

# Comparison of methods for nitrous oxide emission estimation in full-scale activated sludge

Shanna Myers , Anna Mikola , Kati Blomberg ,  
Anna Kuokkanen  and Diego Rosso 

## ABSTRACT

Nitrous oxide (N<sub>2</sub>O) gas transfer was studied in a full-scale process to correlate liquid phase N<sub>2</sub>O concentrations with gas phase N<sub>2</sub>O emissions and compare methods of determining the volumetric mass transfer coefficient, K<sub>L</sub>a. Off-gas and liquid phase monitoring were conducted at the Viikinmäki wastewater treatment plant (WWTP) over a two-week period using a novel method for simultaneous measurement of dissolved and off-gas N<sub>2</sub>O and O<sub>2</sub> from the same location. K<sub>L</sub>a was calculated with three methods: empirically, based on aeration superficial velocity, from experimentally determined O<sub>2</sub> K<sub>L</sub>a, and using a static value of best fit. The findings of this study indicated trends in local emitted N<sub>2</sub>O consistently matched trends in local dissolved N<sub>2</sub>O, but the magnitude of N<sub>2</sub>O emissions could not be accurately estimated without correction. After applying a static correction factor, the O<sub>2</sub> method, using experimentally determined O<sub>2</sub> K<sub>L</sub>a, provided the best N<sub>2</sub>O emission estimation over the data collection period. N<sub>2</sub>O emissions estimated using the O<sub>2</sub> method had a root mean square error (RMSE) of 70.5 compared against measured concentrations ranging from 3 to 1,913 ppm and a maximum 28% error. The K<sub>L</sub>a value, and therefore the method of K<sub>L</sub>a determination, had a significant impact on estimated emissions.

**Key words** | full-scale, gas transfer, greenhouse gases, nitrous oxide, off-gas, wastewater treatment

## HIGHLIGHTS


- The selected method for N<sub>2</sub>O K<sub>L</sub>a determination significantly impacts estimated N<sub>2</sub>O emissions.
- A novel method was developed for continuous, simultaneous measurement of dissolved and emitted O<sub>2</sub> and N<sub>2</sub>O.
- Feasibility of estimating local emissions from dissolved N<sub>2</sub>O measurements and O<sub>2</sub> transfer in a full-scale activated sludge basin was confirmed using this novel method.

## INTRODUCTION

N<sub>2</sub>O released from wastewater treatment plants accounts for 3% of anthropogenic N<sub>2</sub>O emissions worldwide (IPCC 2013). N<sub>2</sub>O is a significant greenhouse gas (GHG) with a 100-year global warming potential nearly 300 times greater than that of CO<sub>2</sub> (IPCC 2013). Current knowledge suggests the majority


of N<sub>2</sub>O production in wastewater treatment occurs during biological denitrification and nitrification processes (Kampschreur *et al.* 2009). There is a desire for increased accuracy in estimating N<sub>2</sub>O emissions from individual treatment plants in order to modify operational strategies to reduce GHG emissions from wastewater treatment.

Emissions of N<sub>2</sub>O can be mathematically modelled with a derivation of the two-film theory (Matter-Müller *et al.* 1981; Von Schulthess *et al.* 1995), but use of this

**Shanna Myers**  (corresponding author)  
Aalto University and Murraysmith,  
888 SW 5th Avenue, Suite #1170, Portland, OR  
97204,  
USA  
E-mail: shanna.myers@murraysmith.us

**Anna Mikola**   
Aalto University,  
P.O. Box 11000, FI-00076 Aalto,  
Espoo,  
Finland

**Kati Blomberg**   
**Anna Kuokkanen**   
Helsinki Region Environmental Services Authority  
(HSY),  
P.O. Box 100, FI-00066 HSY,  
Helsinki,  
Finland

**Diego Rosso**   
University of California,  
Irvine, CA 92697,  
USA

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (<http://creativecommons.org/licenses/by/4.0/>).

doi: 10.2166/wst.2021.033

mathematical model requires an N<sub>2</sub>O K<sub>L</sub>a value. This K<sub>L</sub>a is specific to wastewater conditions, varies with time and location, and limited studies have focused on determining this K<sub>L</sub>a in clean water and wastewater (Foley *et al.* 2010; Domingo-Félez *et al.* 2014; Mampaey *et al.* 2015). An empirical equation for N<sub>2</sub>O K<sub>L</sub>a proposed by Foley *et al.* (2010), referred to within this study as the superficial velocity method, has been employed in estimating N<sub>2</sub>O emissions with decent accuracy (Baresel *et al.* 2016; Fenu *et al.* 2020). N<sub>2</sub>O K<sub>L</sub>a can also be estimated from a known O<sub>2</sub> K<sub>L</sub>a and diffusivity data (Higbie 1935; Fiat 2019), referred to within this study as the O<sub>2</sub> method. Many studies assume the impact of wastewater conditions on O<sub>2</sub> and N<sub>2</sub>O transfer to be analogous (e.g. von Schulthess *et al.* 1995; Foley *et al.* 2010; Fiat 2019), and this is a key assumption in order to calculate N<sub>2</sub>O K<sub>L</sub>a from O<sub>2</sub> K<sub>L</sub>a without having to determine the diffusivities of N<sub>2</sub>O and O<sub>2</sub> in each wastewater matrix. However, the relationship between changes in wastewater quality and changes in N<sub>2</sub>O transfer is relatively unknown compared to water quality impacts on O<sub>2</sub> transfer. The solubility of N<sub>2</sub>O is higher than that of O<sub>2</sub>, and N<sub>2</sub>O has a Henry's coefficient in water that is nearly 20 times larger than for O<sub>2</sub> in water (Sander 2015). Therefore, the accuracy of this assumption of analogous mass transfer impacts needs to be confirmed.

Despite the use of K<sub>L</sub>a estimation methods in N<sub>2</sub>O emissions modelling, there have been mixed results for the accuracy of these methods in differing conditions. Domingo-Félez *et al.* (2014) performed a lab-scale test comparing N<sub>2</sub>O and O<sub>2</sub> K<sub>L</sub>a values, finding that these values were impacted to a different degree by superficial velocity. Foley *et al.* (2010) developed their superficial velocity K<sub>L</sub>a estimation equation based on N<sub>2</sub>O emissions from lab data and full-scale data from the aerated zones of seven treatment plants in Australia, between 3.6 and 6.0 metres deep. Ye *et al.* (2014) tested this superficial velocity method in a system with surface aerators and found it less applicable in high turbulence such as caused by surface aeration. Marques *et al.* (2016) compared the superficial velocity method against the O<sub>2</sub> method in a full-scale treatment plant, continuously monitoring gas and dissolved N<sub>2</sub>O with Clark-type microsensors and calculating O<sub>2</sub> method K<sub>L</sub>a from a static average O<sub>2</sub> transfer rate for the plant. Their study found the O<sub>2</sub> method to be more accurate than the superficial velocity method under the conditions tested at a full-scale WWTP in Spain, using sequencing batch reactors. This study attempts to further assess the impact of K<sub>L</sub>a estimation methods as well as to compare dynamic calculated K<sub>L</sub>a values against a static estimated K<sub>L</sub>a value.

The Viikinmäki WWTP in Helsinki, Finland is well-suited for GHG emission measurements due to the entire plant being enclosed underground. All emissions from Viikinmäki exit from a central exhaust point that is continuously monitored. The Helsinki Region Environmental Services Authority (HSY) began N<sub>2</sub>O and GHG emissions studies at Viikinmäki in 2007, and continuous on-line monitoring of emissions in 2012 (Kosonen *et al.* 2016). Continuous on-line monitoring of dissolved N<sub>2</sub>O began in 2016, using dissolved N<sub>2</sub>O probes in the activated sludge basins of two of the nine treatment lines (Blomberg *et al.* 2018). The continuous measurements taken at Viikinmäki WWTP during this study, though limited in duration, were novel in that they included the continuous collection of dissolved and emitted N<sub>2</sub>O alongside dissolved and emitted O<sub>2</sub> from the same location. This allowed for a more direct comparison of O<sub>2</sub> and N<sub>2</sub>O transfer, as well as of O<sub>2</sub> and N<sub>2</sub>O K<sub>L</sub>a values.

The goal of this paper was to compare multiple methods for N<sub>2</sub>O K<sub>L</sub>a calculation in gas stripping equations and assess the differences attributable to the choice of method. Three calculation methods were used to estimate N<sub>2</sub>O K<sub>L</sub>a: the superficial velocity method, which requires the fewest parameters to calculate K<sub>L</sub>a but does not account for any changes to water quality except as they affect basin aeration; the O<sub>2</sub> method, which requires more data collection and takes into account impacts of water quality on O<sub>2</sub> transfer, but assumes they apply equally to N<sub>2</sub>O transfer; and a static estimation that represented using a static K<sub>L</sub>a for N<sub>2</sub>O emission calculations. The resulting calculated N<sub>2</sub>O emissions were compared against measured emissions to assess accuracy. This study used a novel method to concurrently measure N<sub>2</sub>O and O<sub>2</sub> transfer at a full-scale treatment plant and is one of the first to compare N<sub>2</sub>O and O<sub>2</sub> transfer while considering the dynamic nature of gas transfer K<sub>L</sub>a values.

## MATERIALS AND METHODS

### Process description

The Viikinmäki WWTP treats wastewater for a population equivalent of over 1 million, consisting of 85% residential and 15% industrial wastewater. The average wastewater flow is 270,000 m<sup>3</sup> d<sup>-1</sup> and the influent total nitrogen concentration is 49 mg L<sup>-1</sup>. Viikinmäki WWTP performs physical, chemical, and biological treatment of wastewater, as well as tertiary treatment in denitrifying filters. The Viikinmäki WWTP has nine biological treatment lines with conventional floc-forming sludge, and each line

includes a 12 m deep conventional activated sludge basin that holds 11,500 m<sup>3</sup>. Each activated sludge basin is divided into six zones with fine-bubble membrane disc diffusers for aeration that can be turned on or off to modify the process. The activated sludge basins at Viikinmäki are built into rock tunnels and access to the basins consists of a single path in the middle of each basin.

Aeration can be turned on and off individually for each zone. Under typical conditions, zones 1 and 2 are anoxic, zone 3 aeration is controlled by NH<sub>4</sub><sup>+</sup> loading, and zones 4 through 6 are continuously aerated. During the measurement campaign, dissolved oxygen (DO) in each aerated zone was set to 3.0 mg L<sup>-1</sup>. The hydraulic retention time in the activated sludge basin is typically 8 hours. Prior to exiting the tank and heading to secondary settling, the mixed liquor must pass through a degassing zone due to the depth of the process tanks. The instrumentation layout in the Viikinmäki WWTP line 9 activated sludge basin is shown in Figure 1.

### Measurement campaign and equipment

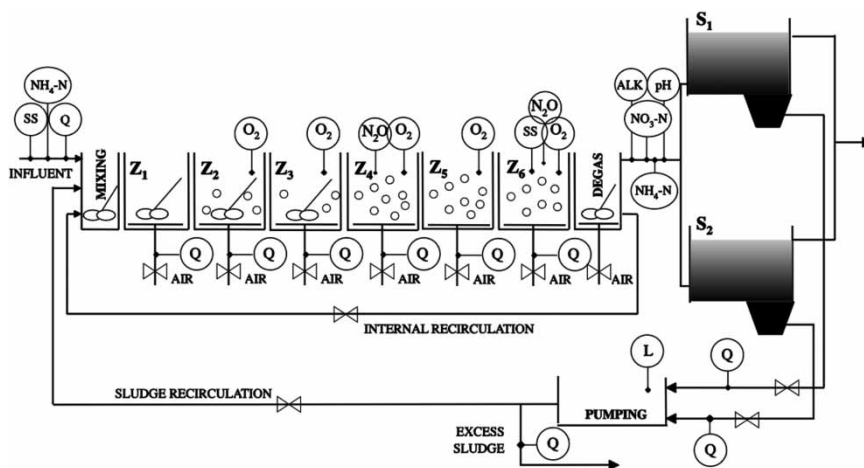
Data were collected from the aerated zones of the activated sludge basins in lines 5 and 9 at Viikinmäki WWTP during two months in late spring of 2019. The longest period of continuous measurement occurred from 14–20 May in the aerated zone 4 of line 9. During spring and summer 2019, Viikinmäki WWTP was experiencing an unprecedented increase in N<sub>2</sub>O production, probably caused by the inhibition of nitrite oxidizing bacteria reflected in high nitrite concentrations (2–7 mg L<sup>-1</sup>). This resulted in significantly higher N<sub>2</sub>O concentrations and emissions (8–20% of the

influent nitrogen load) than recorded in the past 3 years of continuous monitoring.

Off-gas samples were collected using a modular off-gas hood placed near a dissolved N<sub>2</sub>O probe. This modular off-gas hood was constructed at the Aalto University Water Laboratory in Espoo, Finland. The hood was based on a modular design used by Rosso (2018) in prior off-gas experiments, with modifications due to local differences in available materials. For images and dimensions of the modular hood, see section 1 of the supplemental material.

The emissions collected from the activated sludge basin were directed to a mobile measurement array. At this array, multiple parameters were measured and logged continuously. Velocity and air temperature were measured with a datalogging hot wire thermos-anemometer (Extech; Nashua, New Hampshire), and a Gasetm DX4015 Fourier-transform infrared (FTIR) analyser (Gasetm Oy, Finland) measured emitted N<sub>2</sub>O concentrations downstream of velocity measurements. Further downstream, the gas sample was pumped through a desiccating column containing sodium hydroxide pellets for CO<sub>2</sub> removal and desiccant for water vapour removal before being run through an O<sub>2</sub> analyser (AMI model 65; Fountain Valley, CA) to measure the percent O<sub>2</sub> in the sample. An external datalogger (squirrel meter/logger 1,000 series; Grant Instruments, UK) recorded these readings. For images and a table describing the measurement array components, see section 2 of the supplemental material.

Dissolved N<sub>2</sub>O concentrations were measured using online Clark-type microsensors (Unisense; Denmark) located near the modular off-gas hood. DO in the activated sludge basin zones and near the modular hoods was measured using a combination of the Viikinmäki process DO probes



**Figure 1** | Schematic layout of the Viikinmäki line 9 activated sludge basin with location of probes and chemical analysers for online measurements (modified from Haimi 2016). ALK = alkalinity. SS = Suspended solids. L = Level sensor.

(Hach LDO2: Hach Lange, Loveland, Colorado), a handheld Hach LDO103 probe, and a handheld YSI 550A probe (YSI, Yellow Springs, Ohio).

### Data analysis and gas stripping calculations

Continuous data were consolidated into 5-minute averages, and erroneous values removed. Identified erroneous values included impossible values (readings from probes with temperature readings that varied by more than 10 °C from the average basin readings of 15–17 °C, dissolved gas readings above the solubility limit, and concentration measurements below zero) as well as values collected during movement or calibration of probes. Consolidated data were then compared against 3 standard deviations from the same data set. Outliers were removed except for in situations when three or more consecutive outliers would have been removed, in which case data within a 6 standard deviation outlier check remained and data not within 6 standard deviations were removed.

Data from the FTIR analyser were sent to Gasmeter for review to ensure accuracy. Gasmeter data were measured on a 1-minute interval, so all data collected within the established 5-minute intervals were averaged to produce data on a 5-minute interval. FTIR data that had been affected by daily calibration or a known communication error were removed.

It was necessary to minimize the number of data gaps in order to compare data sets. For data gaps lasting no more than 20 minutes (4 contiguous blank values), including those created by deleting erroneous values, approximate values were extrapolated based on preceding and following values using Equation (1) below. In cases where data gaps exceeded 20 minutes or where data could not be extrapolated due to no preceding or following data, gaps were left unchanged.

$$x_n = \frac{\sum_{i=j+1}^{k+1} [x_{n-i}] + \sum_{i=k+1}^{j+1} [x_{n+i}]}{j + k + 2} \quad (1)$$

where:

$x_n$  = blank value to fill;

$i$  = summation index, determined by variables  $j$  and  $k$ ;

$j$  = number of blank values preceding  $x_n$ ; and

$k$  = number of blank values following  $x_n$ .

Emitted N<sub>2</sub>O was calculated from dissolved N<sub>2</sub>O using a derivation of the two-film theory (Equation (2)) proposed by Matter-Müller *et al.* (1981). To solve for gas concentrations, the correct K<sub>L</sub>a value for mass transfer must be

used. In this study, three methods were used to estimate the K<sub>L</sub>a value for N<sub>2</sub>O: solving for a static K<sub>L</sub>a value, calculating K<sub>L</sub>a using an empirical relationship based on superficial velocity, and theoretical determination from O<sub>2</sub> K<sub>L</sub>a values. In the static method, a static K<sub>L</sub>a was solved for that minimized the sum of square errors (SSE) between measured N<sub>2</sub>O emissions and estimated emissions calculated using Equation (2). This K<sub>L</sub>a was subject to temperature corrections per the Arrhenius equation (Equation (3)) but was otherwise kept constant in order to compare the impact of static and dynamic K<sub>L</sub>a estimates. The K<sub>L</sub>a constant for N<sub>2</sub>O in wastewater at 20 °C was estimated from Equations (2) and (3) using the Microsoft Excel Solver add-in GRG non-linear method with Multistart to minimize the sum of the absolute error between calculated and measured values.

$$C_{G,out} = C_{G,in} * e^{-\frac{K_L a V_L}{H * Q_A}} + H * C_L * \left(1 - e^{-\frac{K_L a V_L}{H * Q_A}}\right) \quad (2)$$

where:

$C_{G,in}$  = influent gas-phase concentration [ppm];

$C_{G,out}$  = effluent gas-phase concentration [ppm];

$C_L$  = concentration dissolved in liquid [ppm];

$H$  = unitless Henry's coefficient;

$K_L a$  = volumetric mass transfer coefficient [d<sup>-1</sup>];

$V_L$  = volume of bulk liquid [m<sup>3</sup>]; and  $Q_A$  = air flowrate [m<sup>3</sup> d<sup>-1</sup>].

$$K_L a_T = K_L a_{T=20C} * \theta^{(T-20)} \quad (3)$$

where:

$K_L a_T$  = volumetric mass transfer coefficient [d<sup>-1</sup>] at temperature  $T$ ;

$T$  = temperature in °C;

$\theta$  = unitless temperature conversion factor, typically equal to 1.024 (ASCE 2007).

K<sub>L</sub>a values for N<sub>2</sub>O were also estimated using an empirical relationship proposed by Foley *et al.* (2010) based on data from a combination of lab-scale and full-scale N<sub>2</sub>O transfer tests (Equation (4)):

$$K_L a_F^* = \left(\frac{d_R}{d_L}\right)^{-0.49} * 34\,500 * v_g^{0.86} \quad (4)$$

where:

$K_L a_F^*$  = field-determined N<sub>2</sub>O volumetric mass transfer coefficient [d<sup>-1</sup>];

$d_L$  = depth of the lab reactor from which this equation was established, defined by Foley *et al.* (2010) as 0.815 m;

$d_R$  = depth of the reactor the  $K_{L,a}$  is being solved for [m]; and  
 $v_g$  = superficial gas velocity [ $\text{m}^3 \text{m}^{-2} \text{s}^{-1}$ ], equal to air flow in  $\text{m}^3 \text{s}^{-1}$  divided by aerated area in  $\text{m}^2$ .

This equation is heavily dependent on the aeration superficial velocity, which is why this method of  $K_{L,a}$  calculation was referred to as the superficial velocity method.

The remaining method calculated  $K_{L,a}$  using penetration theory (Higbie 1935) and the calculated O<sub>2</sub>  $K_{L,a}$  values (Equation (5)). This was referred to as the O<sub>2</sub> method due to its reliance on O<sub>2</sub> mass transfer data. This method required the assumption that the effects of contaminants on O<sub>2</sub> and N<sub>2</sub>O are the same:

$$K_{L,a_{N_2O}} = K_{L,a_{O_2}} * \sqrt{\frac{D_{N_2O}}{D_{O_2}}} \quad (5)$$

where:

$D_{N_2O}$  = diffusion coefficient of N<sub>2</sub>O in clean water [ $1.84 * 10^{-9} \text{m}^2 \text{d}^{-1}$  (Tamimi *et al.* 1994)];

$D_{O_2}$  = diffusion coefficient of O<sub>2</sub> in clean water [ $1.98 * 10^{-9} \text{m}^2 \text{d}^{-1}$  (Ferrell & Himmelblau 1967)]; and

$K_{L,a}$  = volumetric mass transfer coefficient (for N<sub>2</sub>O and O<sub>2</sub>, per subscripts) [ $\text{d}^{-1}$ ].

Oxygen transfer efficiency (OTE, %) was calculated from the collected O<sub>2</sub> data using the mole ratio of O<sub>2</sub> to inert gas (Equation (6)), as outlined by the ASCE protocol for in-process testing (ASCE 1997). The measured OTE and O<sub>2</sub> mass flow rate were then used to calculate the oxygen transfer rate (OTR,  $\text{kg}_{\text{O}_2} \text{h}^{-1}$ ) with the same equation. Empirically observed mass transfer coefficients for O<sub>2</sub> (treated as one variable,  $K_{L,a}$ , that included wastewater impacts) were determined using a steady-state solution of the two-film theory equation for liquid-phase limited mass transfer (Lewis & Whitman 1924) using the calculated OTR (Equation (7)).

$$OTE = \frac{OTR}{W_{O_2}} \sim \frac{O_{2,in} - O_{2,out}}{O_{2,in}} \quad (6)$$

where:

$W$  = mass flow rate [ $\text{kg h}^{-1}$ ]; and

$O_{2,in}$  and  $O_{2,out}$  are mole ratios of O<sub>2</sub> to inert gases in and out of the system, respectively.

$$OTR = \frac{1}{24} K_{L,a} * (C_s - C_L) * V_L * 10^{-3} \quad (7)$$

where:

$K_{L,a}$  = liquid-side volumetric mass transfer coefficient for O<sub>2</sub> [ $\text{d}^{-1}$ ];

$C_s$  = saturated DO at operating temperature and pressure [ $\text{mg L}^{-1}$ ];

$C_L$  = measured DO [ $\text{mg L}^{-1}$ ]; and

$V$  = aerated tank volume [ $\text{m}^3$ ].

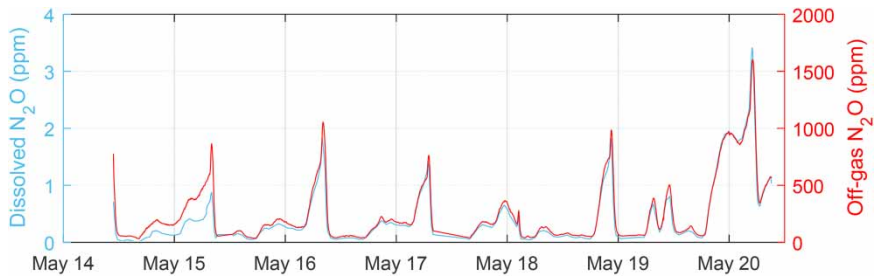
The resulting N<sub>2</sub>O emission estimations from all three methods were then compared against measured off-gas N<sub>2</sub>O concentrations. Correction factors to minimize the sum of absolute error between calculated and measured N<sub>2</sub>O emission concentrations in the O<sub>2</sub> and superficial velocity methods were determined using the Microsoft Excel Solver add-in GRG non-linear method with Multistart. The static  $K_{L,a}$  method solved for a single value that best estimated measured N<sub>2</sub>O emissions during the week of data collection, so no additional correction factors were applied in this method.

## RESULTS AND DISCUSSION

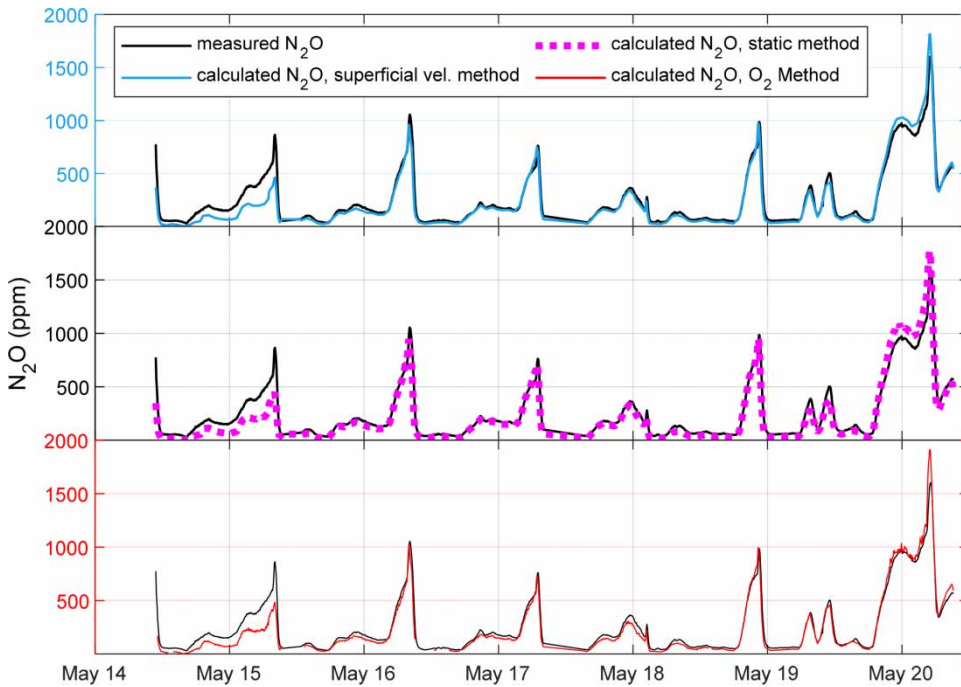
The novel method for simultaneous measurements performed well, with some limitations to locations that could be measured due to turbulence in the activated sludge basin. From collected data, it was clear that off-gas N<sub>2</sub>O concentrations followed the same diurnal pattern as dissolved N<sub>2</sub>O concentrations from the same location (Figure 2). This confirmed the findings from prior studies that dissolved N<sub>2</sub>O monitoring can be used to reveal trends in N<sub>2</sub>O emissions (Baresel *et al.* 2016; Marques *et al.* 2016; Fenu *et al.* 2020). However, linking the dissolved concentration to emitted N<sub>2</sub>O requires calibration and verification. All three N<sub>2</sub>O  $K_{L,a}$  estimation methods accurately represented trends in off-gas of N<sub>2</sub>O due to the correlation between dissolved and emitted N<sub>2</sub>O. In order to better match the magnitude of N<sub>2</sub>O in the off-gas, a static correction factor of 0.58 was applied in the superficial velocity method and a factor of 0.43 was applied to the O<sub>2</sub> diffusivity  $K_{L,a}$  method (Figure 3).

Prior to using a static correction factor to adjust the  $K_{L,a}$  values from the superficial velocity and O<sub>2</sub> methods, N<sub>2</sub>O





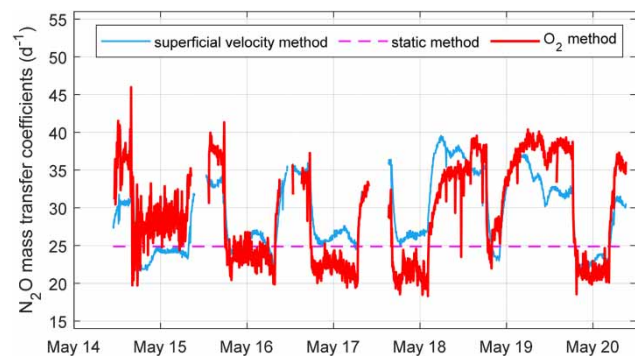
**Figure 2** | Measured dissolved and off-gas N<sub>2</sub>O concentration, 14–21 May 2019. Note the units for dissolved N<sub>2</sub>O are ppm in water, while the units for off-gas N<sub>2</sub>O are ppm in air.



**Figure 3** | Measured N<sub>2</sub>O emissions and calculated emissions from the three K<sub>L</sub>a estimation methods.

emission estimations were less accurate. The superficial velocity calculations resulted in K<sub>L</sub>a values ranging from 34 to 69 d<sup>-1</sup> and the O<sub>2</sub> method calculations estimated a K<sub>L</sub>a ranging from 42 to 107 d<sup>-1</sup> at 20 °C. These K<sub>L</sub>a values overestimated N<sub>2</sub>O emissions when plugged into off-gas estimation calculations (Equation (2)).

After the static correction was applied, calculated K<sub>L</sub>a for N<sub>2</sub>O stripping at 20 °C ranged from 19 to 40 d<sup>-1</sup> when applying the superficial velocity method of calculation, 18 to 46 d<sup>-1</sup> using the O<sub>2</sub> method, and was estimated as 24.9 d<sup>-1</sup> using the static method (Figure 4). The calculated K<sub>L</sub>a values for the superficial velocity and O<sub>2</sub> methods had static correction factors of 0.58 and 0.43, respectively, applied to the dynamic K<sub>L</sub>a values to better fit the



**Figure 4** | Comparison of N<sub>2</sub>O mass transfer coefficients for superficial velocity, static, and O<sub>2</sub> methods. Superficial velocity and O<sub>2</sub> method N<sub>2</sub>O mass transfer coefficients had their respective static correction factors of 0.58 and 0.43 applied prior to graphing.

magnitude of measured N<sub>2</sub>O emissions. The resulting calculated values estimate the measured data well, with the O<sub>2</sub> method showing the closest fit and the superficial velocity method following as the second closest fit (Figure 3).

When comparing against prior studies, there were limited papers with K<sub>L</sub>a values that could be used for comparison. Many N<sub>2</sub>O K<sub>L</sub>a values come from laboratory studies using significantly higher aeration flowrates compared to basin volume. Mampaey *et al.* (2015) found an N<sub>2</sub>O K<sub>L</sub>a of 1,025 d<sup>-1</sup> when aerating a 100 mL stripping flask with 1 L min<sup>-1</sup> airflow. Harper *et al.* (2015) measured an N<sub>2</sub>O K<sub>L</sub>a between 450 and 510 d<sup>-1</sup> aerating a 500 mL vessel with a 1 L min<sup>-1</sup> air flowrate. Domingo-Félez *et al.* (2014) found K<sub>L</sub>a values ranging from 85 d<sup>-1</sup> to 475 d<sup>-1</sup> for air flowrates from 0.25 to 2.5 L min<sup>-1</sup> in a 4 L reactor. In comparison, Viikinmäki's zones are approximately 1.9 \* 10<sup>6</sup> L and the maximum zone aeration during this study was 34,700 L min<sup>-1</sup>.

Data from full-scale studies are even more limited and can also be difficult to compare due to differing conditions. Ye *et al.* (2014) determined N<sub>2</sub>O K<sub>L</sub>a at a full-scale plant with surface aerators using the equivalent of the O<sub>2</sub> method but with a known methane K<sub>L</sub>a instead of an O<sub>2</sub> K<sub>L</sub>a. In their study, K<sub>L</sub>a values were as high as 1,150 d<sup>-1</sup> where the aerators were located and decreased to 12.5 d<sup>-1</sup> in the turbulent zone immediately following the aerators. The surface aerator N<sub>2</sub>O K<sub>L</sub>a value was comparable to laboratory experiments with incredibly high airflow to volume ratios, while the turbulent zone following aeration had lower values than observed in this study because there was no airflow. Foley *et al.*'s study (2010) calculated K<sub>L</sub>a values between approximately 10 and 90 d<sup>-1</sup> in activated sludge basins up to 6 m deep. The tanks at Viikinmäki are 12 metres deep, so even though calculated K<sub>L</sub>a values from this study were within this range, Foley *et al.*'s empirical relationship may not accurately estimate N<sub>2</sub>O K<sub>L</sub>a in deep reactors.

Mass transfer calculated using the O<sub>2</sub> K<sub>L</sub>a and diffusivity had the smallest RMSE (70.5), followed by the superficial velocity method (73.4) and the static method (82.2). The maximum variation between measured and calculated N<sub>2</sub>O in the O<sub>2</sub>, superficial velocity, and static methods were 27.9, 49.1, and 52.0%, respectively. Marques *et al.* (2016) compared methods of K<sub>L</sub>a determination in aerobic and anaerobic conditions and also found the O<sub>2</sub> method of calculating K<sub>L</sub>a to result in more accurate N<sub>2</sub>O emission estimations than the superficial velocity method even though they determined N<sub>2</sub>O K<sub>L</sub>a from a static OTR. Based on the accuracy of calculating N<sub>2</sub>O transfer using

O<sub>2</sub> K<sub>L</sub>a values, similar water quality parameters may have impacted both O<sub>2</sub> and N<sub>2</sub>O transfer. However, the corrected mass transfer coefficient for N<sub>2</sub>O transfer was half as large as was predicted with the clean water diffusivities of O<sub>2</sub> and N<sub>2</sub>O. This suggests that N<sub>2</sub>O stripping and O<sub>2</sub> transfer may be impacted to a different degree by water quality. Domingo-Félez *et al.* (2014) compared K<sub>L</sub>a values for O<sub>2</sub> and N<sub>2</sub>O over varying aeration flowrates and found that the relationship was not linear, suggesting that the different solubilities of N<sub>2</sub>O and O<sub>2</sub> may make the exact relationship between O<sub>2</sub> and N<sub>2</sub>O transfer difficult to correlate. Although this study was not sufficient to prove that the impacts of water quality and superficial velocity on O<sub>2</sub> and N<sub>2</sub>O K<sub>L</sub>a are not analogous, it does cast further doubt on the accuracy of this assumption.

Gas transfer data for N<sub>2</sub>O and O<sub>2</sub> showed daily and weekly fluctuation related to the fluctuations in aeration and water quality at the WWTP, as has been observed in other studies (e.g. Kampschreur *et al.* 2008; Daelman *et al.* 2015; Kosonen *et al.* 2016; Emami *et al.* 2018). OTE was higher at the start and end of the week of measurements, as were N<sub>2</sub>O emissions. Any variations in water quality or operational parameters can impact bubble size and diffusivity, therefore impacting the effective K<sub>L</sub>a and OTE. Oxygen transfer and mass transfer K<sub>L</sub>a values were heavily affected by airflow, and variance between the temporal pattern of O<sub>2</sub> transfer and airflow suggests additional impacts from variations in water quality (Figure 5). However, no one water quality parameter could be decisively linked to impacts on O<sub>2</sub> or N<sub>2</sub>O transfer within this study.

Data used in K<sub>L</sub>a value and N<sub>2</sub>O emission calculations were collected during a single week of unusually high N<sub>2</sub>O concentrations and are not representative of average conditions at Viikinmäki. Due to the limited time scale of this study, there was not a separate calibration and validation period to test the applicability of the calculated static correction factors in different conditions.

Potential sources of error in N<sub>2</sub>O measurements included probe uncertainties and reliability of Gasmeter readings. Probe noise and signal errors caused occasional incorrect readings for probes, but once outliers caused by probe calibration and impossible (negative) concentrations were removed, the remaining variability did not appear to significantly compromise the data. Expected error for Gasmeter DX4015 data is listed in Table 1.

Additional error in N<sub>2</sub>O calculations is possible as a result of errors in readings used for O<sub>2</sub> transfer calculations, for example from noise and drift in the O<sub>2</sub> analyser signal. The AMI model 65 O<sub>2</sub> analyser is reported to have drift

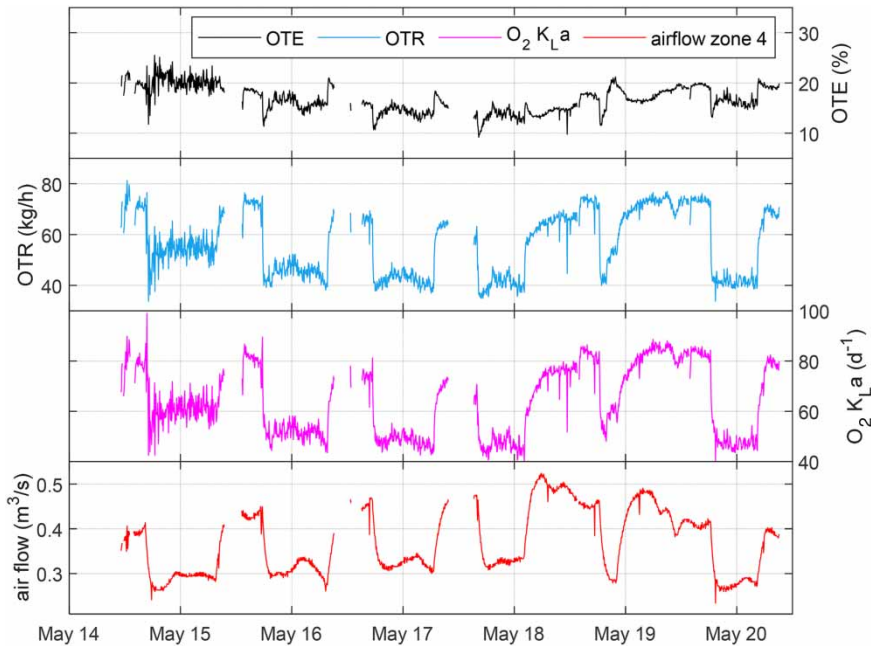


Figure 5 | Air flow rates, OTR, OTE and O<sub>2</sub> K<sub>L</sub>a, 14–21 May 2019.

Table 1 | Gasmeter DX4015 calibration, measurement drift, and deviation (provided by Gasmeter)

Zero-point calibration	Every 24 hours, calibrate with N <sub>2</sub> (5.0 or higher recommended)
Zero-point drift	<2% of measuring range per zero-point calibration interval
Sensitivity drift	None
Linearity deviation	<2% of measuring range
Temperature drifts	<2% of measuring range per 10 K temperature change
Pressure influence	1% change of measuring value for 1% sample pressure change. Ambient pressure changes measured and compensated.

under 1% of the full range over 4 weeks and a repeatability within  $\pm 0.1\%$ . Other sources of uncertainty included temperature probe integrity, temperature variation between the gas hood and the temperature probe, and local variation in aeration air flowrates.

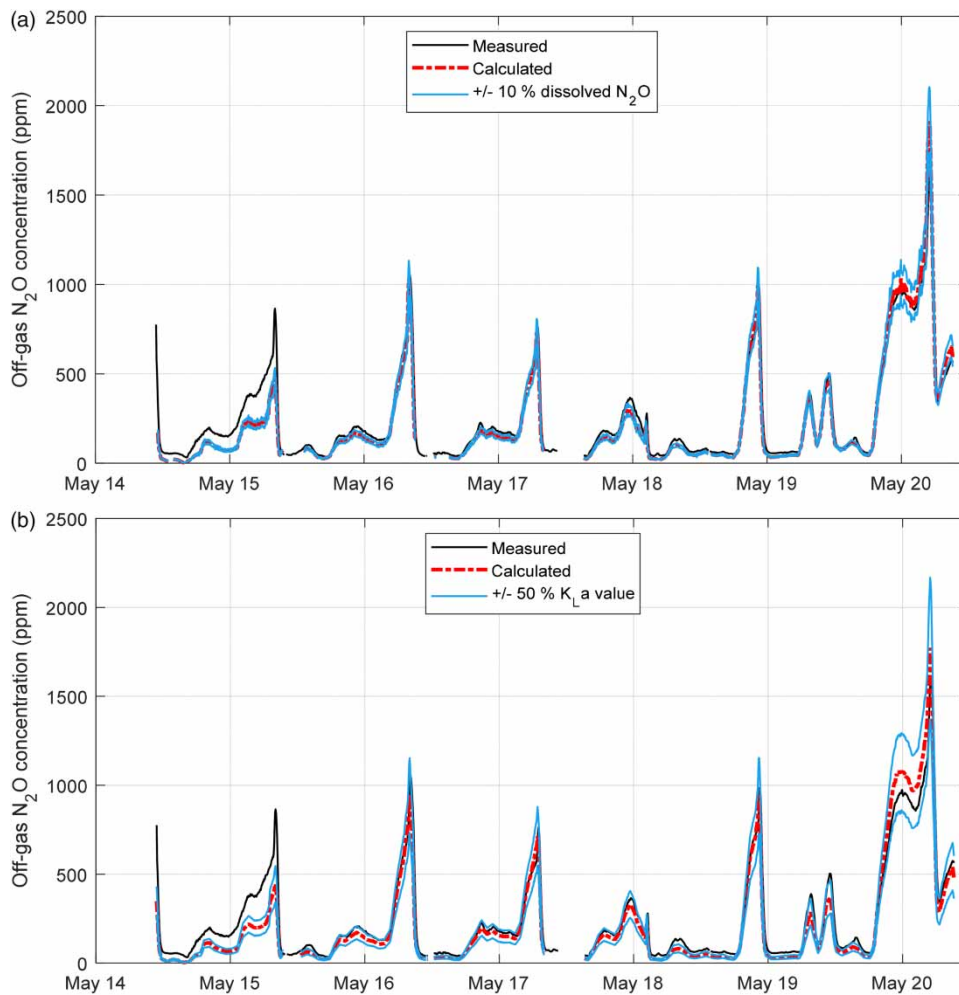
A sensitivity analysis was performed to assess the impact of potential erroneous readings on N<sub>2</sub>O concentration estimations. Probes at the WWTP are calibrated on a regular schedule, so it was assumed that no probe readings deviated by greater than 10% from the true value. The remaining parameters were evaluated using variability similar to what was

observed in this study. Within this sensitivity analysis, variability in calculated K<sub>L</sub>a values and in dissolved N<sub>2</sub>O concentrations both significantly impacted calculated emissions (Figure 6). Dissolved N<sub>2</sub>O variations up to observed levels of  $\pm 10\%$  resulted in changes up to  $\pm 10\%$  in calculated N<sub>2</sub>O emissions. The relationship between dissolved and emitted N<sub>2</sub>O was effectively linear when K<sub>L</sub>a was held constant due to negligible N<sub>2</sub>O in process gas entering the activated sludge basins (Equation (2)). The K<sub>L</sub>a values that best fit measured N<sub>2</sub>O emissions deviated from initial calculated values by an average factor of 0.5. For this range of  $\pm 50\%$  N<sub>2</sub>O K<sub>L</sub>a values, calculated N<sub>2</sub>O emissions varied by  $\pm 25\%$ .

The calculated K<sub>L</sub>a for N<sub>2</sub>O stripping using the O<sub>2</sub> method is dependent on the calculated O<sub>2</sub> K<sub>L</sub>a value and therefore sensitive to variability in airflow and O<sub>2</sub> readings. A 10% air flowrate change resulted in peak differences in O<sub>2</sub> K<sub>L</sub>a that were nearly 15% higher or lower than initial measured values (Figure 7). Erroneous readings of percent O<sub>2</sub> in the off-gas up to 0.2% (twice the listed error for the AMI sensor) had a similar level of impact compared to the 10% difference in air flowrate, suggesting that variability in aeration across an activated sludge basin could skew plant-wide N<sub>2</sub>O emission calculations using the O<sub>2</sub> method.

The impact of changes to the O<sub>2</sub> K<sub>L</sub>a value on calculated N<sub>2</sub>O emissions would be reduced in magnitude, as seen in the sensitivity analysis on impacts of K<sub>L</sub>a variations





**Figure 6** | Impact of (a) dissolved N<sub>2</sub>O readings on calculated off-gas N<sub>2</sub>O using O<sub>2</sub> method compared against measured N<sub>2</sub>O values and (b) mass transfer coefficient on calculated off-gas N<sub>2</sub>O using static method, compared against measured N<sub>2</sub>O values.

(Figure 6). The overall impact on estimated N<sub>2</sub>O emissions would therefore be expected to be closer to a 7–8% difference in N<sub>2</sub>O values for a 10% change in airflow or a 0.2% change in O<sub>2</sub> readings.

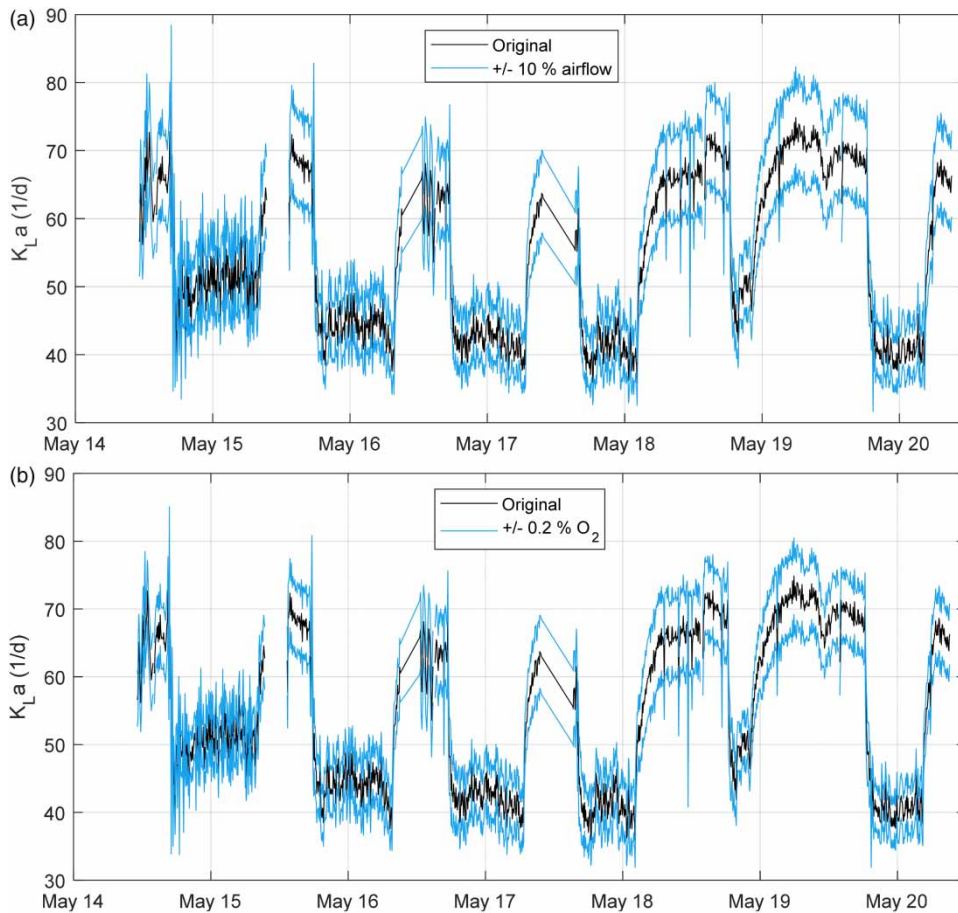
Additional parameters including temperature, DO, and zone dimensions were also analysed for their impact on data integrity, but these did not have as significant an impact.

## CONCLUSIONS

Trends in emissions of N<sub>2</sub>O from WWTPs can be accurately estimated using dissolved N<sub>2</sub>O concentrations, and with sufficient calibration and validation dissolved N<sub>2</sub>O concentrations could be used to estimate the magnitude of emissions as well.

The method of determining mass transfer coefficients for modelling of N<sub>2</sub>O stripping significantly impacts the resulting calculations, and therefore calculation accuracy.

This study introduces a novel method to concurrently measure N<sub>2</sub>O and O<sub>2</sub> transfer in aerated zones of full-scale treatment plants. Within this study, the N<sub>2</sub>O K<sub>L</sub>a calculation method based on O<sub>2</sub> mass transfer had the lowest RMSE and lowest estimation error, making it the most accurate. However, the necessary application of a site-specific correction factor suggests that either additional factors such as basin depth or water quality influenced N<sub>2</sub>O emissions or the K<sub>L</sub>a estimation methods were unable to accurately represent the gas transfer. Although the assumption of analogous impacts of wastewater conditions on N<sub>2</sub>O and O<sub>2</sub> transfer may not be fully accurate, it is clear that O<sub>2</sub> transfer can provide useful information for estimating N<sub>2</sub>O



**Figure 7** | Impact of variation in (a) airflow readings on calculated O<sub>2</sub> K<sub>L</sub>a compared against O<sub>2</sub> K<sub>L</sub>a values calculated in this study and (b) off-gas O<sub>2</sub> readings on calculated O<sub>2</sub> K<sub>L</sub>a compared against values from this study.

transfer. Additional research is still necessary to determine the exact impacts of deep basins and changes in water quality on O<sub>2</sub> transfer and N<sub>2</sub>O stripping, as well as to determine more accurate methods of K<sub>L</sub>a calculation that do not require empirically determined correction factors.

## ACKNOWLEDGEMENTS

The authors of this study would like to thank the operators and engineers at the Viikinmäki WWTP for assisting during the sampling campaigns.

## FUNDING

This research was financially supported by Helsinki Region Environmental Services Authority (HSY), Aalto University,

and the Finnish Water Utilities Association (FIWA) development fund.

## DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

## REFERENCES

- ASCE. 1997 *Standard Guidelines for In-Process Oxygen Transfer Testing*. ASCE Standard. American Society of Civil Engineers, Reston, Virginia. doi:10.1061/9780784401149.
- ASCE. 2007 *Measurement of Oxygen Transfer in Clean Water*. ASCE Standard. American Society of Civil Engineers, Reston, Virginia. doi:10.1061/9780784408483.
- Baresel, C., Andersson, S., Yang, J. & Andersen, M. H. 2016 Comparison of nitrous oxide (N<sub>2</sub>O) emissions calculations at a Swedish wastewater treatment plant based on water

- concentrations versus off-gas concentrations. *Adv. Clim. Change Res.* **7** (3), 185–191. doi:10.1016/j.accre.2016.09.001.
- Blomberg, K., Kosse, P., Mikola, A., Kuokkanen, A., Fred, T., Heinonen, M., Mulas, M., Lübken, M., Wichern, M. & Vahala, R. 2018 Development of an extended ASM3 model for predicting the nitrous oxide emissions in a full-scale wastewater treatment plant. *Environ. Sci. Technol.* **52** (10), 5803–5811. doi:10.1021/acs.est.8b00386.
- Daelman, M., van Voorthuizen, E., van Dongen, U., Volcke, E. & van Loosdrecht, M. 2015 Seasonal and diurnal variability of N<sub>2</sub>O emissions from a full-scale municipal wastewater treatment plant. *Sci. Total Environ.* **536**, 1–11. doi:10.1016/j.scitotenv.2015.06.122.
- Domingo-Félez, C., Mutlu, A. G., Jensen, M. & Smets, B. 2014 Aeration strategies to mitigate nitrous oxide emissions from single-stage nitrification/anammox reactors. *Environ. Sci. Technol.* **48** (15), 8679–8687. doi:10.1021/es501819n.
- Emami, N., Sobhani, R. & Rosso, D. 2018 Diurnal variations of the energy intensity and associated greenhouse gas emissions for activated sludge processes. *Water Sci. Technol.* **77** (7), 1838–1850. doi:10.2166/wst.2018.054.
- Fenu, A., Wambecq, T., de Gussem, K. & Weemaes, M. 2020 Nitrous oxide gas emissions estimated by liquid-phase measurements: robustness and financial opportunity in single and multi-point monitoring campaigns. *Environ. Sci. & Pollut. Res.* **27**, 890–898. doi:10.1007/s11356-019-07047-0.
- Ferrell, R. T. & Himmelblau, D. M. 1967 Diffusion coefficients of nitrogen and oxygen in water. *J. Chem. Eng. Data* **12**, 111–115. doi:10.1021/je60032a036.
- Fiat, J. 2019 *Analyse et modélisation des émissions de protoxyde d'azote par les biofiltres nitrifiants tertiaires à échelle industrielle (Analysis and Modelling of Nitrous Oxide Emissions From Tertiary Nitrifying Biofilters on an Industrial Scale)*. Toulouse, France: s.n.
- Foley, J., de Haas, D., Yuan, Z. & Lant, P. 2010 Nitrous oxide generation in full-scale biological nutrient removal wastewater treatment plants. *Water Res.* **44** (3), 831–844. doi:10.1016/j.watres.2009.10.033.
- Haimi, H. 2016 *Data-derived Soft Sensors in Biological Wastewater Treatment with Application of Multivariate Statistical Methods*. Espoo, Finland: s.n. ISBN: 978-952-60-6650-9 (electronic).
- Harper, W., Takeuchi, Y., Riya, S., Hosomi, M. & Terada, A. 2015 Novel abiotic reactions increase nitrous oxide production during partial nitrification: modeling and experiments. *Chem. Eng. J.* **281**, 1017–1023. doi:10.1016/j.cej.2015.06.109.
- Higbie, R. 1935 The rate of absorption of a pure gas into a still liquid during short periods of exposure. *Trans. Am. Inst. Chem. Eng.* **31**, 365–388.
- IPCC. 2013 *Climate Change 2013: The Physical Science Basis*. Cambridge University Press, Cambridge, UK and New York, NY, USA. ISBN: 978-92-9169-138-8.
- Kampschreur, M. J., van der Star, W. R., Wienders, H. A., Mulder, J. W., Jetten, M. S. & van Loosdrecht, M. C. 2008 Dynamics of nitric oxide and nitrous oxide emission during full-scale reject water treatment. *Water Res.* **42** (3), 812–826. doi:10.1016/j.watres.2007.08.022.
- Kampschreur, M. J., Temmink, H., Kleerebezem, R., Jetten, M. S. & van Loosdrecht, M. C. 2009 Nitrous oxide emission during wastewater treatment. *Water Res.* **43** (17), 4093–4103. doi:10.1016/j.watres.2009.03.001.
- Kosonen, H., Heinonen, M., Mikola, A., Haimi, H., Mulas, M., Corona, F. & Vahala, R. 2016 Nitrous oxide production at a fully covered wastewater treatment plant: results of a long-term online monitoring campaign. *Environ. Sci. Technol.* **50** (11), 5547–5554. doi:10.1021/acs.est.5b04466.
- Lewis, W. & Whitman, W. 1924 Principles of gas transfer absorption. *Ind. Eng. Chem.* **16** (12), 1215–1237. doi:10.1021/ie50180a002.
- Mampaey, K. E., van Dongen, U. G., van Loosdrecht, M. C. & Volcke, E. I. 2015 Novel method for online monitoring of dissolved N<sub>2</sub>O concentrations through a gas stripping device. *Environ. Technol.* **36** (13), 1680–1690. doi:10.1080/09593330.2015.1005029.
- Marques, R., Rodriguez-Caballero, A., Oehman, A. & Pijuan, M. 2016 Assessment of online monitoring strategies for measuring N<sub>2</sub>O emissions from full-scale wastewater treatment systems. *Water Res.* **99**, 171–179. doi:10.1016/j.watres.2016.04.052.
- Matter-Müller, C., Gujer, W. & Giger, W. 1981 Transfer of volatile substances from water to the atmosphere. *Water Res.* **15** (11), 1271–1279. doi:10.1016/0043-1354(81)90104-4.
- Rosso, D. 2018 *Aeration, Mixing, and Energy: Bubbles and Sparks*. IWA Publishing, London. ISBN: 9781780407838.
- Sander, R. 2015 *Compilation of Henry's law constants (version 4.0) for water as solvent*. *Atmos. Chem. Phys.* **15** (8), 4399–4981. doi:10.5194/acp-15-4399-2015.
- Tamimi, A., Rinker, E. B. & Sandall, O. C. 1994 Diffusion coefficients for hydrogen sulfide, carbon dioxide, and nitrous oxide in water over the temperature range 293–368 K. *J. Chem. Eng. Data* **39**, 330. doi:10.1021/je00014a031.
- von Schulthess, R., Kuhn, M. & Gujer, W. 1995 Release of nitric and nitrous oxides from denitrifying activated sludge. *Water Res.* **29** (1), 215–226. doi:10.1016/0043-1354(95)00204-9.
- Ye, L., Ni, B. J., Law, Y., Byers, C. & Yuan, Z. 2014 A novel methodology to quantify nitrous oxide emissions from full-scale wastewater treatment systems with surface aerators. *Water Res.* **48**, 257–268. doi:10.1016/j.watres.2013.09.037.

First received 16 September 2020; accepted in revised form 13 January 2021. Available online 27 January 2021