NITROUS OXIDE MEASUREMENTS ON A PILOT SCALE MABR

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ABSTRACT

Nitrous Oxide is a potent greenhouse gas with a global warming potential of nearly 300 times that of carbon dioxide. Emissions of nitrous oxide from Watercare's wastewater treatment plants account for about 70% of our operational emissions based on IPCC 2016 emission factors. Understanding how much nitrous oxide is emitted from our treatment plants and how it might be mitigated are keys aspects of meeting our commitments of 50% reduction in emissions by 2030 and net zero by 2050.

Membrane Aerated Biofilm Reactors or MABR's are a new technology for the treatment of wastewater. The process is energy efficient and ideal for process intensification where total nitrogen removal or nitrification is required. The MABR process is claimed to have lower nitrous oxide emissions than processes such as activated sludge. Therefore, the technology has the potential to reduce emissions on both existing and new wastewater treatment plants.

Both MABR technology and the quantification of N2O emissions are relatively new areas of focus in wastewater treatment, and there are few studies that have been conducted that quantify emissions from MABR. Most have looked at MABR as a standalone unit and there are very few studies in the literature that have looked at a complete system (MABR with activated sludge reactors).

This paper presents monitoring undertaken on a pilot scale hybrid Membrane Aerated Biofilm Reactor, using a combination of gas and liquid phase measurements. The paper presents some lessons learned that can be applied to monitoring N2O in general. Some key differences in monitoring approaches for reporting of emissions and determining cause and effect are presented as well as a proposed emissions factor for the MABR process.

KEYWORDS

Nitrous Oxide, Pilot Trial, Greenhouse Gas emissions

PRESENTER PROFILE

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1.0 INTRODUCTION

Watercare has pledged to reduce operational carbon emissions by 50% by 2030 and to be net carbon zero by 2050.

Operational emissions consist of scope one and scope two as defined by the IPCC. Scope one emissions are those directly emitted from treatment and conveyance of water and wastewater and scope two emissions are derived from energy and power use.

Our scope one emissions are mainly emitted from wastewater conveyance and treatment. During the collection and conveyance of wastewater, fugitive methane may be produced from the breakdown of organic matter under anerobic conditions. This methane can be released to the atmosphere where flows become turbulent and methane strips from the water into the air. In a treatment plant, methane can be generated during primary sedimentation, sludge conditioning and thickening and is often generated at large facilities and is used as a fuel source for combined heat and power engines (CHP).

The second and potentially more significant scope one emission from wastewater treatment is nitrous oxide or N2O. This is formed during nitrogen removal via nitrification and/or denitrification. Nitrous Oxide has a global warming potential of about 300 times that of carbon dioxide (*USEPA 2023*).

Emissions of nitrous oxide can be quantified by either direct measurement, by factors supplied by the IPCC, or country specific emission factors. In New Zealand the water industry currently uses a factor from the IPCC 2019 guidelines that are based on the intensity of treatment.

Nitrous oxide emissions reporting is currently undertaken by Watercare by measuring the average load of nitrogen treated at a facility and multiplying this by the appropriate WaterNZ/IPCC factor. While this method is effective for reporting, it gives no information on the nature of emissions, type of plant, or how the facility is operated. Furthermore, an emission factor based on load treated does not allow mitigation strategies to be quantified, new technologies that may have lower emissions or operational or physical changes in the plant to be accounted for. Watercare are therefore undertaking a program of monitoring existing plants and measuring emissions from new technologies to inform our path to net zero.

This paper presents the results of intensive monitoring for nitrous oxide on a pilot Membrane aerated Bioreactor and suggests an emissions factor for this type of process, how it can be applied, and some lessons learnt of our fist nitrous oxide monitoring campaign. Since this paper was drafted further research has been undertaken into identifying N2O emission pathways and mitigation strategies for nitrous oxide.

2.0 BACKGROUND

The membrane aerated biofilm reactor (MABR) process is an innovative technology that offers for a wide range of applications. The MABR process employs a gas permeable media to deliver oxygen to a biofilm that is attached to the surface of the media. Oxygen is delivered to the biofilm by molecular diffusion, without the use of bubbles, resulting in energy efficient treatment independent of tank depth. This bubble-less oxygen transfer produces a unique environment within the biofilm where oxygen enters from one side and substrate (ammonia, organics) enter from the other side. This creates a range of process opportunities, including performing nitrification in reactors that are not otherwise aerated and developing different strata of microbes through the depth of the biofilm.

Figure 1 shows the structure of an MABR membrane and biofilm versus that of a conventional carrier process such as MBBR.

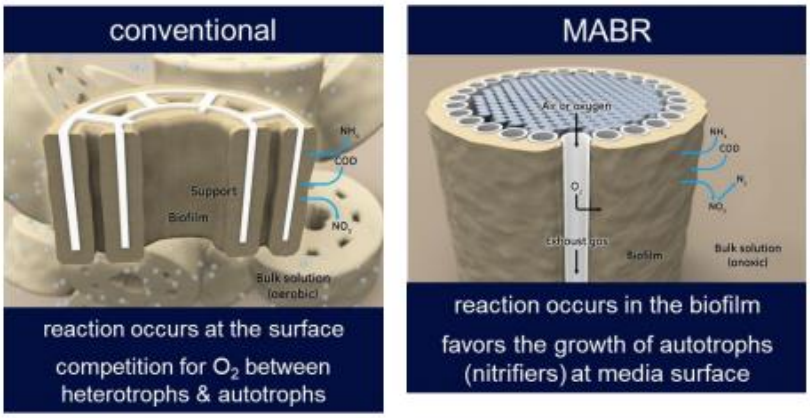


Figure 1: MABR compared to Conventional Biofilm

2.1 MABR TECHNOLOGY

MABR technology can be used in a range of applications. The most common is the upgrade of conventional activated sludge (CAS) plants for nutrient removal and capacity expansion in existing tank volumes (Kunetz et al., 2016). In this application, MABR intensifies treatment capacity and improves performance by increasing the biomass inventory while also significantly reducing the energy required for aeration. For this hybrid configuration, MABR media is installed into an activated sludge reactor, typically in the anoxic zone. A biofilm grows on the media surface and increases the total inventory in the system at the same suspended growth mixed liquor concentration.

MABR has been reported (*Houweling & Uri-Carreno*) as having lower nitrous oxide emissions when compared to conventional activated technology. There have been some studies (*Houweling & Uri-Carreno*) on the emission of N2O from MABR, however the small amount of literature available makes it very difficult to use emissions factors measured elsewhere in the New Zealand context.

There is also some literature (Kinh 2017) that suggests that operational conditions may have an impact on emission rates, hence measuring emissions under specific controlled operating conditions may help to remove this bias if it exists.

2.2 MABR PILOT TRIALS

Watercare has been running pilot trials on MABR technology over the past two years at our innovation centre located at the Mangere Wastewater Treatment plant. These trials initially focused on proof of concept for Pure MABR and hybrid systems, and the setup we have is ideal for measuring nitrous oxide.

Given that hybrid MABR is claimed to have lower scope one emissions than other activated sludge systems, we wanted to measure nitrous oxide emissions and develop an emissions factor to inform our future planning. We also wanted to learn how to monitor and to trail some of the liquid and gas phase sensors for nitrous oxide measurement that are available on the market. An additional goal of the pilot was to determine if we could apply lessons learnt to the full scale and to try and understand some of the cause-and-effect mechanisms with nitrous oxide production in activated sludge systems in general.

2.3 PILOT PLANT SET UP

The pilot plant at the Mangere innovation centre consists of an MABR tank, with three Zeelung modules, a downstream activated sludge reactor configured with an anoxic zone with a mixer and an aerated reactor with diffused aeration, followed by a conventional clarifier. Return activated sludge is pumped from the clarifier back to the MABR tank.

A simplified PFD of the pilot is shown in figure 2 below.

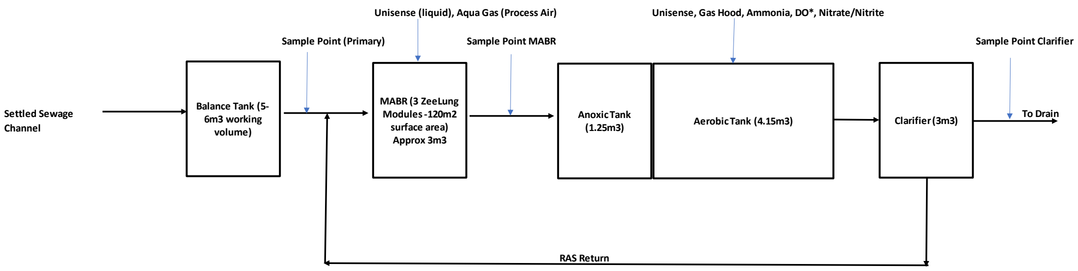


Figure 2: Pilot Plant PFD

Photo 1 shows a membrane module installed in its support from before installation and Photo 2 shows the pilot skid awaiting installation at the innovation centre.

Photo 1: Membrane Modules and Support Frame

The membrane modules are arranged in a frame with air connections at the top and bottom. Process air is connected to the base of the support frame and is drawn off from the top of the modules. Process air is applied at a constant rate of 4-5L/min or approximately 8m^3/hr per full scale cassette.

Photo 2:   MABR Before Installation

Wastewater is pumped from the settled sewage channel at Mangere into an 8m^3 balance tank via a self-priming dry mounted pump. From the balance tank a pump fitted with variable speed drive delivers between 4 and 10m^3/d of primary settled wastewater to the pilot tank. Process air is supplied via site compressed air. This process air is filtered, and pressure is reduced from 5-6 bar to between 0.6 and 0.7 bar. Exhaust air oxygen, CO_2 and nitrous oxide content are measured via MAMOS gas analysers (see photo 3)

Photo 3: Gas Analyser

In addition to the process air, the pilot has mixing air and scour air. These are used to mix the contents of the reactor to minimise any solids settling and to ensure that substrate is "refreshed" at the membrane liquid interface. This minimises the risk of diffusion limiting treatment performance. Scour air is applied to the membranes via a LEAP aerator (the same as on MBR systems). This provides a stream of course bubbles that scour biomass off the membrane surface to manage its thickness. Both systems on this pilot are run via timers and control valves that are operator adjustable.

Effluent from the MABR reactor flows over a weir and flows by gravity to a downstream activated sludge tank and a clarifier. Clarified effluent is discharged to drain and settled sludge (RAS) is returned to the MABR via a fixed speed pump.

3.0 METHODS AND MATERIALS

3.1 NITROUS OXIDE MEASUREMENTS

Nitrous oxide can be dissolved in the liquid within a treatment plant or in the gas leaving the surface of the process tanks. Dissolved N2O (liquid phase) will usually only be emitted to the atmosphere where there is a flow of gas through the liquid, such as in an aeration tank. In an MABR, nitrous oxide can be discharged from the process air exhaust of from the tank surface.

3.2 MABR

3.2.1 PROCESS AIR

Process air is applied to the MABR membranes at the top of each module. This air travels through the membrane lumen, is collected and discharged to atmosphere. The inlet process air contains approximately 21% oxygen and the exhaust air typically contains 12-14% oxygen, the difference being the amount consumed by the process. In addition to oxygen, the exhaust air also contains nitrous oxide and carbon dioxide. This concept is shown figure 3.

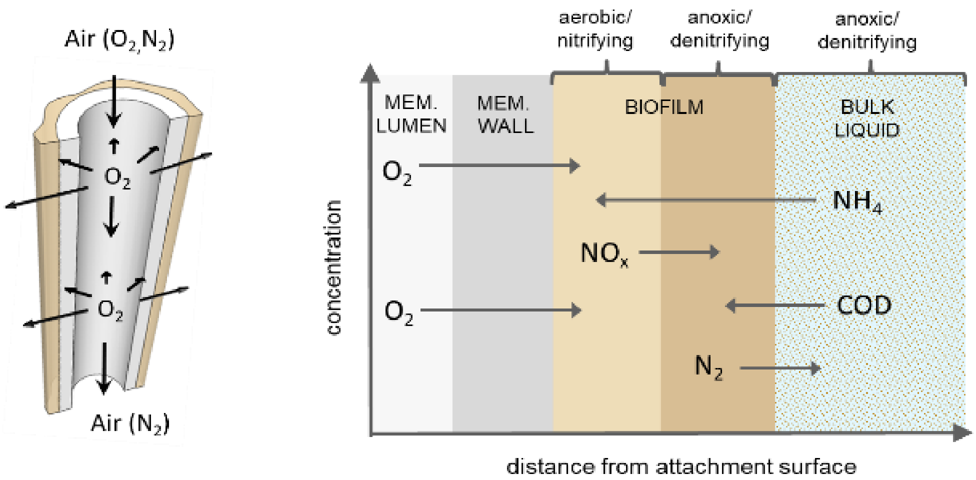


Figure 3: MABR Oxygen and Substrate Consumption

The exhaust air from the MABR was monitored using an Aquagas N2O/CO2 analyser, with data recorded in the on site SCADA.

3.2.2 MABR SCOUR AND MIXING AIR

Coarse bubble aeration is used within the MABR to mix the reactor and to scour the membrane surface for biofilm thickness control. Scour and mixing air exits to the atmosphere via the surface of the MABR tank. This air may contain N2O if there is dissolved N2O present in the MABR liquid. In the pilot setup mixing/scour air was sampled by placing a lid over the top of the MABR tank. Offgas was collected via gas tubing and pumped to a Picarro CRDS analyser. Note that because this air stream is not operated continuously this source of N2O emission is periodic.

3.2.3 MABR LIQUID

Dissolved nitrous oxide may be present in the liquid phase of the MABR tank due to biological reactions occurring in the biofilm or in the bulk liquid. To measure the N2O dissolved in the liquid phase inside the MABR tank, a Unisense N2O probe was used. This liquid measurement allowed us to correlate the gas and liquid phases and determine if N2O was being formed in the biofilm or in the bulk liquid or both.

3.3 ACTIVATED SLUDGE REACTOR

3.3.1 ACTIVATED SLUDGE AERATION

Within the aeration tank air is applied to supply oxygen to the process to oxidise residual COD and ammonia from the MABR. Note that the MABR is a diffusion driven process and low concentrations of substrate will slow reaction rates quite significantly. To achieve maximum nitrification rates in the biofilm, the residual ammonia in the MABR tank needs to be between 5- 10mgN/l, hence some additional ammonia oxidation is needed in the downstream activated sludge tank to reduce ammonia to low levels in the final effluent.

In the pilot plant aeration air was supplied through a series of diaphragm blowers, with one, two or three blowers operated at once to maintain the desired dissolved oxygen concentration. Air flow to the diffusers was measured using a rotameter and recorded each day (airflow was constant unless blowers were started or stopped). Off gas was measured through a gas hood (see photo 4) with the gas being analysed in a Picarro CRDS analyser. The flow of air through the hood was measured with a rotameter and recorded each day.

Photo 4: Gas Hood on Aeration Tank

3.3.2 LIQUID MEASUREMENTS

A second Unisense liquid phase N2O probe was installed in the aeration tank of the activated sludge reactor. This probe could also be moved to the unaerated portion of the reactor to determine if N2O production or reduction was happening within the unaerated tank.

3.3.3 ADDITIONAL MEASUREMENTS

In addition to measurements of the liquid and gas phase N2O, the pilot activated sludge tank was fitted with dissolved oxygen, ammonia and nitrate/nitrite sensors that were connected to SCADA. Samples of COD, TSS, VSS, TKN, ammonia and phosphorous were taken from the influent wastewater, MABR tank and clarifier each day during a series of intensive sampling campaigns. These were used to quantify loads and removal rates of the different wastewater characteristics.

A log was also kept during the trials of influent flow, airflows, offgas oxygen and reactor temperature and any operational changes were noted including any equipment failures.

4 RESULTS AND DISCUSSION

4.1 LIQUID AND GAS PHASE RESULTS

Figure 4 presents a plot of dissolved and gas phase nitrous oxide measured within the MABR pilot tank. Data from March to early April 2023 have been excluded as during this period a series of experiments were run to look at cause and effect of how nitrous oxide may be formed and removed in the MABR.

As shown in the figure the amount of N2O measured is quite variable with significant and regular peaks of both liquid and gas phase N2O. It can also be noted that there are periods where the N2O is present in the gas phase, but very little (or none) is present in the liquid. During these periods, back diffusion of N2O is likely to be very small, due to low or no concentration gradient, and back diffusion must be equal or more than the rate of production in the liquid. These periods where N2O is detected in the gas and not the liquid may also represent the emission profile of the biofilm only and not generation from the bulk liquid.

Measurements were also taken from the MABR headspace during this time as described above to try and quantify how much (if any N2O) was stripped from the reactor during either mixing or scour cycles. These measurements showed that while there was N2O and methane stripping occurring, the amount of nitrous oxide emitted over a period of time was very small compared to that emitted from the process air exhaust.

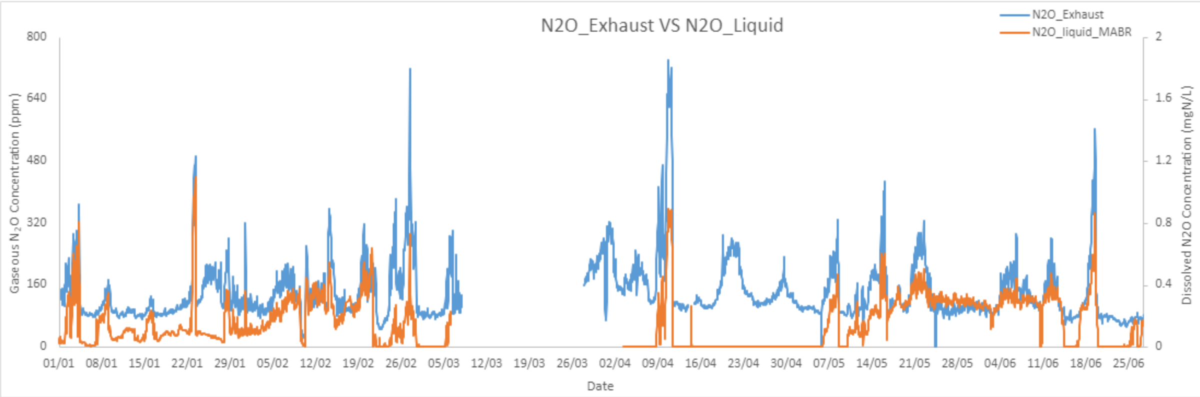


Figure 4: Liquid and Gas Phase Measurements from MABR

Figure 5 shows a plot of nitrous oxide in the process exhaust gas (blue line) and oxygen in the offgas (green line). The trends show the effect of air scour on both gases. This is hypothesised to be due to diffusion of gas from the membrane and biofilm into the liquid as the scour bubbles pass over the membrane surface, changing the diffusion dynamics of the system.

Figure 5: Oxygen and N2O offgas Measurements from MABR

Several key learnings were made with the MABR tank measurements, and these are described below.

4.1.1 HEADSPACE

Analysis of the headspace offgas data showed that the air coming out the volume between the MABR liquid surface and the tank lid always had significant amounts of N2O and that the concentrations in the gas were very stable between scour events. After further investigation and analysis, it was identified that the turnover of gas in the headspace was negligible, hence the analyser was constantly measuring the gas present in this zone, not that emitted from the process.

Key Learning – a carrier gas is essential for good N2O measurements where there is no consistent flow of air through a process headspace, this applies to offgas measurements on anoxic zones, ponds and covered tanks.

4.1.1 MASS TRANSFER

The effect of the scour shown in figure 5 highlights that the gas to liquid and liquid to gas mass transfer occurring in the MABR influences measurement. These relationships need to be considered when looking at where and how to measure nitrous oxide as gases can diffuse backwards and forwards between phases depending on the reactor conditions.

Key Learning – Mass transfer of gas to liquid and liquid to gas need to be considered when measuring nitrous oxide.

4.2 N2O FLUX

Figure 6 presents the nitrous oxide flux (gN2)/hr) emitted from the exhaust gas from the MABR (orange) and from the surface of the activated sludge process via the gas hood (blue).

The data shows that the emissions from the activated sludge process are similar or greater than the MABR with very significant spikes in the N2O flux from the activated sludge tanks in June 2023. Data from March/April has been excluded due to batch tests and experiments being conducted on cause and effect of nitrous oxide production.

Given that the MABR does most of the nitrification (about 70% in this study) the emissions from the activated sludge process are very significant when compared to the MABR based on ammonia removed.

With reference to figure 4, when N2O is elevated in the MABR off gas there is a significant amount of dissolved N2O in the liquid phase of the MABR tank. As this dissolved N2O is not all stripped, some of it is transferred to the downstream anoxic and aerated tanks where it can be stripped out of solution by aeration. This stripped N2O is then measured as an emission from the activated sludge process, however based on the liquid phase measurements in both tanks, most of this emitted N2O did not form in the activated sludge tanks.

It is very important to note that while N2O is stripped from the activated sludge tank because of aeration, this does not necessarily mean that the N2O was formed in the same place. This is an extremely important aspect to consider if cause and effect rather than the amount of emissions is being investigated. If cause and effect is being considered (and potential mitigation) the source of N2O may be more important than the emission rate. To determine the total emissions factor the whole system must be considered not either part in isolation.

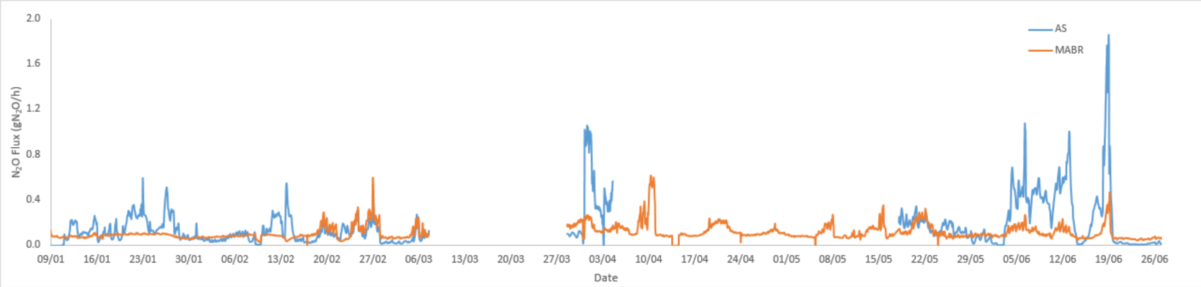


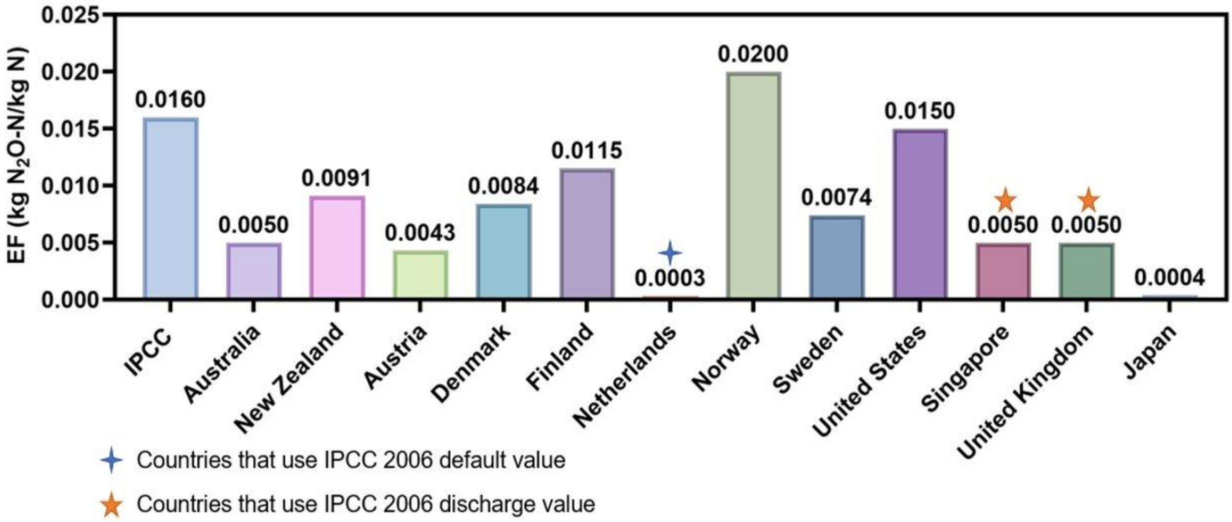
Figure 6: Nitrous Oxide Flux

Key Learning – high N2O emissions from a portion of a process do not always mean that the N2O was formed in the same part of the process. The whole system must be considered.

4.3 EMISSIONS FACTOR

Figure 7 presents the measured emissions factor from the MABR process over the study period. Note that the factor is only reported for periods where intensive sampling was undertaken and the mass of ammonia in and out of the process was fully quantified daily. The emissions factor measured in this study averages about 2% or 0.02gN2O/gN treated. This is significantly higher than reported by other authors and greater than the IPCC factor for activated sludge processes. There are several reasons for this higher-than-expected emissions factor:

- The gas analyser used for the MABR gas measurements was found to have an offset at low (<50ppmV) N2O concentrations. The instrument has since been calibrated, however the results presented above have not been corrected for the offset
- The study at the innovation centre at Mangere is the only study we are aware of that has measured the MABR and activated sludge process as a system rather than individual units. Hence there is limited or no data to compare this study against. The measured factor is within the range of those measured for activated sludge plants in other studies that have been reported (see figure 7 below)



- Subsequent work on the pilot and experiments into cause and effect of how nitrous oxide is produced and what pathways appear to dominate production and consumption has been undertaken. This work will be presented at a later date, however mitigation can be applied and we have been able to reduce emissions by 50-80%

- The work presented above and our subsequent work on mitigation shows that the N2O emission rates may depend more on the operation of the facility or plant being tested than its configuration or even the process type

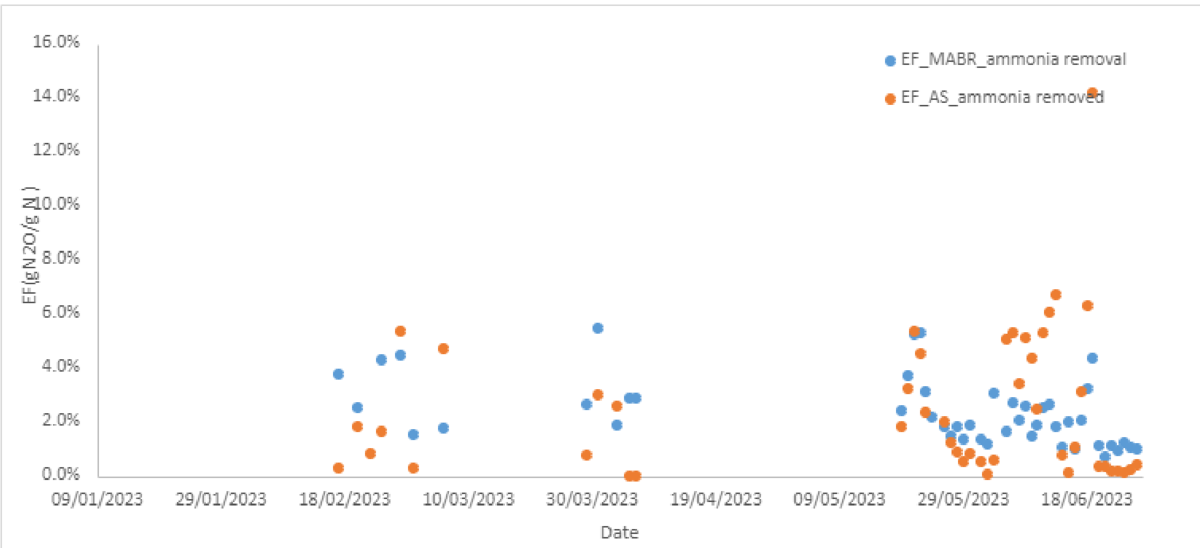


Figure 7: Oxygen and N2O offgas Measurements from MABR

Key Learning – Consideration of Operational conditions are essential to understand emissions and to compare studies and data to each other. Operation *of a plant has a very significant impact on results and may be more important than process configuration.*

CONCLUSIONS

This paper has presented monitoring undertaken on a pilot scale hybrid Membrane Aerated Biofilm Reactor, using a combination of gas and liquid phase measurements. An emissions factor for an MABR system has been determined and key lessons learnt for future studies and investigations into N2O emissions.

A key result of this study is that there is a difference in measurement for investigating why N2O formation occurs and measurement for mitigation. The study has also highlighted that the operational conditions of the plant are an essential aspect of nitrous oxide emissions and must be understood for comparisons between different studies to be made.

Further work has been undertaken on investigating cause and effect of N2O production in a hybrid MABR and a successful mitigation strategy has been developed.

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