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 (N₂O) gas transfer was studied in a full-scale process to correlate liquid phase N₂O concentrations with gas phase N₂O emissions and compare methods of determining the volumetric mass transfer coefficient, K_La. 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 N₂O and O₂ from the same location. K_La was calculated with three methods: empirically, based on aeration superficial velocity, from experimentally determined O₂ K_La, and using a static value of best fit. The findings of this study indicated trends in local emitted N₂O consistently matched trends in local dissolved N₂O, but the magnitude of N₂O emissions could not be accurately estimated without correction. After applying a static correction factor, the O₂ method, using experimentally determined O₂ K_La, provided the best N₂O emission estimation over the data collection period. N₂O emissions estimated using the O₂ 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_La value, and therefore the method of K_La 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 N₂O K_La determination significantly impacts estimated N₂O emissions.
- A novel method was developed for continuous, simultaneous measurement of dissolved and emitted O₂ and N₂O.
- Feasibility of estimating local emissions from dissolved N₂O measurements and O₂ transfer in a full-scale activated sludge basin was confirmed using this novel method.

INTRODUCTION
N₂O released from wastewater treatment plants accounts for 3% of anthropogenic N₂O emissions worldwide (IPCC 2013). N₂O is a significant greenhouse gas (GHG) with a 100-year global warming potential nearly 300 times greater than that of CO₂ (IPCC 2013). Current knowledge suggests the majority of N₂O production in wastewater treatment occurs during biological denitrification and nitrification processes (Kampschreur et al. 2009). There is a desire for increased accuracy in estimating N₂O emissions from individual treatment plants in order to modify operational strategies to reduce GHG emissions from wastewater treatment.

Emissions of N₂O 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...
mathematical model requires an N₂O K_La value. This K_La is specific to wastewater conditions, varies with time and location, and limited studies have focused on determining this K_La in clean water and wastewater (Foley et al. 2010; Domingo-Félez et al. 2014; Mampaey et al. 2015). An empirical equation for N₂O K_La proposed by Foley et al. (2010), referred to within this study as the superficial velocity method, has been employed in estimating N₂O emissions with decent accuracy (Baresel et al. 2016; Fenu et al. 2020). N₂O K_La can also be estimated from a known O₂ K_La and diffusivity data (Highie 1935; Fiat 2019), referred to within this study as the O₂ method. Many studies assume the impact of wastewater conditions on O₂ and N₂O transfer to be analogous (e.g. von Schulthes et al. 1995; Foley et al. 2010; Fiat 2019), and this is a key assumption in order to calculate N₂O K_La from O₂ K_La without having to determine the diffusivities of N₂O and O₂ in each wastewater matrix. However, the relationship between changes in wastewater quality and changes in N₂O transfer is relatively unknown compared to water quality impacts on O₂ transfer. The solubility of N₂O is higher than that of O₂, and N₂O has a Henry’s coefficient in water that is nearly 20 times larger than that for O₂ in water (Sander 2015). Therefore, the accuracy of this assumption of analogous mass transfer impacts needs to be confirmed.

Despite the use of K_La estimation methods in N₂O 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 N₂O and O₂ K_La values, finding that these values were impacted to a different degree by superficial velocity. Foley et al. (2010) developed their superficial velocity K_La estimation equation based on N₂O 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 O₂ method in a full-scale treatment plant, continuously monitoring gas and dissolved N₂O with Clark-type microsensors and calculating O₂ method K_La from a static average O₂ transfer rate for the plant. Their study found the O₂ 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_La estimation methods as well as to compare dynamic calculated K_La values against a static estimated K_La 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 N₂O 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 N₂O began in 2016, using dissolved N₂O 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 N₂O alongside dissolved and emitted O₂ from the same location. This allowed for a more direct comparison of O₂ and N₂O transfer, as well as of O₂ and N₂O K_La values.

The goal of this paper was to compare multiple methods for N₂O K_La calculation in gas stripping equations and assess the differences attributable to the choice of method. Three calculation methods were used to estimate N₂O K_La: the superficial velocity method, which requires the fewest parameters to calculate K_La but does not account for any changes to water quality except as they affect basin aeration; the O₂ method, which requires more data collection and takes into account impacts of water quality on O₂ transfer, but assumes they apply equally to N₂O transfer; and a static estimation that represented using a static K_La for N₂O emission calculations. The resulting calculated N₂O emissions were compared against measured emissions to assess accuracy. This study used a novel method to concurrently measure N₂O and O₂ transfer at a full-scale treatment plant and is one of the first to compare N₂O and O₂ transfer while considering the dynamic nature of gas transfer K_La 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 m³ d⁻¹ and the influent total nitrogen concentration is 49 mg L⁻¹. 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$^3$. 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$_4^+$ 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$^{-1}$. 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$_2$O production, probably caused by the inhibition of nitrite oxidizing bacteria reflected in high nitrite concentrations (2–7 mg L$^{-1}$). This resulted in significantly higher N$_2$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$_2$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 Gasmet DX4015 Fourier-transform infrared (FTIR) analyser (Gasmet Oy, Finland) measured emitted N$_2$O concentrations downstream of velocity measurements. Further downstream, the gas sample was pumped through a desiccating column containing sodium hydroxide pellets for CO$_2$ removal and desiccant for water vapour removal before being run through an O$_2$ analyser (AMI model 65; Fountain Valley, CA) to measure the percent O$_2$ 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$_2$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

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**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.
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 where 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 Gasmet for review to ensure accuracy. Gasmet 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 temperature readings that varied by more than 10 °C were then compared against 3 standard deviations 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 where 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.

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.

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

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 \( x_n \).

Ejected \( \text{N}_2\text{O} \) was calculated from dissolved \( \text{N}_2\text{O} \) using a derivation of the two-film theory (Equation (2)) proposed by Matter-Müller et al. (1981). To solve for gas concentrations, the correct \( K_{L_A} \) value for mass transfer must be used. In this study, three methods were used to estimate the \( K_{L_A} \) value for \( \text{N}_2\text{O} \); solving for a static \( K_{L_A} \) value, calculating \( K_{L_A} \) using an empirical relationship based on superficial velocity, and theoretical determination from \( O_2 \) \( K_{L_A} \) values. In the static method, a static \( K_{L_A} \) was solved for that minimized the sum of square errors (SSE) between measured \( \text{N}_2\text{O} \) emissions and estimated emissions calculated using Equation (2). This \( K_{L_A} \) 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 \( K_{L_A} \) estimates. The \( K_{L_A} \) constant for \( \text{N}_2\text{O} \) 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.

\[
C_{G,out} = C_{G,in} e^{-\frac{x_n n_{fl}}{h L}} + H C_{L} \left(1 - e^{-\frac{x_n n_{fl}}{h L}}\right)
\]

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 \(^{-1}\)];
\( V_L \) = volume of bulk liquid [m\(^3\)]; and
\( Q_A \) = air flow rate [m\(^3\) d \(^{-1}\)].

\[
K_{L_A} = K_{L_A}T_{20°C} \times \theta^{(T-20)}
\]

where:
\( K_{L_A} \) = volumetric mass transfer coefficient [d \(^{-1}\)] at temperature \( T \);
\( T \) = temperature in °C;
\( \theta \) = unitless temperature conversion factor, typically equal to 1.024 (ASCE 2007).

\( K_{L_A} \) values for \( \text{N}_2\text{O} \) 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 \( \text{N}_2\text{O} \) transfer tests (Equation (4)):

\[
K_{L_A} = \left(\frac{d_B}{d_L}\right)^{-0.49} \times 34,500 \times 7^{0.88}
\]

where:
\( K_{L_A} \) = field-determined \( \text{N}_2\text{O} \) volumetric mass transfer coefficient [d \(^{-1}\)].
\( d_L \) = 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 \( K_La \) is being solved for [m]; and  
\( v_s \) = superficial gas velocity \([m^3 m^{-2} s^{-1}]\), equal to air flow in \( m^3 s^{-1} \) divided by aerated area in \( m^2 \).

This equation is heavily dependent on the aeration superficial velocity, which is why this method of \( K_La \) calculation was referred to as the superficial velocity method.

The remaining method calculated \( K_La \) using penetration theory (Higbie 1935) and the calculated O2 \( K_La \) values (Equation (5)). This was referred to as the O2 method due to its reliance on O2 mass transfer data. This method required the assumption that the effects of contaminants on O2 and N2O are the same:

\[
K_{La_{N2O}} = K_{La_{O2}} \times \sqrt{\frac{D_{N2O}}{D_{O2}}} \tag{5}
\]

where:

- \( D_{N2O} \) = diffusion coefficient of N2O in clean water \([1.84 \times 10^{-9} m^2 d^{-1}] \) \( \text{(Tamimi et al. 1994)} \);  
- \( D_{O2} \) = diffusion coefficient of O2 in clean water \([1.98 \times 10^{-9} m^2 d^{-1}] \) \( \text{(Ferrell & Himmelblau 1967)} \); and  
- \( K_{La} \) = volumetric mass transfer coefficient (for N2O and O2, per subscripts) \([d^{-1}] \).

Oxygen transfer efficiency (OTE, \%) was calculated from the collected O2 data using the mole ratio of O2 to inert gas (Equation (6)), as outlined by the ASCE protocol for in-process testing (ASCE 1997). The measured OTE and O2 mass flow rate were then used to calculate the oxygen transfer rate (OTR, kgO2 h\(^{-1}\)) with the same equation. Empirically observed mass transfer coefficients for O2 (treated as one variable, \( K_{La} \), 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)).

\[
OTE = \frac{OTR}{W_{O2}} \times \frac{O_{2, in} - O_{2, out}}{O_{2, in}} \tag{6}
\]

where:

- \( W \) = mass flow rate \([kg h^{-1}] \); and  
- \( O_{2, in} \) and \( O_{2, out} \) are mole ratios of O2 to inert gases in and out of the system, respectively.

\[
OTR = \frac{1}{24} K_{La} \times (C_s - C_L) \times V_L \times 10^{-3} \tag{7}
\]

where:

- \( K_{La} \) = liquid-side volumetric mass transfer coefficient for O2 \([d^{-1}] \);  
- \( C_s \) = saturated DO at operating temperature and pressure \([mg L^{-1}] \);  
- \( C_L \) = measured DO \([mg L^{-1}] \); and  
- \( V \) = aerated tank volume \([m^3] \).

The resulting N2O emission estimations from all three methods were then compared against measured off-gas N2O concentrations. Correction factors to minimize the sum of absolute error between calculated and measured N2O emission concentrations in the O2 and superficial velocity methods were determined using the Microsoft Excel Solver add-in GRG non-linear method with Multistart. The static \( K_{La} \) method solved for a single value that best estimated measured N2O 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 N2O concentrations followed the same diurnal pattern as dissolved N2O concentrations from the same location (Figure 2). This confirmed the findings from prior studies that dissolved N2O monitoring can be used to reveal trends in N2O emissions (Baresel et al. 2016; Marques et al. 2016; Fenu et al. 2020). However, linking the dissolved concentration to emitted N2O requires calibration and verification. All three N2O \( K_{La} \) estimation methods accurately represented trends in off-gas of N2O due to the correlation between dissolved and emitted N2O. In order to better match the magnitude of N2O 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 O2 diffusivity \( K_{La} \) method (Figure 3).

Prior to using a static correction factor to adjust the \( K_{La} \) values from the superficial velocity and O2 methods, N2O...
emission estimations were less accurate. The superficial velocity calculations resulted in $K_{L_A}$ values ranging from 34 to 69 d$^{-1}$ and the O$_2$ method calculations estimated a $K_{L_A}$ ranging from 42 to 107 d$^{-1}$ at 20°C. These $K_{L_A}$ values overestimated N$_2$O emissions when plugged into off-gas estimation calculations (Equation (2)).

After the static correction was applied, calculated $K_{L_A}$ for N$_2$O stripping at 20°C ranged from 19 to 40 d$^{-1}$ when applying the superficial velocity method of calculation, 18 to 46 d$^{-1}$ using the O$_2$ method, and was estimated as 24.9 d$^{-1}$ using the static method (Figure 4). The calculated $K_{L_A}$ values for the superficial velocity and O$_2$ methods had static correction factors of 0.58 and 0.43, respectively, applied to the dynamic $K_{L_A}$ values to better fit the

![Figure 2](image1.png) Measured dissolved and off-gas N$_2$O concentration, 14-21 May 2019. Note the units for dissolved N$_2$O are ppm in water, while the units for off-gas N$_2$O are ppm in air.

![Figure 3](image2.png) Measured N$_2$O emissions and calculated emissions from the three $K_{L_A}$ estimation methods.

![Figure 4](image3.png) Comparison of N$_2$O mass transfer coefficients for superficial velocity, static, and O$_2$ methods. Superficial velocity and O$_2$ method N$_2$O mass transfer coefficients had their respective static correction factors of 0.58 and 0.43 applied prior to graphing.
magnitude of measured N₂O emissions. The resulting calculated values estimate the measured data well, with the O₂ 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 KLa values that could be used for comparison. Many N₂O KLa values come from laboratory studies using significantly higher aeration flowrates compared to basin volume. Mampaey et al. (2015) found an N₂O KLa of 1,025 d⁻¹ when aerating a 100 mL stripping flask with 1 L min⁻¹ airflow. Harper et al. (2015) measured an N₂O KLa between 450 and 510 d⁻¹ aerating a 500 mL vessel with a 1 L min⁻¹ air flowrate. Domingo-Félez et al. (2014) found KLa values ranging from 85 d⁻¹ to 475 d⁻¹ for air flowrates from 0.25 to 2.5 L min⁻¹ in a 4 L reactor. In comparison, Viikinmäki’s zones are approximately 1.9 * 10⁶ L and the maximum zone aeration during this study was 34,700 L min⁻¹.

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 N₂O KLa at a full-scale plant with surface aerators using the equivalent of the O₂ method but with a known methane KLa instead of an O₂ KLa. In their study, KLa values were as high as 1,150 d⁻¹ where the aerators were located and decreased to 12.5 d⁻¹ in the turbulent zone immediately following the aerators. The surface aerator N₂O KLa 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 KLa values between approximately 10 and 90 d⁻¹ in activated sludge basins up to 6 m deep. The tanks at Viikinmäki are 12 metres deep, so even though calculated KLa values from this study were within this range, Foley et al.’s empirical relationship may not accurately estimate N₂O KLa in deep reactors.

Mass transfer calculated using the O₂ KLa 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 N₂O in the O₂, superficial velocity, and static methods were 27.9, 49.1, and 52.0%, respectively. Marques et al. (2016) compared methods of KLa determination in aerobic and anaerobic conditions and also found the O₂ method of calculating KLa to result in more accurate N₂O emission estimations than the superficial velocity method even though they determined N₂O KLa from a static OTR. Based on the accuracy of calculating N₂O transfer using O₂ KLa values, similar water quality parameters may have impacted both O₂ and N₂O transfer. However, the corrected mass transfer coefficient for N₂O transfer was half as large as was predicted with the clean water diffusivities of O₂ and N₂O. This suggests that N₂O stripping and O₂ transfer may be impacted to a different degree by water quality. Domingo-Félez et al. (2014) compared KLa values for O₂ and N₂O over varying aeration flowrates and found that the relationship was not linear, suggesting that the different solubilities of N₂O and O₂ may make the exact relationship between O₂ and N₂O transfer difficult to correlate. Although this study was not sufficient to prove that the impacts of water quality and superficial velocity on O₂ and N₂O KLa are not analogous, it does cast further doubt on the accuracy of this assumption.

Gas transfer data for N₂O and O₂ 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 N₂O emissions. Any variations in water quality or operational parameters can impact bubble size and diffusivity, therefore impacting the effective KLa and OTE. Oxygen transfer and mass transfer KLa values were heavily affected by airflow, and variance between the temporal pattern of O₂ 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 O₂ or N₂O transfer within this study.

Data used in KLa value and N₂O emission calculations were collected during a single week of unusually high N₂O 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 N₂O measurements included probe uncertainties and reliability of Gasmet 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 Gasmet DX4015 data is listed in Table 1.

Additional error in N₂O calculations is possible as a result of errors in readings used for O₂ transfer calculations, for example from noise and drift in the O₂ analyser signal. The AMI model 65 O₂ analyser is reported to have drift
under 1% of the full range over 4 weeks and a repeatability within ±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 N₂O 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_{La} values and in dissolved N₂O concentrations both significantly impacted calculated emissions (Figure 6). Dissolved N₂O variations up to observed levels of +/- 10% resulted in changes up to +/- 10% in calculated N₂O emissions. The relationship between dissolved and emitted N₂O was effectively linear when K_{La} was held constant due to negligible N₂O in process gas entering the activated sludge basins (Equation (2)). The K_{La} values that best fit measured N₂O emissions deviated from initial calculated values by an average factor of 0.5. For this range of +/- 50% N₂O K_{La} values, calculated N₂O emissions varied by +/- 25%.

The calculated K_{La} for N₂O stripping using the O₂ method is dependent on the calculated O₂ K_{La} value and therefore sensitive to variability in airflow and O₂ readings. A 10% air flowrate change resulted in peak differences in O₂ K_{La} that were nearly 15% higher or lower than initial measured values (Figure 7). Erroneous readings of percent O₂ 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 N₂O emission calculations using the O₂ method.

The impact of changes to the O₂ K_{La} value on calculated N₂O emissions would be reduced in magnitude, as seen in the sensitivity analysis on impacts of K_{La} variations.

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

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero-point calibration</td>
<td>Every 24 hours, calibrate with N₂ (5.0 or higher recommended)</td>
</tr>
<tr>
<td>Zero-point drift</td>
<td>&lt;2% of measuring range per zero-point calibration interval</td>
</tr>
<tr>
<td>Sensitivity drift</td>
<td>None</td>
</tr>
<tr>
<td>Linearity deviation</td>
<td>&lt;2% of measuring range</td>
</tr>
<tr>
<td>Temperature drifts</td>
<td>&lt;2% of measuring range per 10 K temperature change</td>
</tr>
<tr>
<td>Pressure influence</td>
<td>1% change of measuring value for 1% sample pressure change. Ambient pressure changes measured and compensated.</td>
</tr>
</tbody>
</table>

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**Figure 5** | Air flow rates, OTR, OTE and O₂ K_{La}, 14–21 May 2019.
The overall impact on estimated N₂O emissions would therefore be expected to be closer to a 7–8% difference in N₂O values for a 10% change in airflow or a 0.2% change in O₂ 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 N₂O from WWTPs can be accurately estimated using dissolved N₂O concentrations, and with sufficient calibration and validation dissolved N₂O concentrations could be used to estimate the magnitude of emissions as well.

The method of determining mass transfer coefficients for modelling of N₂O stripping significantly impacts the resulting calculations, and therefore calculation accuracy.

This study introduces a novel method to concurrently measure N₂O and O₂ transfer in aerated zones of full-scale treatment plants. Within this study, the N₂O KLa calculation method based on O₂ 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 N₂O emissions or the KLa estimation methods were unable to accurately represent the gas transfer. Although the assumption of analogous impacts of wastewater conditions on N₂O and O₂ transfer may not be fully accurate, it is clear that O₂ transfer can provide useful information for estimating N₂O

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*(Figure 6)* Impact of (a) dissolved N₂O readings on calculated off-gas N₂O using O₂ method compared against measured N₂O values and (b) mass transfer coefficient on calculated off-gas N₂O using static method, compared against measured N₂O values.
transfer. Additional research is still necessary to determine the exact impacts of deep basins and changes in water quality on O₂ transfer and N₂O stripping, as well as to determine more accurate methods of KLa calculation that do not require empirically determined correction factors.

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DATA AVAILABILITY STATEMENT

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

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