Spatial and short-term temporal distribution of fugitive methane and nitrous oxide emission from a decentralised sewage mining plant: a pilot study

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ABSTRACT

The decentralisation of wastewater treatment operations exposes several environmental consequences. This includes the fugitive emission of two greenhouse gases, nitrous oxide (N₂O) and methane (CH₄). The magnitude of these emissions is presently unclear. Therefore, it is necessary to measure the extent of the release of N₂O and CH₄ gas from decentralised wastewater treatment plants (WWTPs) in order to quantify the impact these emissions will have on the environment and to determine strategies to reduce them. Specifically, this pilot study employed an online non-dispersive infrared (NDIR) gas analyser and flux hood to evaluate the spatial and short-term temporal distribution of N₂O and CH₄ flux over half a day, from an aeration tank system within a decentralised sewage mining plant. The aeration tank system was able to emit N₂O fluxes of up to 11.6 g N₂O m⁻² day⁻¹ and CH₄ fluxes of up to 1.1 g CH₄ m⁻² day⁻¹. The N₂O and CH₄ fluxes varied rapidly over short time intervals in the same position (as high as 45% for N₂O and 36% for CH₄) and could almost triple in magnitude between two different positions across the surface of the aeration tank (within a distance no greater than 1.5 to 2 m).

Key words | decentralised, fugitive, gas, spatial, temporal, wastewater

INTRODUCTION

Atmospheric nitrous oxide (N₂O) and methane (CH₄) are both known to directly enhance the greenhouse effect, and as such they are regarded as greenhouse gases (GHGs). Recently obtained data show that current tropospheric concentrations are between 322 and 323 parts per billion (10⁹) (ppb) for N₂O and are between 1750 and 1871 ppb for CH₄ (Blasing 2012). Despite existing in lower concentrations in the troposphere in comparison to carbon dioxide (CO₂) (that has a current tropospheric concentration of 390.5 parts per million (ppm)), N₂O and CH₄ are much more effective at trapping infrared radiation (heat) in comparison to CO₂, and as a result can have a greater influence upon positive radiative forcing. More precisely, N₂O has 298 times greater atmospheric heating potential over 100 years in comparison to CO₂, and CH₄ has 25 times greater atmospheric heating potential over 100 years in comparison to CO₂ (Intergovernmental Panel on Climate Change 2007). Additionally, N₂O can breakdown and eliminate ozone (O₃) in the stratosphere. This has a negative impact upon the Earth’s ecosystem, as the reduction of O₃ results in greater levels of biologically damaging downwelling solar ultra violet (UV) radiation being able to penetrate the atmosphere and reach the surface of the Earth (McKenzie et al. 2011). Both UVB (short wavelength) and UVA (long wavelength) radiation can harm both humans and animals by initiating topical, cellular and even DNA damage to unprotected living tissue (Parisi et al. 2004).

During the sewage treatment process, N₂O is produced in and released from wastewater containing a concentration of nitrogen-based organic material, typically originating from waste matter produced by humans. N₂O can be generated and emitted via two pathways: the oxidation of...
ammonia to nitrate under aerobic conditions (nitrification) and the reduction of nitrate to dinitrogen gas under anaerobic conditions (denitrification). Generally, 0.5 and 1% of all nitrogen (N) entering a wastewater treatment plant (WWTP) is converted and emitted as N₂O gas (Townsend-Small et al. 2011). This N to N₂O gas conversion percentage can vary greatly from WWTP to WWTP and can be correlated to a number of biochemical and physical parameters such as: acidity (pH), air stripping, dissolved oxygen (DO) level, rapid changes in treatment system conditions, chemical oxygen demand (COD), influent N concentration and spikes in ammonium and nitrite (Kampschreur et al. 2009a; Law et al. 2012). Across a WWTP, fugitive N₂O gases are most likely to be measured from anaerobic/anoxic tanks, effluent holding lagoons and activated sludge aeration tanks (from which the highest N₂O emissions are expected to occur) (Global Water Research Commission 2011). The emissions of N₂O from a vast cross-section of wastewater treatment facilities has been extensively detailed in the literature, with some examples being: Czepiel et al. (1995); Ho Ahn et al. (2010); Global Water Research Commission (2011); Townsend-Small et al. (2011); and Winter et al. (2012).

The production of CH₄ at a WWTP occurs in anaerobic wastewater treatment processes and is a resultant by-product of anaerobic decomposition performed by methanogenic bacteria. Once produced, CH₄ gas can be ejected into the atmosphere by either mechanical aeration or surface diffusion. Several physical and biochemical parameters can be used to indicate the potential for CH₄ production: pH, sewage temperature, levels of sulphate reducing bacteria and toxicants, competition between methanogenic bacteria, wastewater treatment degree and retention time (El-Fadel & Massoud 2001; Wang et al. 2011). Fugitive CH₄ emissions most commonly take place in the influent works, primary clarifiers/sedimentation, aeration tanks, sludge processing/digestion and in effluent holding lagoons (Global Water Research Commission 2011). In addition, large amounts of CH₄ have been found to be produced and released within sewer systems (Guisasola et al. 2008). After being generated in sewers, dissolved CH₄ can continue to travel into WWTPs and may be stripped out and emitted into the atmosphere. This CH₄ stripping can take place extensively in artificially aerated systems, such as aeration tanks. Numerous investigations have been performed measuring the emission of CH₄ from a variety of wastewater treatment systems treating sewage derived from human activity, such as the following: Czepiel et al. (1995); Foley et al. (2009); Diaz-Valbuena et al. (2011); Wang et al. (2011); Global Water Research Commission (2011); and Daelman et al. (2012).

The vast majority of the preceding gas flux studies have been made at large-scale WWTPs treating sewage for extensive catchment areas and sizeable populations (at times greater than one million people). One study has estimated the carbon footprint of two small-scale decentralised WWTPs using mass balance modelling and a software package (Chong et al. 2011). However, there has been no attempt made to measure the emission of fugitive N₂O and CH₄ using any online gas analysis techniques from small-scale decentralised WWTPs servicing small catchments (Sharma et al. 2009). As a result, there is a significant gap in the literature that needs to be addressed. The installation of decentralised WWTPs is rapidly increasing worldwide, particularly in new residential greenfield and infill developments and in small-scale self-sufficient communities, such as retirement villages and sustainable townships (Sharma et al. 2012). As such, there is a requirement to investigate and quantify the environmental impact and GHG footprint associated with the ongoing development and operation of these particular sites. By doing this it can be determined if decentralised WWTPs have a measurable influence upon positive atmospheric radiative forcing, and ultimately climate change. By identifying the biochemical and physical processes occurring at these decentralised WWTPs that correlate to these fugitive emissions, various mitigation strategies to limit or eliminate these emissions may be developed and applied by site engineers and water management authorities in the future. These outcomes may also assist in the development of innovative fugitive gas capture and recycling technologies. Additionally, gas flux data sets obtained from the campaigns performed at decentralised WWTPs could be used to validate and calibrate synthetic GHG emissions data calculated from current models (with one such example being the National Greenhouse and Energy Reporting System (NGERS) implemented by the Australian Government). Doing this will help to greatly improve the accuracy of GHG and
carbon footprint reporting conducted by water management authorities.

The objective of this pilot study is to improve upon the currently minimal amount of information available on the extent and magnitude of GHG emissions released from decentralised WWTPs. The formal hypothesis that this study specifically aimed to evaluate was as follows: is there a measurable variation in the spatial distribution of the N₂O and CH₄ gas fluxes across the length of an aeration tank running an activated sludge treatment regime, and do N₂O and CH₄ gas fluxes vary by any amount over a short-term temporal interval? In order to test this hypothesis, N₂O and CH₄ gas fluxes were measured in real-time (using a portable online gas analysis system) from an aeration tank system operating at a decentralised sewer mining plant (servicing a small population catchment of no more than 3,000 people), over the time span of a single day during its window of peak operation. As no previous investigation has attempted to directly determine if the distribution of GHG flux is isotropic or anisotropic across the surface of a treatment tank/reactor, there is a need to resolve this.

**MATERIALS AND METHODS**

**Treatment plant description and specifications**

The WWTP selected for analysis is a modern (commissioned in 2007) sewer mining plant that has been built on site at a suburban 18 hole public golf course located in the western suburbs of Melbourne, Australia (37° 47' 39" S, 144° 46' 49" E, Altitude: 44 m). The function of the sewer mining plant is to extract a relatively small amount of domestic wastewater from a main sewer line and to treat it to safe standard so it can be used to continuously irrigate the golf course throughout an entire year by using biological nutrient removal (BNR) methods. In general, the WWTP operates by mechanically pumping in raw wastewater through a bar screen. Following this, the wastewater is sent to a balance tank and then to two aeration tanks working in parallel. Return activated sludge is cycled between the two aeration tanks and a settling tank. Any excess solids that are produced during this stage are sent back into the sewer line. After this, the clarified water is passed through a buffer tank and a sand filter tank. Final disinfection is performed by a UV unit. A percentage of the disinfected water is sent to a backwash tank, where it is treated with a chemical mix (sodium hypochlorite and caustic soda) and is returned back to the sand filter in order to clean the sand and to prevent bacterial growth. Finally, the treated water is stored in a 32.5 ML holding pond from which it can be readily accessed by the greenkeepers. Figure 1 displays a simplified sewage treatment flowchart from entry to exit for the sewer mining plant, and Table 1 shows a summary of its operational metadata and annual flow characteristics.

**Field fugitive gas analysis procedure**

The field gas analysis detailed in this project followed a methodology similar to that employed by Tremblay *et al.* (2004) based on the original measurement system detailed by Carignan (1998). Gas capture was made on the surface of the sewage with a buoyant airtight flux hood (Ac‘Scent Flux Hood, St Croix Sensory Inc., USA) connected to a primary standard calibrated (traceable to the National Institute of Standards and Technology) non-dispersive infrared (NDIR) gas analysis unit (VA-3000 Series, Horiba Ltd, Japan). Surface off-gases were trapped inside the flux hood.
and passed through to a gas conditioning system (VS-3000 Series, Horiba Ltd, Japan) via an internal pump working at a constant flow rate. The gas conditioning system removed any water vapour and other particulates from the gas stream before it entered the NDIR gas analysis unit. After the N2O and CH4 constituent gas concentrations had been evaluated by the NDIR gas analysis unit, the sampled gases were sent back into the flux hood so that they were mixed continuously, enabling a more accurate estimation of gas concentration to be obtained over time (Lambert & Frechette 2005; Tremblay et al. 2009).

Gas concentrations were recorded over 10 (±5) minutes at evenly spaced intervals to reduce the influence of the ‘chamber effect’ (Venterea et al. 2009). In order to determine the spatial distribution of the N2O and CH4 gas fluxes, the gas concentration measurements were made successively in seven separate sections across one of the aeration tanks (in this study it was assumed that the N2O and CH4 gas fluxes emitted from both of the aeration tanks were symmetrical as both tanks have the same influent intake and operate under the same conditions and specifications simultaneously). These seven sections are displayed and labelled in Figure 2. The sections were each separated by a distance of approximately 1.5 to 2 m, and each section had its own characteristic DO content due to the uneven oxygen distribution supplied by the submerged aeration system in operation at the bottom of the aeration tank. This aeration system was in constant operation throughout the entire measurement series. Specifically, in this study N2O and CH4 gases were measured from the aeration tank only, as it has the most substantial physical footprint (48 m² surface area for one aeration tank; 96 m² for both aeration tanks) and was the most atmospherically exposed (i.e. it has the largest uncovered surface area) of all the treatment systems/tanks on site, and as a result it had the highest potential to deliver the most substantial cumulative emissions. Supplementary N2O and CH4 emissions measurements were made on the settling, buffer and filter tanks over a time span of 1 to 2 hours. Both N2O and CH4 emissions were found to be negligible on each of these tanks.

A tightened rope was used to hold the flux hood in the same position and to reduce the effect of wave action on the sewage surface. After each measurement, the flux hood was removed from the sewage surface so that gas concentrations could return to ambient levels before the next measurement. The gas concentration data were recorded continuously to a laptop computer starting at 11:07 AM until 3:15 PM (27 March 2012). From this sampling regime, temporal gas flux patterns could be readily determined over the time of day at which the influent organic loading was most likely to be at its peak. A full 24 hour interval of gas flux measurements could not be made at the sewer mining plant due to strict workplace health and safety restrictions that are enforced by the sewer mining plant operations management authority.

### Table 1 | Sewer mining plant operational metadata and parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Function</td>
<td>Sewer mining for golf course irrigation</td>
</tr>
<tr>
<td>Predominant influent type</td>
<td>Domestic</td>
</tr>
<tr>
<td>Catchment population (approximate)</td>
<td>3,000</td>
</tr>
<tr>
<td>Yearly COD mass load (metric tonnes)</td>
<td>88</td>
</tr>
<tr>
<td>Yearly BOD mass load (metric tonnes)</td>
<td>46.4</td>
</tr>
<tr>
<td>Yearly total N mass load (metric tonnes)</td>
<td>11</td>
</tr>
<tr>
<td>Yearly inflow (ML) (daily inflow (ML))</td>
<td>100 (0.274)</td>
</tr>
</tbody>
</table>

### Figure 2 | The seven separate sections from which gas fluxes were measured across the aeration tank. The sections are in numerical order from the influent point of entry.
One of these restrictions is a complete ban on any onsite work performed by external contractors after daylight hours. As such, it was not possible for the measurement series to be expanded to run over a complete 24 hour time period in order to obtain a full diurnal gas emission analysis. Figure 3(a) displays the deployment of the flux hood on top of the aeration tank and Figure 3(b) shows the NDIR gas analyser, the gas conditioner and the laptop computer used as a data logger throughout the measurement campaign.

Continuous measurement of various water quality parameters were made simultaneously to the gas flux measurements using a novel online water quality measurement system (Sewer Sentinel, Commonwealth Scientific and Industrial Research Organisation, Australia). Sewage was extracted from the aeration tank to the online water quality measurement system via a masticating pump (Piranha 08 Grinding Pump, ABS-Sulzer, Switzerland). The pump was positioned in close proximity to the flux hood at all times during each measurement and was lowered approximately 0.5 to 1 m under the sewage surface. The water quality parameters that were measured included: temperature, pH and DO. More water quality data and operational data such as influent flow rate, influent total N mass load, influent total COD, DO delivery profiles and inflow pump timings were obtained from the WWTP site engineers as required. Mean values for the water quality parameters as measured in each particular section of the aeration tank (by the online water quality measurement system) and mean raw fugitive emissions from each section of the aeration tank (measured by the NDIR gas analysis unit) are shown in Table 2.

Data analysis procedure

In order to calculate N₂O and CH₄ gas fluxes, linear regression was applied to the gas concentration data over the sampling time. Only data sets with a coefficient of determination ($R^2$ value) greater than 0.5 were employed for flux calculations. The average $R^2$ calculated over the CH₄ gas concentration data sets was $0.78 \pm 0.14$ ($\pm 1 \sigma$) and the average $R^2$ calculated across the N₂O gas concentration data sets was $0.79 \pm 0.11$ ($\pm 1 \sigma$). Specifically, over the entire measurement campaign, 96% of all 24 CH₄ emission concentration data sets had an $R^2$ of over 0.5, and 100% of all 24 N₂O emission concentration data sets had an $R^2$ of 0.5 or greater. Following the application of linear regression, gas flux was calculated directly using the following equation (Tremblay et al. 2004):

$$\text{Flux} = \frac{m \times V \times \alpha \times \beta}{A \times \gamma}$$

where $m$ is the slope from the line of best fit set to the gas concentration data over the sampling time (ppm second$^{-1}$); $V$ is the volume under the flux hood (m$^3$); $\alpha$ is a gas concentration conversion factor (for CH₄: 655.47 μg m$^{-3}$ ppm$^{-1}$; for N₂O: 1798.56 μg m$^{-3}$ ppm$^{-1}$); $\beta$ is a temporal conversion factor (86400 seconds day$^{-1}$); $A$ is the area under the flux hood (m$^2$) and $\gamma$ is a magnitude conversion factor ($1 \times 10^6$ μg g$^{-1}$).
Flux is given in g m⁻² d⁻¹. To evaluate the total daily carbon footprint for the sewer mining plant, the calculated CH₄ and N₂O fluxes were converted to their equivalent CO₂ (CO₂e) values by multiplying them by their respective 100 year global warming potential conversion factors (25 for CH₄ and 298 for N₂O) currently purported by the Intergovernmental Panel on Climate Change (2007).

To directly compare the N₂O and CH₄ emissions from the aeration tank to those made in other studies, the fluxes must first be normalised to a specific water quality parameter and converted to an emission factor. As such, to make a rudimentary emission factor estimation, the mean N₂O emission measured over the sampling period across each section in the aeration tank was extrapolated over 365 days and normalised to the total annual NᵢNFLUENT, and the mean CH₄ emission recorded over the sampling period in each section of the aeration tank was extrapolated over 365 days and normalised to the total annual CODᵢNFLUENT using the following two respective equations:

\[
\text{N₂OEF} = \left( \frac{(\text{N₂O})_{\text{MEAN}}}{(\text{NᵢNFLUENT})_{\text{ANNUAL TOTAL}}} \right) \times 100\% ;
\]
\[
\text{CH₄EF} = \left( \frac{(\text{CH₄})_{\text{MEAN}}}{(\text{CODᵢNFLUENT})_{\text{ANNUAL TOTAL}}} \right) \times 100\% ;
\]

where N₂OEF and CH₄EF are the annual emission factors for N₂O and CH₄ respectively; (N₂O)MEAN is the mean of the N₂O flux measurements (metric tonnes) integrated over the tank surface area made over the sampling period (extrapolated over 365 days); (NᵢNFLUENT)ANNUALTOTAL is the annual total N (metric tonnes) arriving in the influent at the sewer mining site; (CH₄)MEAN is the mean of the CH₄ flux measurements (metric tonnes) integrated over the tank surface area made over the sampling period (extrapolated over 365 days) and (CODᵢNFLUENT)ANNUALTOTAL (metric tonnes) is the annual total COD arriving in the influent at the sewer mining site. These emissions factor calculations assume that the emission of N₂O and CH₄ gas from the aeration tanks remains constant throughout the year.

### RESULTS AND DISCUSSION

**Greenhouse gas measurements – short-term temporal and spatial distribution**

Figure 4 shows the CH₄ and N₂O flux measured throughout the sampling period across each section of the aeration tank system. In this figure the measurements made in the seven separate sections across the aeration tank took place at the following times: Section 1–11:07 AM to 12:10 PM;
Throughout the trial, the sewage temperature remained stable between 22 and 22.5°C. Due to the low temperature differential across the aeration tank (and during the trial period) no discernible link between temperature and N₂O and CH₄ flux could be ascertained. In Figure 4, it is clear that CH₄ flux varied extensively throughout the trial period from Section 1 to Section 7, reaching a peak value of 1.1 g CH₄ m⁻² day⁻¹ in Section 3, and a minimum value of 0.21 g CH₄ m⁻² day⁻¹ in Section 6. Specifically, the average calculated CH₄ flux was 0.55 ± 0.24 g CH₄ m⁻² day⁻¹ (±1σ). The percentage variation (μ/σ×100%) across all of the CH₄ flux measurements was a sizeable 44%. In each separate section the temporal variations in CH₄ flux were at times almost as large as the variation measured across the aeration tank over the entire trial. In particular, CH₄ fluxes varied by as much as 36% in Section 2 and Section 6, throughout relatively short measurement times of 54 minutes and 10 minutes respectively. The average CH₄ flux after conversion to its equivalent CO₂ value was 11.5 ± 5.1 g CO₂e m⁻² day⁻¹ (±1σ), with a daily emission per unit of influent volume of 302 g CO₂e ML⁻¹. Assuming that this average output remains the same each day over the space of a year, the total annual CO₂e footprint due to CH₄ emissions for the sewer mining site is equal to 403 kg (0.13 kg CO₂e person⁻¹), with an associated emission factor (CH₄EF) of 0.022.

From Figure 4, it can be seen that N₂O flux significantly increased in magnitude over the trial period across Section 1 to Section 7, reaching a maximum value of 11.6 g N₂O m⁻² day⁻¹ in Section 7, and a minimum value of 1.01 g N₂O m⁻² day⁻¹ in Section 1. From the sectional values, the average calculated N₂O flux was estimated to be 5.6 ± 3.45 g N₂O m⁻² day⁻¹ (±1σ), with an associated percentage variation of 61%, a value much higher than the percentage variation obtained for the CH₄ measurements. In each separate section the temporal variations in N₂O flux were close to being as large as the variation measured across the aeration tank during the entire trial period. As was the case for the CH₄ fluxes, N₂O fluxes also fluctuated by the greatest amounts in Section 2 (45%) and Section 6 (35%) again over respective measurement intervals of 54 min and 10 min. The average N₂O flux after being converted to its equivalent CO₂ value was 1,761 ± 1,070 g CO₂e m⁻² day⁻¹ (±1σ), with a daily emission per unit of influent volume of 46,320 g CO₂e ML⁻¹. From this, by making the assumption that these emissions remain relatively constant throughout the year, the total annual CO₂e footprint due to N₂O emissions for the site was found to be 61.7×10³ kg (with a related emission factor (N₂OEF) of 1.8), a footprint much greater than the value estimated for the CH₄ emissions. As a result, the total annual CO₂e footprint of 62.1×10³ kg (21 kg CO₂e person⁻¹) for the site is largely dominated by N₂O related emissions by a contribution factor of 154 to 1.
The calculated emission factors for both CH$_4$ (0.022) and N$_2$O (1.8) for the aeration tank at the sewer mining plant fell within the expected range of emission factors that have been previously estimated for large-scale centralised WWTPs using comparable flux measurement techniques and calculation methods (Global Water Research Commission 2011). In particular, the N$_2$O emission factor calculated for the sewer mining site fits well within the generally expected interval of 0 to 4% conversion of influent total N to direct N$_2$O emissions (Kampschreur et al. 2009b; Chong et al. 2011), and the CH$_4$ emission factor is in the same order of magnitude as CH$_4$ emission factors estimated for large-scale WWTPs recently analysed in both France and the Netherlands (0.005 to 0.04) (Global Water Research Commission 2011). Consequently, this outcome implies that at the sewer mining plant, the conversion of influent COD to CH$_4$ gas and influent N to N$_2$O gas occurs at approximately the same efficiency rate as what takes place at large-scale centralised WWTPs. However, the total environmental impact of the resultant N$_2$O and CH$_4$ emissions released from the sewer mining plant will most probably be reduced in comparison to large-scale centralised WWTPs, as the total daily volume of treated wastewater moving through the sewer mining plant is much lower, meaning that there is far less total organic material available that can be readily converted into N$_2$O and CH$_4$ gas.

The distribution of averaged N$_2$O and CH$_4$ fluxes across each section of the aeration tank as measured is shown in Figure 5. It is clear from Figure 5 that both the averaged N$_2$O and CH$_4$ fluxes did not display a definite homogenous (even) distribution across the length of the aeration tank. Instead all of the fluxes vary by a measurable amount from the inlet (Section 1) to the outlet (Section 7), with large discrepancies measured across small distances (no greater than 1.5 to 2 m). For example, sizeable differences in CH$_4$ flux were seen to occur most considerably from Section 2 to Section 3, where a near threefold increase in flux was measured (from 0.39 g CH$_4$ m$^{-2}$ day$^{-1}$ up to 1 g CH$_4$ m$^{-2}$ day$^{-1}$), and from Section 5 to Section 6, across which a 48% decrease in flux occurred (from 0.51 g CH$_4$ m$^{-2}$ day$^{-1}$ down to 0.27 g CH$_4$ m$^{-2}$ day$^{-1}$). Also, a doubling of N$_2$O flux was measured between Section 1 and Section 2 (from 1.86 g N$_2$O m$^{-2}$ day$^{-1}$ to 3.78 g N$_2$O m$^{-2}$ day$^{-1}$), and again between Section 2 and Section 3 (from 3.78 g N$_2$O m$^{-2}$ day$^{-1}$ up to 6.31 g N$_2$O m$^{-2}$ day$^{-1}$). As such, the distribution of the N$_2$O and CH$_4$ fluxes across the aeration tank can be regarded as anisotropic (i.e. the fluxes change with direction lengthways across the tank). In particular, the spatial distribution of the CH$_4$ fluxes did not follow any recognisable pattern from entry to exit, while the N$_2$O fluxes displayed a definite gradual increase. This suggests that the emissions of CH$_4$ generally occur at random across the surface area of the aeration tank, while emissions of N$_2$O do not take place stochastically, and may be loosely correlated to the positioning of the bubblers/oxygen supply in the aeration system and to the distribution of the sludge/nutrient loading within the water column. However, it is unclear whether these N$_2$O and CH$_4$ emission patterns take place consistently like this throughout each day of the year, or are entirely an artefact of the particular organic load entering the sewer mining plant at that time of day. Consequently, further measurements of the spatial distribution of the N$_2$O and CH$_4$ emissions are required throughout different seasons in order to conclusively determine their overall variability.

The objective of the research performed in this investigation was only to measure the N$_2$O and CH$_4$ emissions released from the aeration tank system in order to determine if the spatial and temporal distribution of gas flux in an activated sludge aeration system was variable over a short time period. However, at the sewer mining site it is predicted that
not only do N₂O and CH₄ emissions emerge from the aeration tanks, but they may also be released from the final effluent holding pond, which may be significant due to its substantial volume and surface area. Further emissions of N₂O gas may be prevalent in this final treatment stage, as the solubility of N₂O in water is high, and as such N₂O generated upstream in other treatment processes may remain in the effluent for an indefinite period of time. In addition, reactive nitrogen that is present in final effluent may be applied across the golf course (via watering performed by the greenkeepers), and as such will be available for nitrification and denitrification resulting in further possible N₂O emissions, adding further to the GHG footprint related to the sewer mining plant. Consequently, in further studies detailing the total site GHG footprint, these factors should be taken into account and quantified appropriately.

**Greenhouse gas measurements – correlation to wastewater physical parameters**

Figure 6(a) and Figure 6(b) show respectively the measured CH₄ and N₂O fluxes versus the measured dissolved oxygen concentration for each section across the aeration tank and the measured CH₄ and N₂O fluxes versus the measured pH value for each section across the aeration tank. In Figure 6(a) there appears to be only a very weak positive linear correlation between both DO level and the N₂O and CH₄ fluxes, with the R²
value being slightly greater for the relationship between DO level and N\textsubscript{2}O flux (0.18) in comparison to the relationship between DO level and CH\textsubscript{4} flux (0.07). In the aeration tank it is assumed that the majority of the emitted CH\textsubscript{4} is not being generated inside the tank, but is arriving into the tank via the sewer and is being agitated and stripped out via aeration. As such, the weak link between the increasing CH\textsubscript{4} flux and increasing DO may moderately imply that the sections of the aeration tank where greater levels of aeration/oxygenation are occurring is also where the highest amounts of CH\textsubscript{4} gas stripping is taking place. The link between oxygen concentration and N\textsubscript{2}O generation and emission has been tested and detailed previously in a number of studies performed in aeration tanks at real-world WWTPs. These investigations have shown highly conflicting results, with some illustrating that DO levels are positively correlated with N\textsubscript{2}O emissions ([Schulthess et al. 1994; Ho Ahn et al. 2010]), while others reported that DO levels are negatively correlated to N\textsubscript{2}O emissions ([Kampschreur et al. 2009a; Winter et al. 2012]). Due to the relatively low DO levels (<1 mg L\textsuperscript{-1}) existent across the entire aeration tank, it is thought that the high levels of N\textsubscript{2}O were primarily generated during the nitrification stage, in the nitrifier denitrification process, which takes place following poor and inadequate aeration or during a large peak in ammonium ([Global Water Research Commission 2001]). As such the site operators may wish to increase the output of the aeration system (if possible) in order to reduce the occurrence of this scenario, and possibly reduce the generation of N\textsubscript{2}O.

In Figure 6(b) it can be seen that a weak negative linear relationship exists between pH and CH\textsubscript{4} flux ($R^2 = 0.14$). Conversely, a relatively strong positive linear relationship developed between pH and N\textsubscript{2}O flux ($R^2 = 0.68$). Previous investigations have shown that variations in the pH of sampled activated sludge can be directly linked to emissions of N\textsubscript{2}O gas ([Thorn & Sorensen 1994]), with lower pH readings correlating to higher N\textsubscript{2}O production. The results obtained in the aeration tank at the sewer mining plant display the opposite of this, with higher pH readings generally correlating to higher N\textsubscript{2}O fluxes. From this, it may be possible that in the aeration tank at the sewer mining plant, online pH measurements could be employed as a simple indicator by site engineers to determine the probability of high or low N\textsubscript{2}O emissions occurring at that particular point in time.

**CONCLUSIONS**

This pilot study is the first of its kind to present both fugitive N\textsubscript{2}O and CH\textsubscript{4} emissions data as measured by an online infrared gas analysis system at a decentralised sewer mining plant. The continuation of monitoring and analysis of fugitive GHG emissions made at various types of decentralised WWTPs is important, as there are very few data currently available on the total GHG footprint related to these sites. Measurements similar to what has been presented in this study can be used to calibrate and optimise existing GHG modelling frameworks (such as the current Australian NGERS) in order to improve the accuracy of carbon footprint reporting performed by water management authorities and operators, which has been shown to be too general in application and at times highly inaccurate ([Global Water Research Commission 2001]). In addition, the detailed measurement of fugitive emissions at decentralised WWTPs not only helps to better quantify the magnitude and extent of fugitive N\textsubscript{2}O and CH\textsubscript{4} emissions over time but can also assist in determining how N\textsubscript{2}O and CH\textsubscript{4} gases are produced and released from wastewater. As a result, they can also aid in the development of innovative strategies on how N\textsubscript{2}O and CH\textsubscript{4} fugitive emissions can be reduced, captured and recycled. However, further evaluation is required to determine if decentralised WWTPs, such as the sewer mining site evaluated in this study, are capable of being continuously self powered by the conversion of their emissions into a sustainable energy supply. An economic assessment is also needed to determine if such an energy recycling scheme would be financially viable.

The formal hypothesis originally detailed in the Introduction section appears to have been proven, as the spatial and temporal distributions of N\textsubscript{2}O and CH\textsubscript{4} flux directly measured in real-time across the aeration tank were found to vary significantly over both short distances and time intervals. The anisotropic spatial distribution of both N\textsubscript{2}O and CH\textsubscript{4} fluxes suggests that GHG flux measurements made with a flux hood in a single position over an extended time period on an aeration tank surface may not be adequate for
GHG measurements on tanks with a large surface area, such as the aeration tank at the sewer mining site analysed in this study. Failure to acknowledge that the magnitude of both N$_2$O and CH$_4$ fluxes can change by sizeable amounts over short distances across an aeration tank may lead to a considerable misestimation in the averaged N$_2$O and CH$_4$ emissions data, and consequently in the overall GHG footprint calculated for the WWTP under investigation. As such, it is recommended that flux measurements are made in quick staggered time intervals at multiple evenly spaced positions across the entire measurable surface of an aeration tank, in order to better ascertain both temporal and spatial flux variations. Another way to overcome this problem is to deploy an array of separate flux hoods and gas analysis (or gas storage) systems across an aeration tank surface at even separations to take flux measurements simultaneously. However, this solution may be financially prohibitive, logistically difficult and may violate safety regulations at some WWTPs. Another possible solution is to position an open-path eddy covariance gas flux measurement unit near to the surface area of an aeration tank to provide high-accuracy continuous measurements of total gas transfer for an extended time period. However, eddy covariance may not be entirely useful due to the fact that emissions from treatment tanks generally do not effect ambient air GHG concentrations in air more than several metres away from the source (Townsend-Small et al. 2011). Also, it must be ensured that the surface under investigation resides within the measurement footprint area of the eddy covariance unit. This can be very difficult to maintain, as the shape of the measurement footprint can vary many times over the space of a day, primarily due to fluctuations in wind direction.

From the results provided by this pilot study it is clear that further work is now required to better determine the seasonal and annual N$_2$O and CH$_4$ emissions produced on site, and to determine the sensitivity of the sewer mining plant to short- and long-term variations in influent properties and local environmental conditions. From this, a broad extrapolation could be made to evaluate the overall influence that the ongoing increase in the uptake of decentralised WWTPs and wastewater treatment systems (similar to the sewer mining site) will have on both the Australian and the worldwide carbon budget. Further measurements are also needed to evaluate the total amount and location of the N$_2$O and CH$_4$ generated in the connecting sewers, in order to ascertain if these gases can be captured, reduced or eliminated.

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