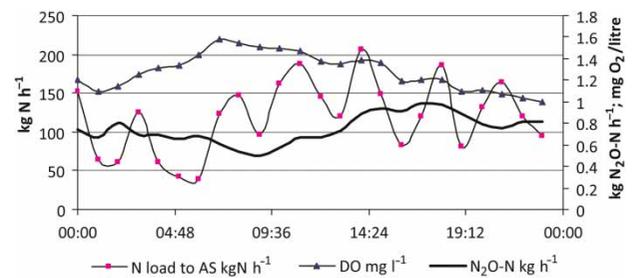**Figure 13** │ Hourly averages of N load, N_2O-N emissions and DO (survey 2).

Figure 14 │ Hourly averages of N load, N_2O-N emissions and DO (survey 3).

year (April 2008–March 2009). On a monthly basis, the 'carbon footprint' from the WWTP was lower during monitoring phase 2 owing to improved plant performance: less imported electricity and a higher electricity generation from CHP.

Replacing the mass of N_2O calculated through the workbook with the mass of N_2O derived from this study (8,523 kg N_2O year^{-1}), it can be calculated that approximately 17.5% of the CO_2e emissions from sewage treatment and pumping and sludge treatment and disposal would be due to N_2O emissions. The contribution of N_2O to the CO_2e emissions was higher (19%) in month 5 and 6 than in month 12 and 1 (15%). This was only partly due to the increase in N_2O emissions but also due to the reduced 'carbon footprint' of Reading WWTP as discussed above.

It should be noted that the estimated annual measured emissions are based on the measurements taken during phase 1 and 2, including the measurements during November 2008 and April 2009. The estimated annual emissions calculated from the UKWIR workbook was based on the period of April 08–March 09.

Interpretation of the results

The contribution of nitrous oxide emissions estimated from this study from wastewater treatment accounted for approximately 17.5% of the CO_2e process emissions from the WWTP. The emission factor was 0.0056 kg N_2O-N emitted/kg N load on secondary treatment. This was a factor of 2.8 higher than the emission factor used in the UKWIR GHG workbook. Importantly it was also within the range of emission factors that are reported in literature and within the range of uncertainty of 30–300% reported by UKWIR (2009a).

The emission factor from the UKWIR GHG workbook relates to nitrification only. Since the biological treatment processes at Reading WWTP remove nitrogen through nitrification followed by denitrification, it was likely that the emission factor derived from this work was higher than the theoretical because N_2O is formed during nitrification as well as denitrification. UKWIR (2008) assumes a 50:50 split for N_2O emissions between the two pathways of nitrification and denitrification.

Factors that influence the emissions of N_2O addressed in this research were the DO in the aeration lanes and the nitrogen load to the AS plant. Literature suggests that a low positive DO in the aeration lanes (i.e. during nitrification) provides favourable conditions for N_2O emissions. The analysis of the 24-hour surveys showed that, frequently, the DO in the beginning of the aeration lanes decreased to levels below 1 mg l^{-1} in the afternoon. During the same period of time, nitrous oxide emissions increased. Linear regression analysis confirmed an inverse relationship between DO and N_2O; however, the correlation did not provide sufficient ground to prove or disprove the relationship. However the objective of this research was to capture emission data from an operating large-scale WWTP, rather than from an artificially controlled small-scale environment. This inevitably resulted in data sets with a relatively large scatter owing to contributing mechanisms such as plant performance and variation in wastewater quality and quantity. In addition, dissolved oxygen levels are closely related to wastewater temperature. The influence of temperature on the DO was not discussed in this paper; however the project was conducted in two phases to capture seasonal variation.

It has been reported that incomplete denitrification can lead to N_2O emissions (Kampschreur *et al.* 2009). The N_2O emissions from the anoxic zone, where denitrification takes place, were found to be insignificant during phase 1. However this does not mean that no N_2O was produced during this stage of the process. N_2O, which was produced in the anoxic zones, may be carried over to the aerated zones in a dissolved or suspended state where it is readily transferred into the gaseous phase via the action of air stripping. The DO in the anoxic zones was not monitored as part of this research. It is therefore not possible to assess the impact of denitrification on N_2O emissions from this work.

Clear diurnal differences were not seen during phase 1 with N_2O emissions spread relatively evenly throughout 24 h. However, in general, the majority of peak concentrations occurred p.m. This was more pronounced during phase 2, with the majority of days showing a N_2O emission peak in the afternoon.

The 24-h surveys confirmed the trend of increasing N_2O emissions during the day. This may have been related to the decrease of DO. Factors influencing DO may have been the nitrogen load to the plant which resulted in a high oxygen demand and wastewater temperature. The DO levels

peaked between 8 a.m. and noon before decreasing in the afternoon. The nitrogen load was more erratic; however highest loads occurred between 13:00 and 14:00 h. N_2O-N emissions appear to be highest in the afternoon with peaks between 17:00 (survey 3) and 23:00 (survey 1). The surveys suggested that the increasing nitrogen load to the plant resulted in a decrease of DO in the aeration lanes, which in turn favours the formation of N_2O emissions.

The DO could be altered with the aim of reducing N_2O emissions without compromising the overall performance of the WWTP. The DO target at the WWTP for the high rate zone is $2\,mg\,l^{-1}$; however this was not achieved for the majority of the monitoring period. Increasing the aeration capacity and providing more air to the system would, however, increase the electricity requirements, which would increase the GHG emissions of the WWTP.

The data from the two monitoring phases indicated that, overall, N_2O emissions were higher during phase 2 than during phase 1. However, they were, in general, within two standard deviations of the mean (Tables 2 and 3). Therefore, a seasonal variation was not established from the data gained during this research.

The extrapolated annual N_2O-N emissions, nitrogen load to the AS plant and mass of nitrogen in the effluent are depicted in Figure 15. The data are derived from the average data of both monitoring phases. The annual mass of N_2O-N emitted was 5.5 tonnes (8.6 tonnes N_2O).

The estimated annual nitrogen load to the AS plant was 973 tonnes. The AS process removed 78% of the nitrogen in the wastewater during phase 1 and 68% during phase 2. Approximately 700 tonnes of nitrogen were converted to nitrogen gas.

The UKWIR GHG workbook (2009a) generates a lower value for N_2O emissions than derived from this research. Importantly, the emission factor derived from this work was within the range of emission factors that are reported in literature and within the range of uncertainty reported by UKWIR (2009a).

Using the UKWIR GHG workbook (UKWIR 2009a) and boundary conditions, Thames Water's overall GHG emissions for 2008/2009 were calculated to be 848,130 tCO_2e (Thames Water 2009). Based on the data from this research, Reading WWTP contributes 1.8% of the total emissions and the N_2O emissions from the AS plant contribute 0.3% of the company's GHG emissions. For carbon accounting, Reading WWTP would contribute 1.6% and the emissions from the AS plant would contribute 0.15% of the company's GHG emissions.

Establishing a single emission factor is exceptionally difficult because the processes used in biological wastewater treatment are diverse and complex involving nitrification and denitrification. It is therefore important to understand the origin of any published emission factor. Other factors such as geographic influences and how the economic recession could have affected nitrogen in wastewater and subsequent emissions may need to be considered for the derivation of a robust emission factor. The data reported here contributes to the knowledge of GHG emissions from wastewater treatment; however this site-specific case study is not sufficient to confirm a UK-wide emission factor. By referencing this study it would suggest that the costs of undertaking the recommendation by UKWIR (2009a) for the UK water industry to conduct a wider sampling programme on a large number of WWTPs with the aim to derive an improved, UK-specific emission factor and to reduce the uncertainty would be significantly above the suggested £220,000 and therefore prohibitively expensive.

CONCLUSIONS

The research provided several months of robust data from a large-scale WWTP with a design population equivalent of 285,000 to improve understanding of the significance of N_2O emissions from wastewater treatment. The ability to monitor and representatively sample the entire off gas stream for several weeks at a time has allowed for robust emission data to be collected relevant to this plant
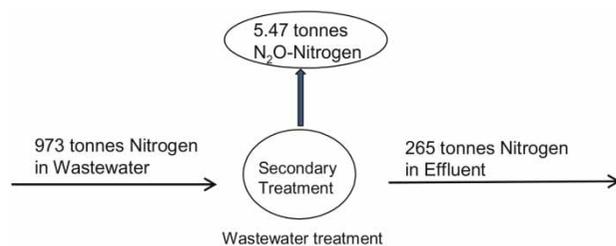
Figure 15 | Estimated annual N_2O-N emissions and mass of nitrogen in wastewater and effluent.

configuration (nitrogen removal activated sludge). However, as discussed in the interpretation section, a single site- and process-specific case study is not sufficient to confirm a UK-wide emission factor.

In this study the contribution of N_2O emissions from wastewater treatment to the GHG emissions of the WWTP from the AS process accounted for approximately 17.5% of the CO_2e process emissions from the WWTP.

The N_2O-N emission factor derived from this research was 0.0056 kg N_2O-N emitted/kg N load on secondary treatment (0.56%). The emission factor used in the UKWIR GHG workbook is lower, because it relates only to nitrification. It is important to note that the emission factor derived from this work was within the range of emission factors that are reported in literature and within the range of uncertainty reported by UKWIR (2009b). The processes at Reading WWTP remove nitrogen through nitrification followed by denitrification, and it is established that both pathways contribute to the N_2O emissions.

Diurnal profiles indicated that DO in the aeration lanes and the nitrogen load to the AS plant influenced N_2O emissions. However the measurements from a large operating WWTP resulted in data sets of variable nature. A significant seasonal variation of N_2O emissions could not be established from this research. The DO in the high rate zone of the aeration lanes should be kept above 1 mg l^{-1} to avoid favourable conditions for N_2O emissions during nitrification.

DISCLAIMER

This work was carried out as part of the Thames Water Innovation programme. The views expressed in the paper are those of the authors and not necessarily those of Thames Water.

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