PREDICTION OF WASTEWATER TREATMENT GREENHOUSE GAS EMISSIONS USING A REAL-TIME MODEL

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ABSTRACT

Nitrous oxide (N_2O) is the major contributor to greenhouse gas (GHG) emissions from activated sludge plants, with a global warming potential 298 times that of carbon dioxide (CO_2). The underlying biological mechanisms leading to its production are complex and not fully understood. At present, fixed emission factors are typically used to estimate N_2O emissions. However, these factors do not reflect the high level of uncertainty around how emissions are affected by a number of influences, including wastewater characteristics, the type of treatment process, and how the process is operated and controlled. Whilst mechanistic models have been developed for predicting GHG emissions, these are not yet well proven, or widely adopted by water utilities for predicting and reporting emissions. Additionally, these models typically represent a fixed point in time, and don't benefit from real-time data inputs and control opportunities. Further emissions monitoring data is required to support the development of such models.

The Rosedale Wastewater Treatment Plant (WWTP) achieves biological nitrogen removal through nitrification and denitrification using the Modified Ludzack-Ettinger (MLE) process. As with all biological treatment plants, the operation results in direct emissions of greenhouse gases such as CO_2, CH_4, and N_2O.

To support commissioning of the fourth MLE reactor in 2020, a digital twin of Rosedale WWTP was developed to provide real-time insights into plant performance. Subsequently, Watercare Services Ltd (WSL) wanted to extend the digital twin to include live reporting of GHG emissions. The specific aims were to assist with planning and benchmarking and to help achieve its aim of reducing operational emissions by 50% by 2030. This would require comparing the biological model with site-measured emissions data.

A survey was performed to gather data on process emissions using a Picarro G2508 off-gas concentration analyser. Aqueous phase N_2O was also analysed to provide information on where in the process N_2O was generated. Real-time data was captured in SCADA and surfaced to a dashboard in the digital twin. The digital twin will provide ongoing real-time predictions of GHG emissions in the absence of permanent off-gas analysers, allowing these to be redeployed to other sites, where similar models will be established.

The project will provide key insights into the factors that contribute to N_2O emissions at Rosedale WWTP and will assist in the generation of mitigation strategies and scenario analysis for reducing these in future. The proving of this approach will also allow similar emissions measurement and digital twin models to be established at other treatment plants throughout New Zealand.

This paper will document the development of the model, the practical challenges of collecting and interpreting measurement data, discuss the key factors influencing the production of GHG emissions in the Rosedale MLE process, and the reliability of the real-time model for predicting emissions.

KEYWORDS

GREENHOUSE GAS EMISSIONS, NITROUS OXIDE, WASTEWATER TREATMENT, DIGITAL TWIN, PROCESS MODELLING

PRESENTER PROFILE

David is a Principal Process Engineer in Mott MacDonald's Water team. He is a wastewater specialist with design, commissioning, process optimisation and troubleshooting experience. David has a long history of process design of significant wastewater treatment plant projects in New Zealand and the UK.

INTRODUCTION

Nitrous oxide (N_2O) is the major contributor to greenhouse gas (GHG) emissions from activated sludge plants, contributing some 90% of the total site wide GHG emissions. Mitigation of these emissions is therefore considered fundamental to achieving water utilities' GHG reduction targets. However, emission factors and control strategies are likely to vary with specific plant configurations, operating conditions, and wastewater characteristics. Therefore, site specific measurement and prediction of the N_2O emissions should be considered as part of a mitigation strategy.

Watercare has a target to reduce operational greenhouse gas emissions by 50% by the year 2030. Current estimates indicate approximately 70% of Watercare's operational GHG emissions is generated from WWTP process emissions. It is therefore crucial to increase our understanding of GHG sources to enable improved control and reduction.

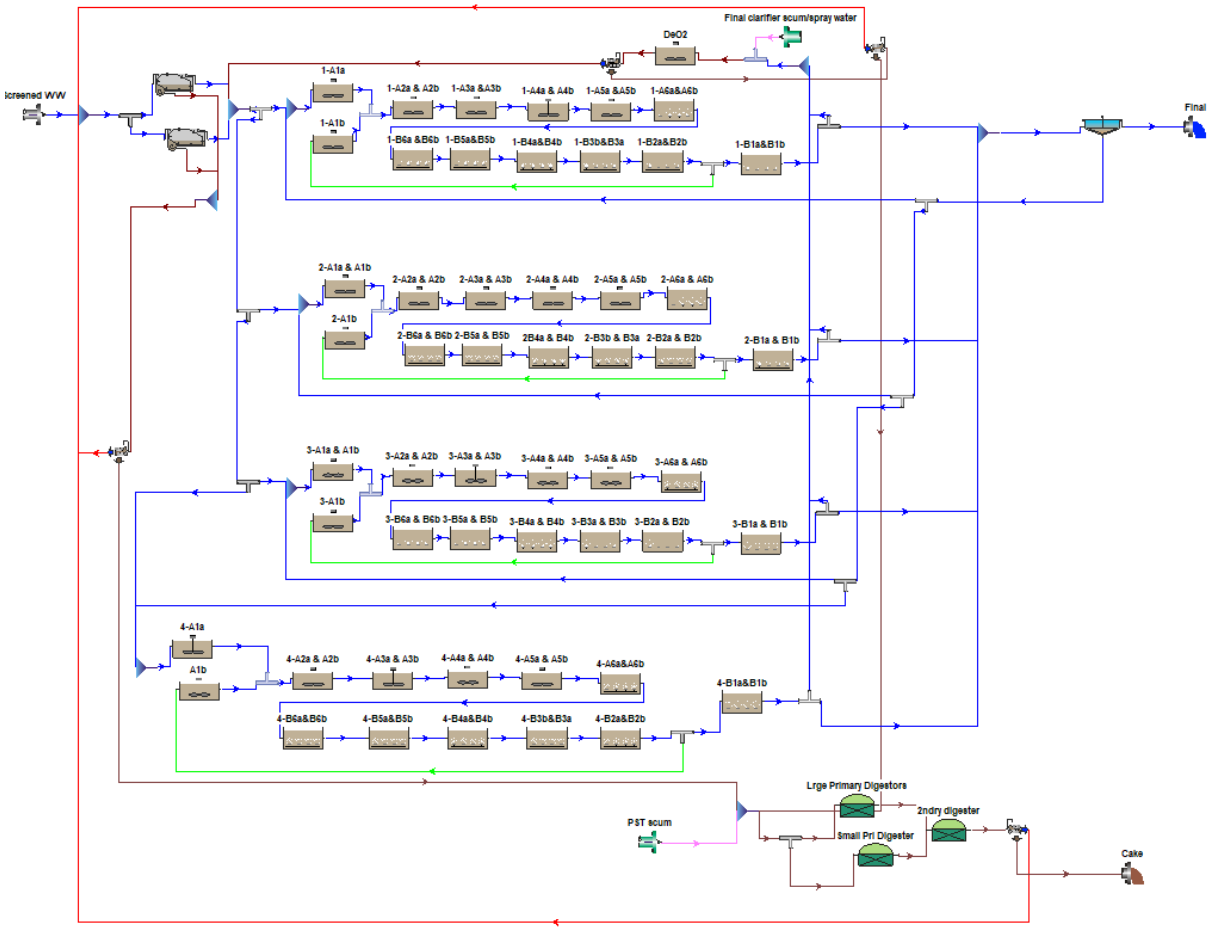
The Watercare Rosedale Wastewater Treatment Plant (WWTP) consists of primary sedimentation, biological treatment through the Modified Ludzack-Ettinger (MLE) process, clarification, UV disinfection, and anaerobic digestion for solids stabilisation. The wastewater is predominantly domestic with a small industrial component.

A digital twin of Rosedale WWTP was developed in 2020 to provide real-time insights into plant performance and scenario testing, to support commissioning of the fourth MLE reactor (MLE4). The solution combines biological modelling and machine learning with real-time data and dashboards, underpinned by the Moata platform.

A core component of the Rosedale WWTP Digital Twin is a live BioWin Model. BioWin is a wastewater treatment process simulator that ties together biological, chemical, and physical process models. BioWin is created by EnviroSim Limited and used world-wide to design, upgrade, and optimise wastewater treatment plants.

The BioWin model was operationalised with an Application Programming Interface (API) developed between Moata and BioWin to push/pull plant data and model results. The real-time inputs into the BioWin model come from online instrumentation including measured influent flow rates, temperature, dissolved oxygen concentrations, and sludge wasting rates. The outputs from the model are compared with actual plant data from the plant historian through the dashboards and adjustments made to improve the accuracy of the model. Currently the influent mass load profile in the model is a fixed input based on historical sample data and the concentrations are varied within the model based on the actual flow rates. Therefore, model results may differ at times from reality if the actual loads differ, for example during first flush storm events. A proposed improvement to the digital twin is to introduce online analysis of influent concentrations, such as ammonia, as a model input to improve accuracy.

Figure 1: Rosedale WWTP BioWin Model



Through the Rosedale Innovation Programme the decision was made to leverage the Rosedale digital twin to identify, control and reduce WWTP Greenhouse Gas (GHG) emissions.

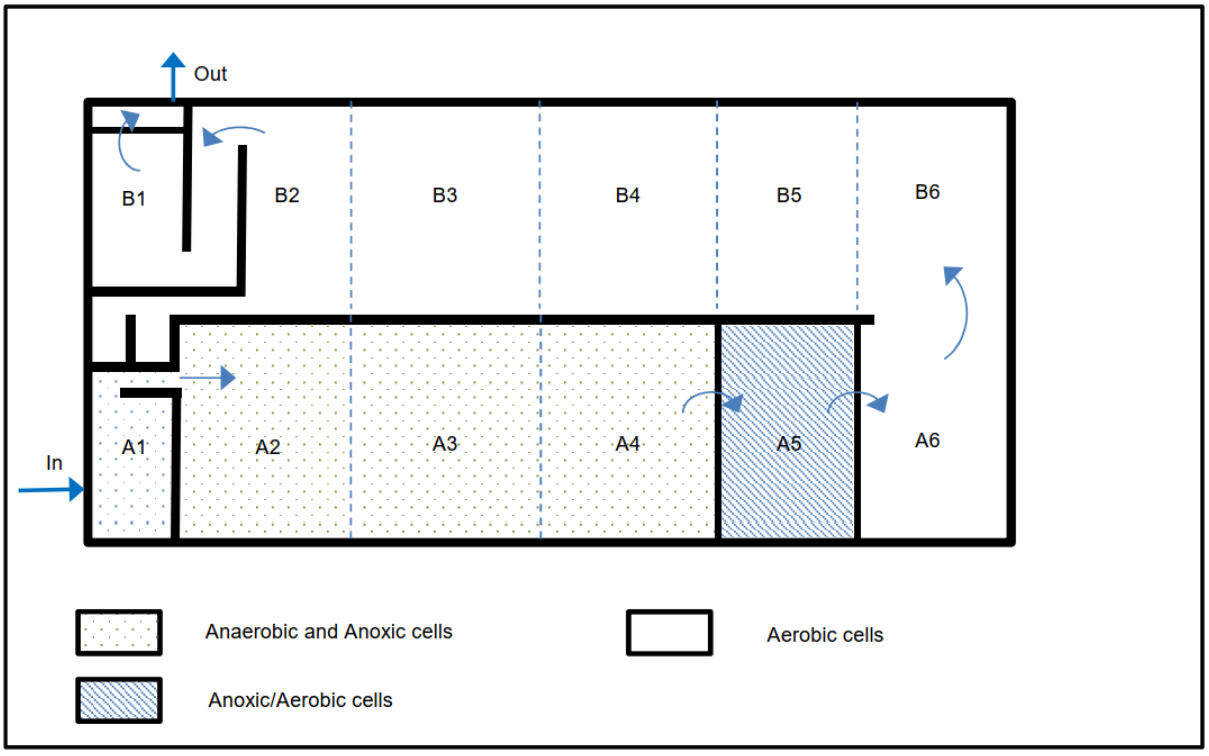
Watercare has recently purchased two Picarro G2508 analysers for measuring GHG concentrations. The Picarro unit uses cavity ring-down spectroscopy (CRDS) technology to measure N_2O concentration along with CH_4, CO_2, NH_3 and H_2O. This provided the ideal opportunity to implement a measuring campaign at Rosedale WWTP.

MATERIALS AND METHODS

PROCESS DESCRIPTION

Rosedale WWTP achieves biological nitrogen removal through nitrification and denitrification using the Modified Ludzack-Ettinger (MLE) process. A simplified representation of the new MLE4 at Rosedale is presented in Figure 2.

Figure 2: Simplified representation of MLE4



Wastewater enters MLE4 in cell A1 and flows by gravity through the various treatment compartments and exits the last compartment, cell B1. The compartments are called cells and are arranged in the order of flow as follows:

a) Anaerobic selector A1
b) Anoxic cell A2
c) Anoxic cell A3
d) Anoxic cell A4
e) Anoxic/aerobic cell A5 (currently operates as an anoxic cell)

f) Aerobic cell A6
g) Aerobic cell B6
h) Aerobic cell B5
i) Aerobic cell B4
j) Aerobic cell B3
k) Aerobic cell B2
l) Aerobic cell B1

MLE4 has an influent wastewater flow meter as well as influent airflow measurements for each of the three zones A5/A6, B5/B6 and B2/B3/B4. This allows monitoring of the influent flow and load, and the airflow split between the different aerobic zones.

The three aerated zones are serviced by individual DO probes, control valves and flow meters (A5/A6 DO probe in A6; B5/B6 DO probe in B5; and B2/B3/B4 DO probe in B2). The final zone B1 has its own DO probe and control valve but no flow meter. However, there is a flow meter on the main air header to MLE4 so the air flow to B1 can be calculated by difference between this flow rate and the flows to the other three zones. The current DO set points are 2 mg/L in A6, 2 mg/L in B5/B6, 1 mg/L in B2/B3/B4 and 1.5 mg/L in B1. Cell B2 runs at a slightly lower DO set point to reduce DO in the mixed liquor recycle from B2 to A2. The internal recycle ratio is 4:1.

MEASUREMENT CAMPAIGN AND EQUIPMENT

A sampling campaign was devised to collect appropriate data to baseline the current emission and support the model development. The following equipment was specified.

- Picarro G2508 cavity ring-down spectroscopy (CRDS) unit (for gas phase N_2O)
- 3 x gas hoods (for collecting off-gas)
- Manifold block (for connecting gas hoods to Picarro unit)
- Unisense Clark-type microsensors (two probes, for liquid phase N_2O)
- Sample bottles from Watercare Laboratories for all liquid phase sampling
- Handheld DO probe
- Handheld pH probe

Gas phase sampling

Aerated cells

The gas hood and the Unisense probe were moved progressively through the different aerobic cells, from cell A6 to cell B1 at the outlet of the MLE. This was used to measure the gas-phase and liquid-phase N_2O concentrations, to allow an understanding of both the N_2O generation (liquid phase) and emission (stripping into the gas phase). Coincident liquid and gas-phase concentrations also allow a better understanding of the N_2O mass transfer coefficient.

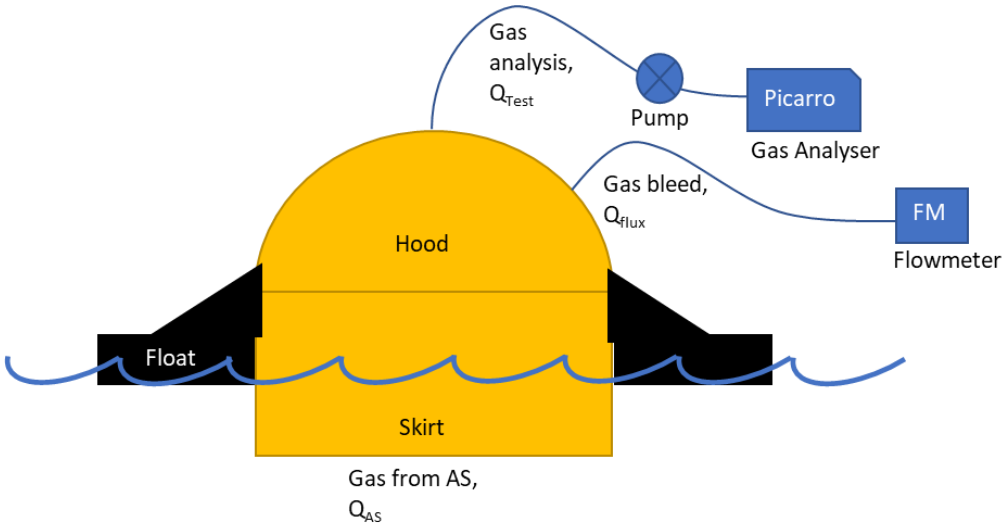
Unaerated cells

Only liquid-phase sampling was performed in the unaerated zones. Ideally liquid- and gas-phase sampling would be performed in the anaerobic and anoxic zones

to allow a full picture of N_2O generation and emission from each cell. However, since off-gas generation from unaerated zones is small, this would require a carrier gas (Chandran, 2011) to allow sample collection, and this has proven too challenging for the scope of this project. It was thought likely that emissions from the anaerobic and anoxic zones will be small in comparison to the aerobic cells and this was supported by the liquid-phase N_2O concentrations measured.

Figure 3 indicates the hood arrangement used for the sampling campaign. The hood was placed in the middle of the selected cell.

Figure 3: Prototype hood design for Rosedale



Measurement of the gas flow through the hood is measured from the flow through the positive displacement pump on the gas analysis line (0.23 L/min) and the flowmeter on the gas bleed line.

The gas bleed line acts as a pressure relief and ensures that the hood does not become pressurised, which could result in some gas escaping from underneath the hood. It is important that all the gas from the hood is measured by the flowmeter (L/min), since when combined with the off-gas N_2O concentration (ppm_v) and the cross-sectional area of the hood (m^2), this will give the emission flux of N_2O from the hood (mg N_2O/m^2.min). This flux can then be correlated with the known flowrate of gas from the hood and applied to the air flow rate in the whole cell to obtain the surface emission flux from that cell. The air flow rate to a cell is estimated by pro-rating the total airflow to that cluster of cells by the number of diffusers in each cell. The dropper valves to the individual diffuser grids were fully open during the monitoring campaign.

Unfortunately, there were issues obtaining reliable readings from the rotameter flowmeters on the gas bleed line. Initially the 12mm flexible tubing had to be reduced considerably in length to reduce friction losses in the line so that the air could reach the flowmeter. However, during the survey the line frequently filled with water from the off-gas which gave unreliable readings despite the operators' best efforts to drain the line. Because of this a different approach to calculating

the N_2O flux had to be taken, by assuming that the measured off-gas concentration in each cell correlates with the total air flow rate to that cell as opposed to the localised air flow rate under the hood. It is recommended that in future larger tubing be used for the gas bleed line and possibly a water trap.

Photograph 1: Prototype hood for Rosedale

Photograph 2: *Picarro* off-gas concentration analyser

Liquid phase sampling

In parallel with the gas phase measurements via the hoods, liquid phase sampling was also performed:

- Liquid phase sampling was performed, in the same cell as the hood (for TSS, VSS, sCOD, ffCOD, NH_3, NO_3, NO_2, DO, Alkalinity, pH, N_2O, and temperature), with one grab sample being taken every 6 hours over the 24-hour period for parameters not covered by online probes.

ffCOD is flocculated and filtered COD which is a measure of soluble COD.

Coincidentally with the above liquid samples taken in the same cell as the hood, grab samples were also taken from the influent to the MLE (e.g. at the influent flow splitter) and the secondary effluent (after the clarifier) and analysed for the same parameters.

The frequency of grab samples was one every 6 hours (at 3pm, 9pm, 3am, and 9am) to make the sampling campaign manageable for the operations team, who also must operate the plant. This timing ensured that sampling captured the morning and evening peaks and troughs in influent load. In addition, while online liquid and gas-phase N_2O monitoring was provided in all cells, the full suite of liquid sampling was only carried out on selected cells. The selected cells and the justification for full sampling is as follows:

- A1 – nitrate recycled here via RAS and zero DO
- A2 – nitrate recycled here via internal recycle and zero DO
- A5 – final anoxic zone
- A6 – first aerobic zone (anoxic/aerobic interface)
- B2 – potentially low DO
- B5 – provides an intermediate point between A6 and B2.

For the duration of the survey, 15-minute flow rate data was obtained from SCADA for:

- Influent to MLE4
- RAS
- WAS
- MLE4 Internal Recycle
- Air Flows to MLE4 and to individual zones

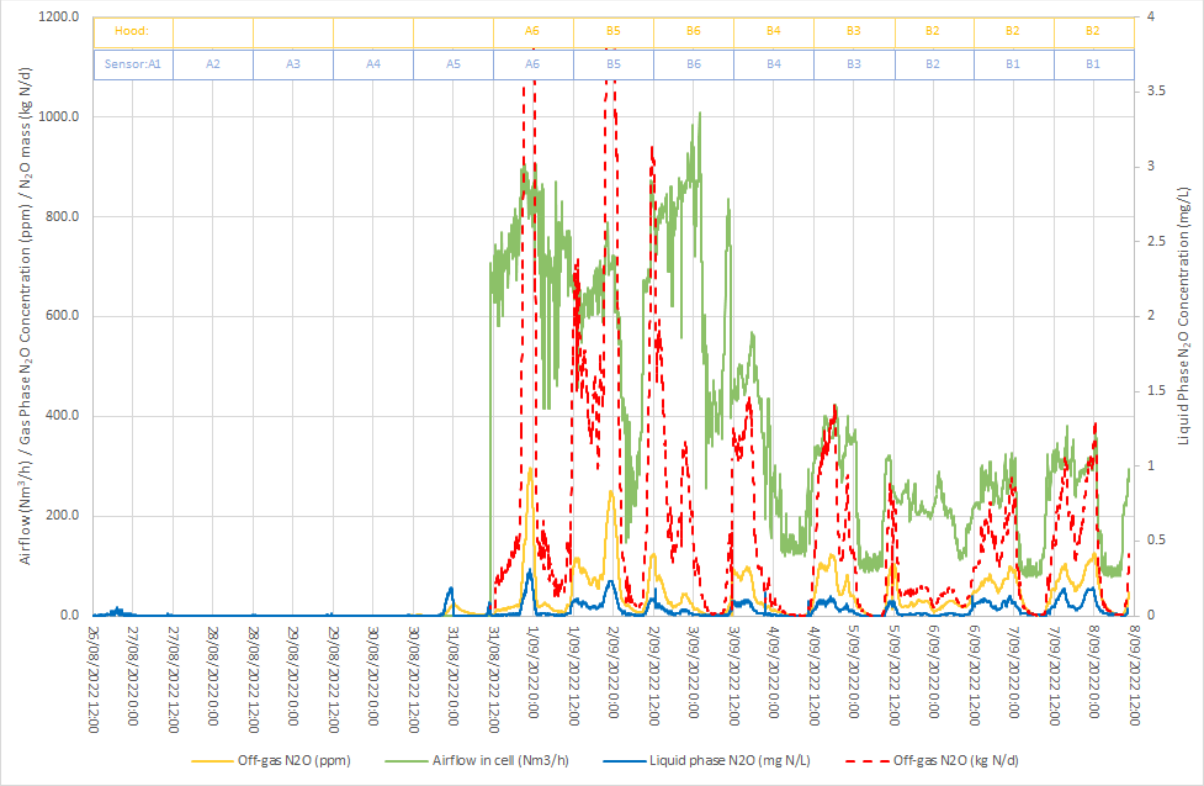
RESULTS AND DISCUSSION

Figure 4 shows the results of the monitoring campaign. This shows the liquid and gas phase N_2O concentrations corresponding to the cells in the bars across the top of the graph, as the hood and Unisense sensor was moved from cell to cell each day.

The air flow rate per cell was calculated based on the measured air flow rate to an aeration zone (comprising multiple cells) and assuming the air is distributed in proportion to the number of diffusers in each cell. The air flow rate increases with

the influent organic and nitrogenous mass load which is generally proportional to the influent flow and varies diurnally.

Figure 4: Results of N_2O sampling



The results indicate that there is typically little dissolved N_2O in the anoxic cells (A2 to A5). The gas phase N_2O in the unaerated cells was not measured, except for cell A5, where the gas phase N_2O was generally low, indicating that N_2O generation and emission from the anoxic cells is low compared with the aerobic cells.

The N_2O generation and emission is higher in the aerobic cells (A6 to B1) than the anoxic cells. In the aerobic cells the N_2O is stripped out of the liquid phase by the air. The data shows that the trend in gas phase N_2O concentration generally follows the trend in dissolved N_2O concentration. The off-gas N_2O mass load is the product of the off-gas concentration and the off-gas flow rate and therefore follows a similar trend.

Figure 5 shows that the reactor ammonia concentration generally follows the influent ammonia mass load and decreases along the length of the reactor as nitrification proceeds. The high ammonia concentration in cell B2 on the 5th September was due to a wet weather event.

Figure 5: Influent flow, ammonia load and reactor concentration

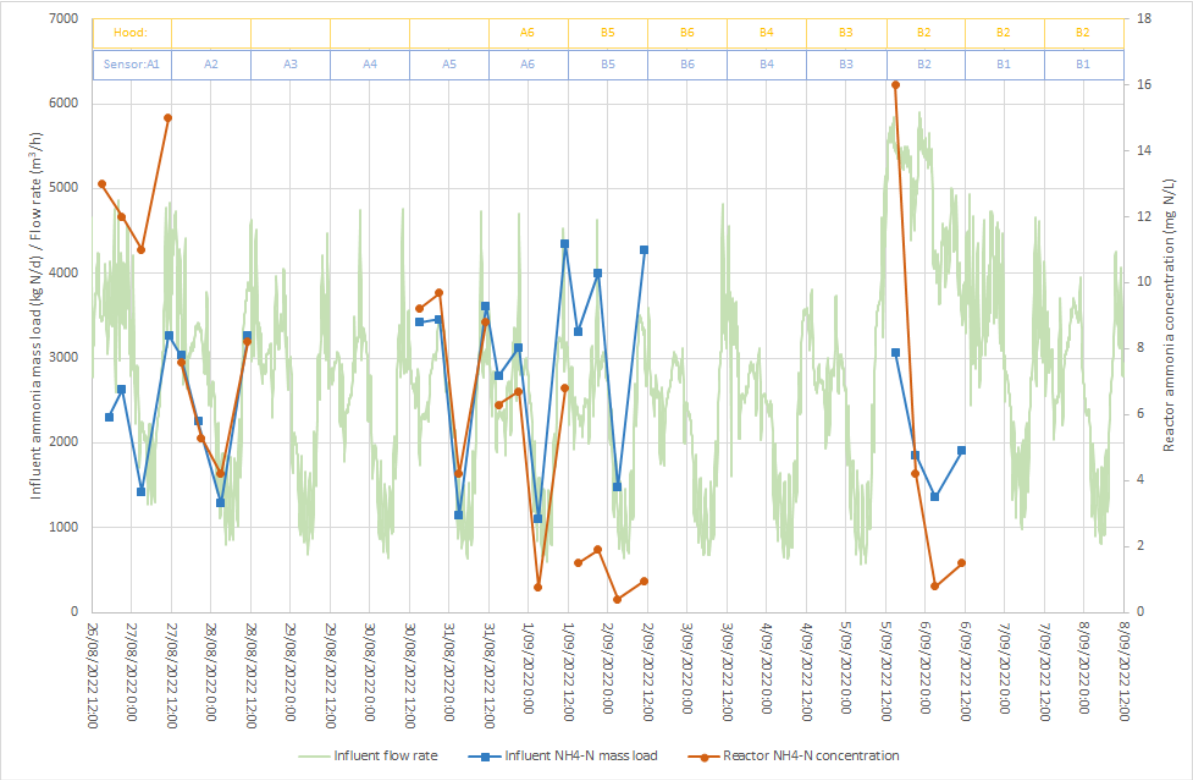
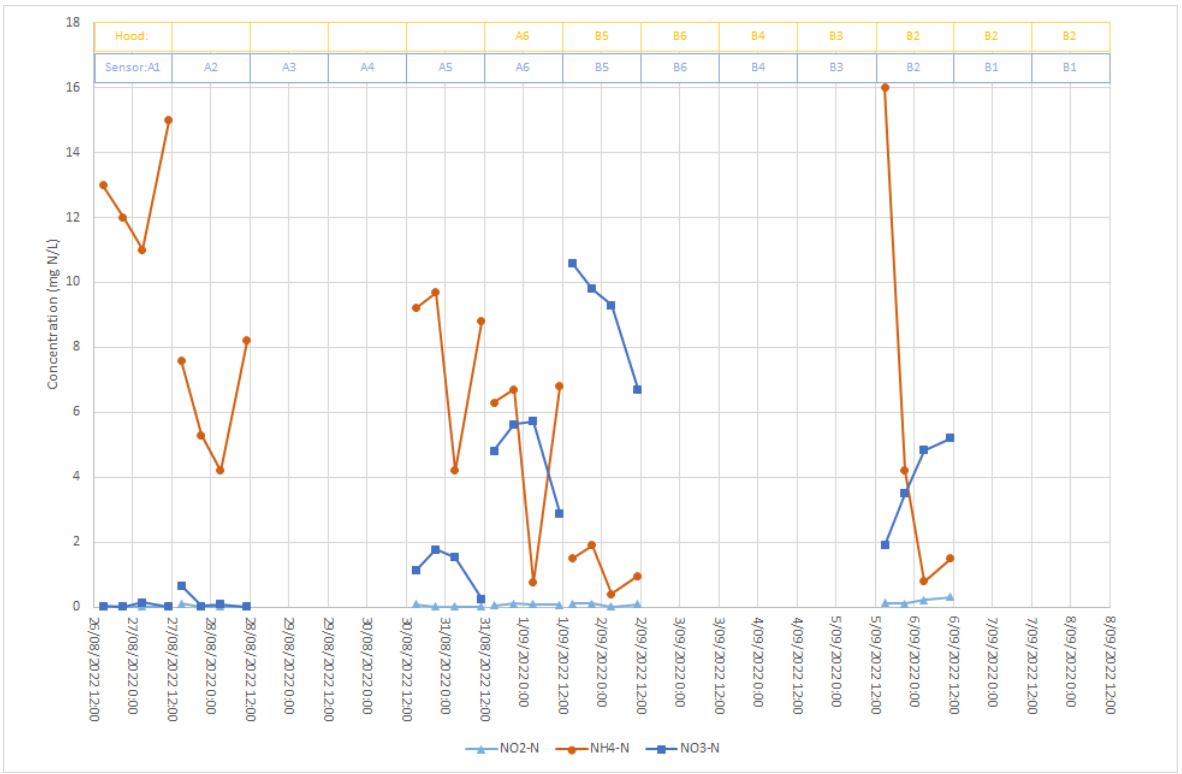


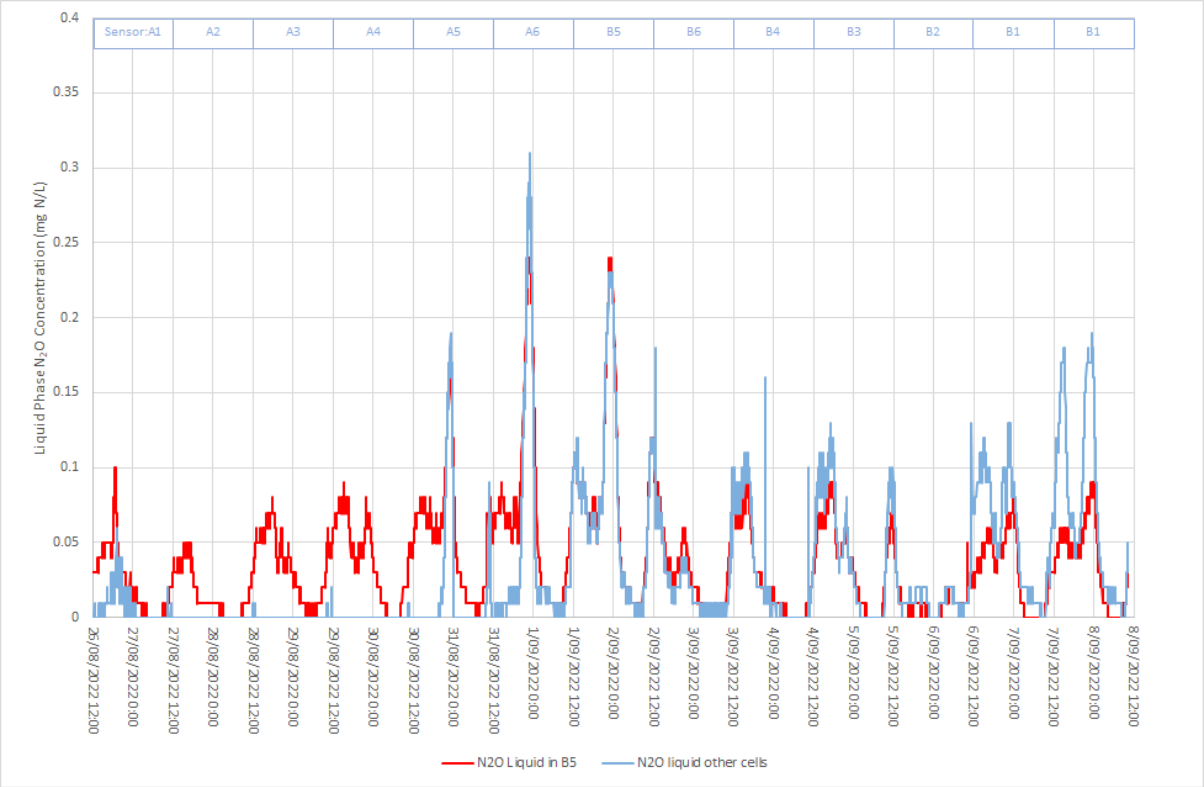
Figure 6 shows that the nitrate and nitrite concentrations increase along the length of the aerobic reactor as expected. Nitrite concentrations generally remain below 0.1 mg N/L indicating there is very little accumulation. The low nitrate concentration in cell B2 on the 5th September was due to a wet weather event.

Figure 6: Reactor ammonia, nitrate and nitrite concentrations



When measuring the liquid phase N_2O, one Unisense probe was left in cell B5 for the duration of the survey while the other was moved from cell to cell. Figure 7 compares the dissolved N_2O concentration in cell B5 with that in other cells. The probes show close agreement when they are both in cell B5, which gives confidence that the probes have been calibrated the same. The dissolved N_2O concentration appears to increase along the length of the reactor from the inlet to the outlet.

Figure 7: Liquid phase N_2O in Cell B5 and other cells



The Unisense manual presents a formula (see Equation 1) for calculating the off-gas N_2O concentration in aerated zones based on the dissolved N_2O concentration and the superficial gas velocity (air flow rate divided by reactor aerated surface area).

$$r_{N_2O} = H_{N_2O} \times S_{N_2O} \left(1 - e^{\frac{k_L a_{N_2O}}{H_{N_2O}} \times \frac{V_R}{Q_A}}\right) \times \frac{Q_A}{V_R} \quad (1)$$

where:

r_{N_2O} = N_2O emission rate (mg N_2O-N m^{-3} d^{-1});

H_{N_2O} = Henry's law constant;

S_{N_2O} = N_2O dissolved concentration (mg N_2O-N m^{-3});

Q_A = total airflow through reactor (m^3 d^{-1});

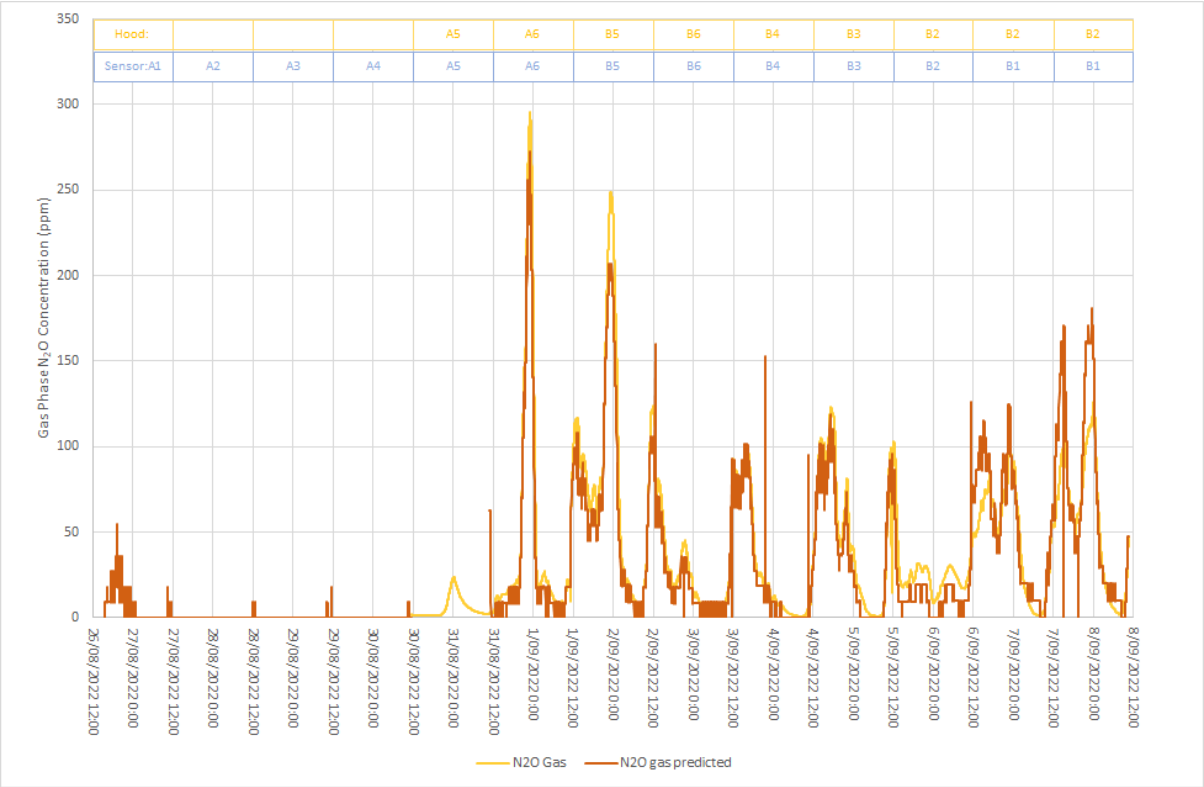
V_R = volume of aerated part of the reactor (m^3);

$k_L a_{N_2O}$ = N_2O mass transfer coefficient (d^{-1});

The complete set of equations including temperature correction is presented in the Unisense manual (Unisense, 2020).

The N_2O concentration in the off-gas was calculated using these equations. Figure 8 shows the comparison between the predicted concentration and the measured concentration.

Figure 8: Predicted versus measured gas phase N_2O concentration



The results indicate good agreement between the predicted and measured gas phase N_2O concentration, indicating that the dissolved N_2O concentration can be used to provide an estimate of N_2O emission rates. Myers et al. (2021) applied an empirically derived site-specific static correction factor to the results to better match the magnitude of N_2O in the off-gas. The authors advise that measurement of both liquid- and gas-phase N_2O concentrations is required to confirm the site-specific correlation between the liquid and gas phase concentrations.

CALCULATION OF N_2O EMISSION RATE

The average N_2O emission rate from MLE4 for the two-week monitoring period was calculated by summing the N_2O emissions from the individual cells. The emission from each cell was found by multiplying the off-gas N_2O concentration from the cell by the measured airflow to that cell. This approach assumes that the off-gas concentration in each cell on the day it was measured, is representative of the emissions from that cell during the two-week monitoring period. This

assumption could lead to inaccuracies in the estimated emission factor. However, for practical reasons it is not possible to measure the off-gas concentration in every cell simultaneously. For the purposes of this study the N_2O emissions from the anoxic zones are assumed to be small and have been ignored.

The average N_2O emission rate for MLE4 for the two-week period was found to be 4.15 kg N_2O-N/d. Based on the average influent total nitrogen load to the works during this period and given that 25% of this goes to MLE4, this gives an emission factor (EF) of 0.005 kg N_2O-N/kg $N_{influent}$ (0.5% N_2O-N/$TN_{influent}$). This is approximately half the value quoted as typical for a wastewater treatment plant (Andrews, 2021). However, it is noted that the survey was conducted over a short period. Therefore, this is viewed as only a snapshot of the N_2O emission rate. It is recommended that longer-term monitoring will provide further confidence in this figure, and monitoring for a period of at least a year would be required to understand the seasonal variations.

BIOWIN SIMULATION

The BioWin Activated Sludge Digestion Model (ASDM) includes three major process mechanisms for potential nitrous oxide production. Two of these are mediated by ammonia oxidizing bacteria (AOBs) and one by heterotrophs, as described below (EnviroSim Associates Ltd, 2014).

#1 Nitrification byproduct: When AOBs are operating at maximum rate in the presence of ammonia excess (NH_3 >> 2 x Ks), and with no oxygen limitation (DO >> 0), a small fraction of the oxidized ammonia is directed to N_2O.

#2 Nitrifier denitrification by AOBs: Under oxygen-limited conditions (0 < DO ≤ 0.4 mg/L) where nitrite is present, free nitrous acid (FNA) can be used as a terminal electron acceptor and is converted to N_2O.

#3 Heterotrophic denitrification: At low DO (0.4 < DO ≤ 0.8 mg/L), and depending on nitrite concentration and pH (pH < 7.5 or > 8), free nitrous acid (FNA) reaches a level where the final step of denitrification is inhibited, and N_2O accumulates.

Figure 9 compares the measured liquid phase N_2O with that predicted by the BioWin model. The model uses the BioWin version 6.2 default kinetic and stoichiometric parameters for nitrous oxide modelling. The model appears to overpredict the concentration in the anoxic cells. The measured data suggests that N_2O does not accumulate in these cells and that any N_2O in the internal recycle is rapidly consumed. The trend in the aerated cells is similar to the measured, but the magnitude of the values is much lower in the model.

Figure 9: Liquid phase N_2O measured versus model

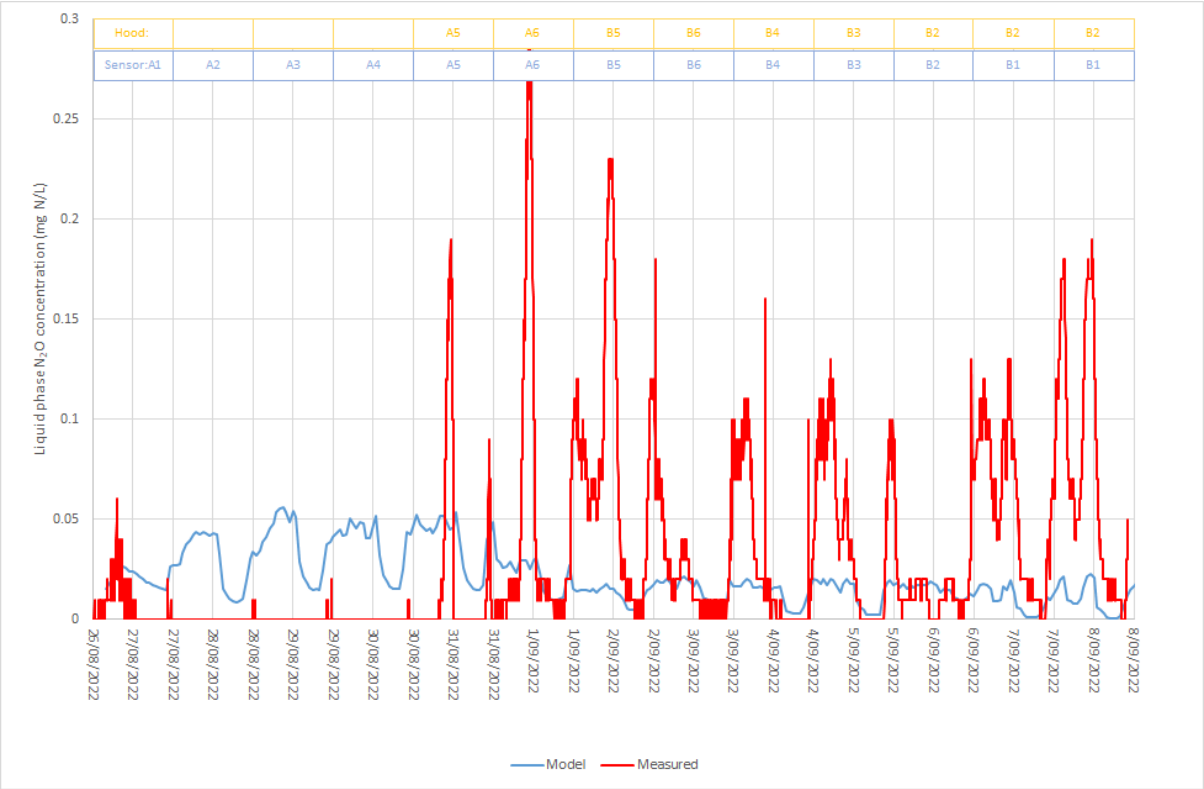


Figure 10 compares the measured gas phase N_2O with that predicted by the model. Again, the trend is similar, but the magnitude of the values in the aerated cells is somewhat different.

Figure 10: Gas phase N_2O measured versus model

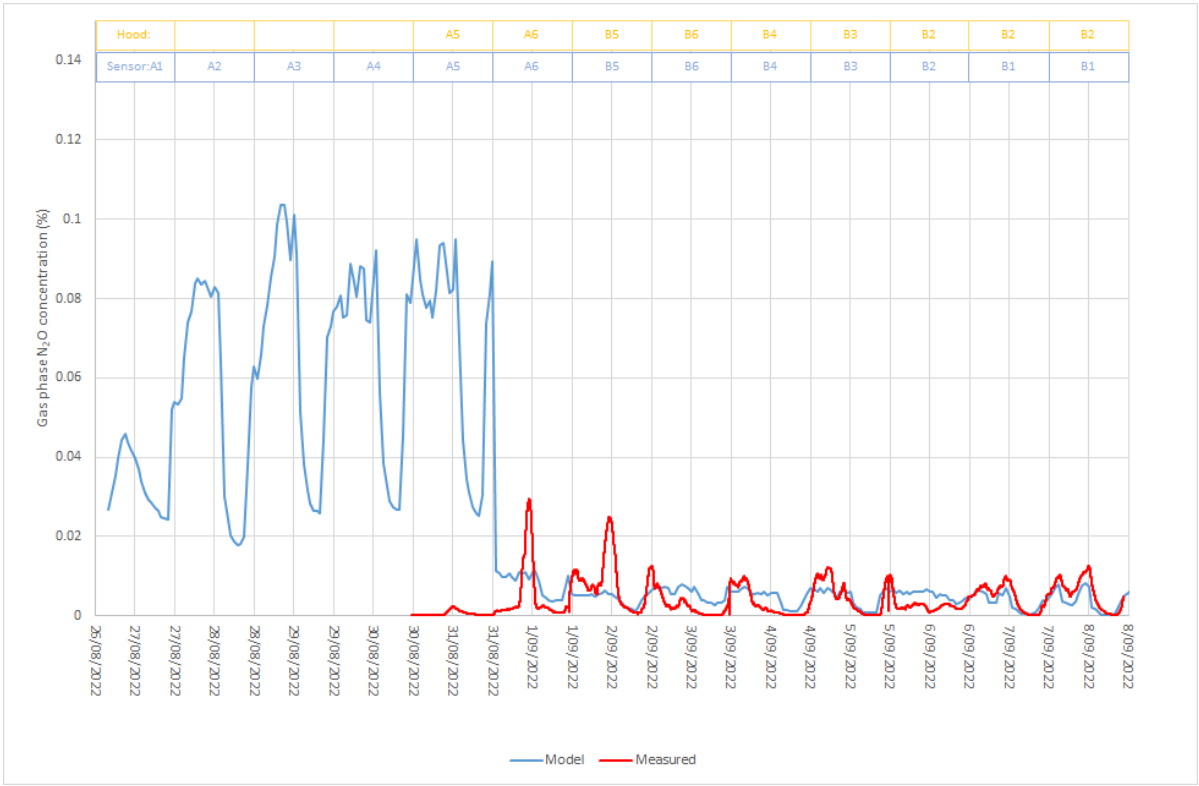
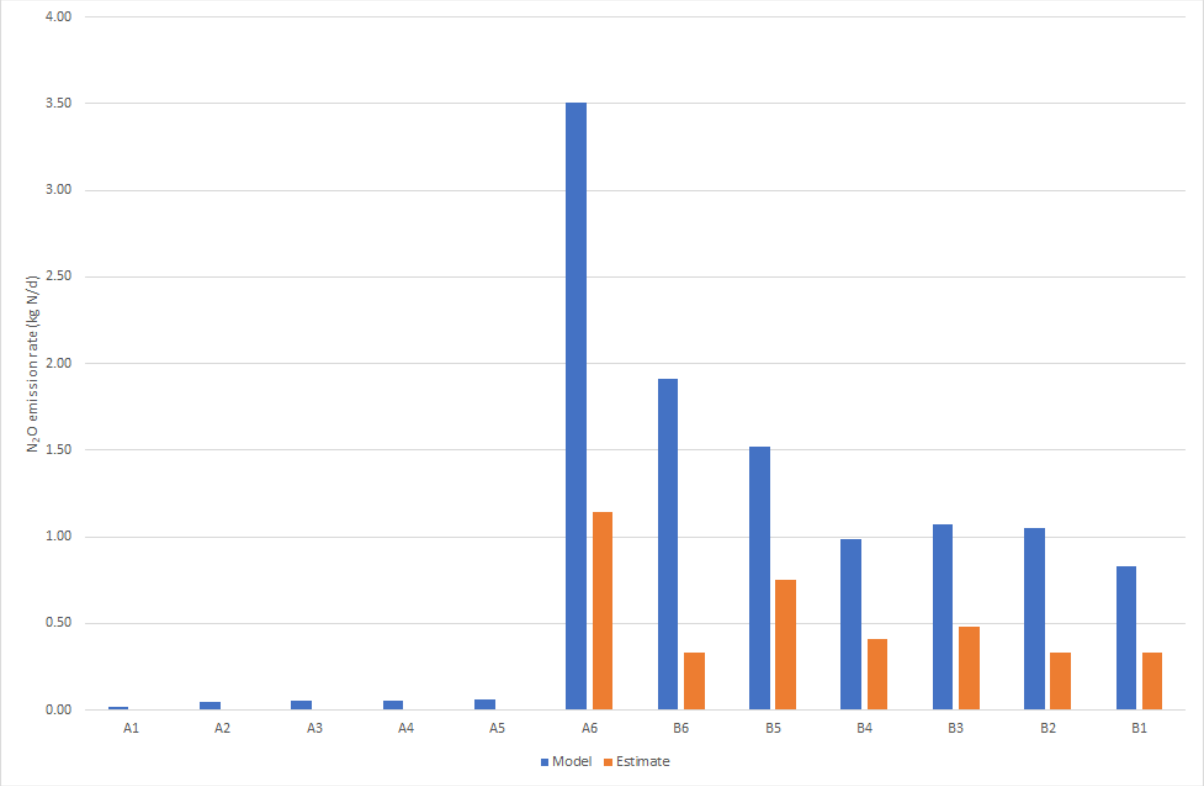


Figure 11 compares the estimated N_2O emission rate based on the site measurements with that predicted by the model.

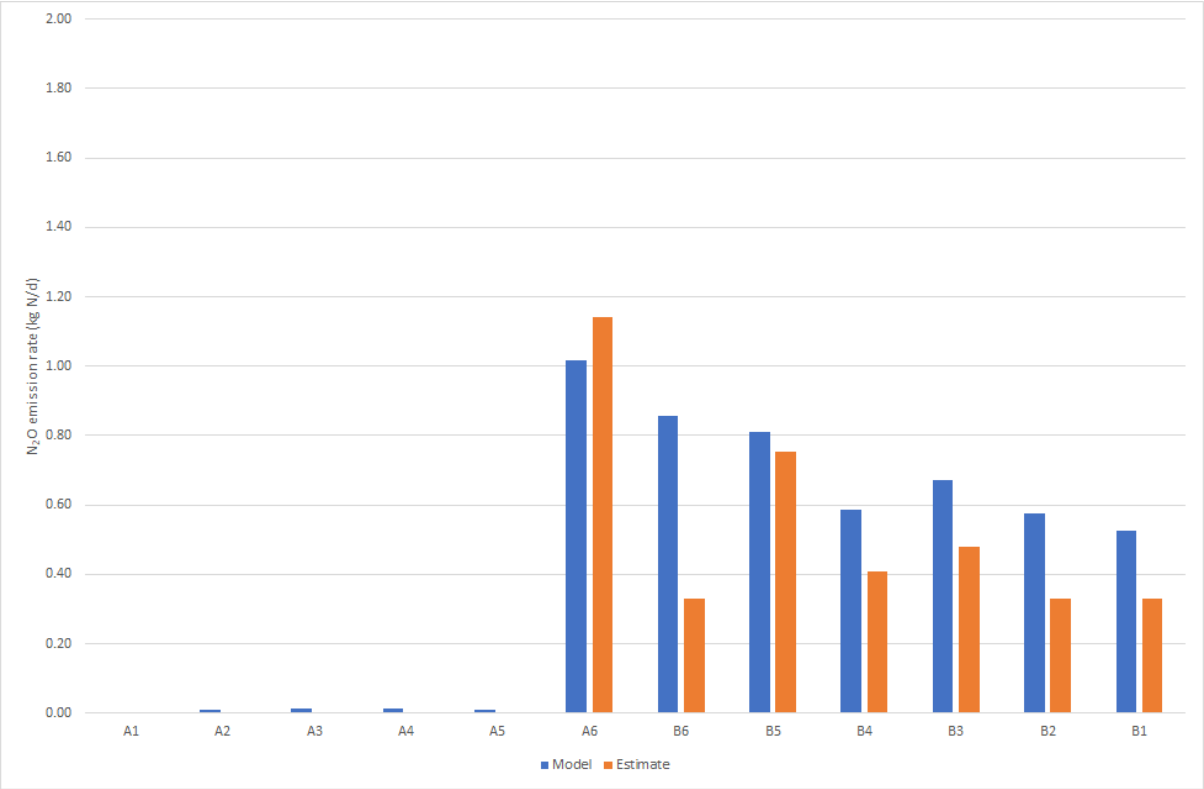
Figure 11: Estimated gas phase N_2O emission rate



The gas-phase N_2O concentration was not directly measured in cell B1 and therefore the estimated N_2O emission rate has been assumed to be equal to that in the adjacent Cell B2.

Figure 12 shows that, with Mechanism #3 (heterotrophic denitrification) switched off in the model, the model predictions agree more closely with the data, which suggests that this might be an area to focus on in the model.

Figure 12: Estimated gas phase N_2O emission with Mechanism #3 switched off



It is noted that the general trend in N_2O emission rates is similar between the model and that estimated based on the measured concentrations, in that the emission rate is highest in the first aerated cell and the declines along the length of the reactor.

At the time of publishing this paper there are ongoing efforts to improve calibration of the BioWin model, including an intensive site-wide sampling campaign being carried out in late 2022.

CONCLUSIONS

A two-week monitoring campaign was performed to gather data on N_2O process emissions from the new MLE4 at Rosedale WWTP. The results indicate that there is typically little dissolved N_2O in the anoxic cells, indicating that in this case N_2O generation and emission from the anoxic cells is low compared with the aerobic cells. In the aerated cells the trend in gas phase N_2O concentration generally follows the trend in dissolved N_2O concentration. The estimated emission factor for the period was 0.005 kg N_2O-N/kg $N_{influent}$ (0.5% N_2O-N/$TN_{influent}$). It is recommended that the monitoring continue for a period of at least a year to understand the longer-term variations.

To quantify the emission factor, in theory it would be necessary to measure the liquid phase- or gas-phase N_2O concentration in every cell simultaneously. However, for practical reasons it is only possible to measure one or two cells at the same time. Therefore, there will always be some assumptions in the calculation of the emission factor. A real-time model offers the potential to

overcome this limitation. However, it is necessary to have a high level of confidence in the model and in the data that goes into it.

Simulations using BioWin show similar trends in dissolved and gas phase N_2O concentrations, but with a different magnitude. There are ongoing efforts to improve calibration of the model. Once this is completed, it is expected that the Rosedale WWTP Digital Twin will provide an invaluable tool for identifying and mitigating process emissions.

ACKNOWLEDGEMENTS

The authors would like to thank the other members of the team for their contribution to this project, including Apra Boyle-Gotla (Watercare), Andrew Kennedy (Watercare), and Glenys Rule (Watercare).

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