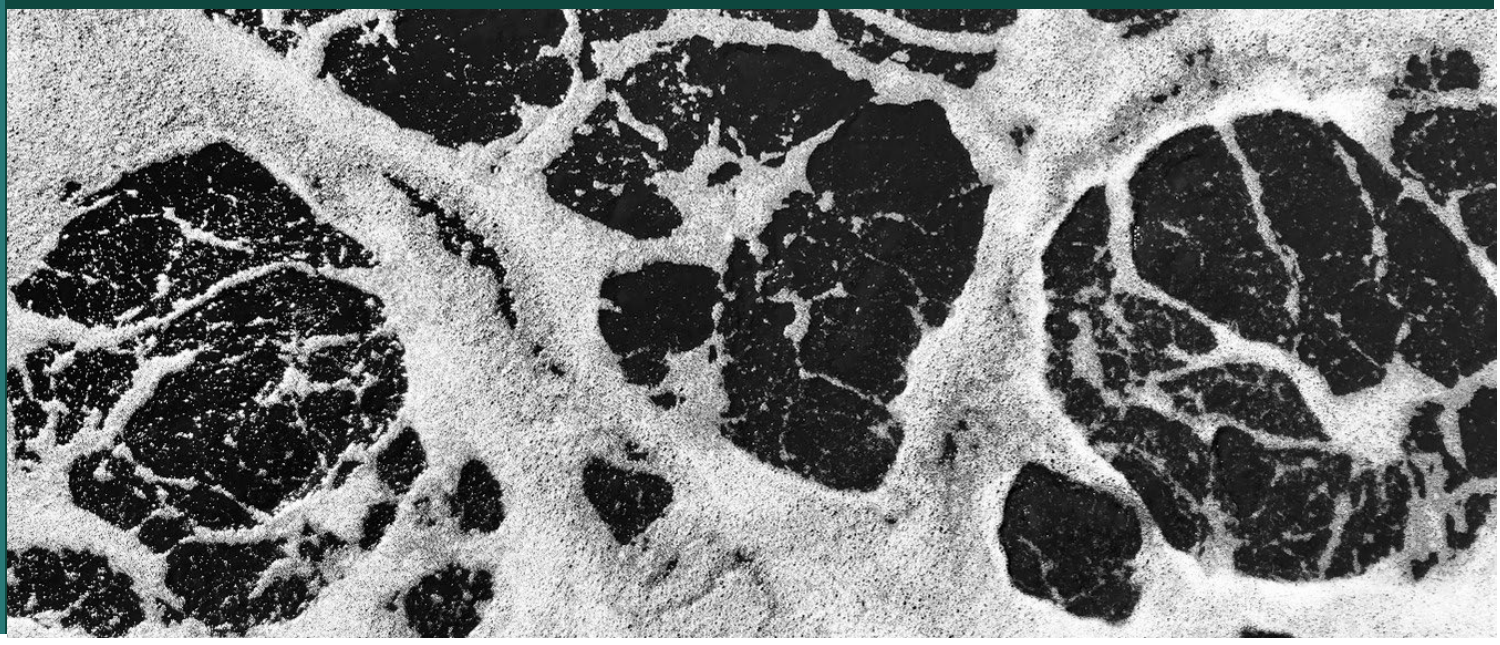
Miljøministeriet
Miljøstyrelsen

AWAIRE

Development and testing of techniques for measuring N2O emissions from wastewater treatment plants - MUDP project

MUDP Report

June 2024



Publisher: The Danish Environmental Protection Agency

Editors:
Luca D. Ledermann; Explicit ApS
Arturo Lewis Lallana; Explicit ApS
Anders M. Fredenslund; DTU Sustain
Charlotte Scheutz; DTU Sustain
Konstantinos Kissas; DTU Sustain
Mikkel Stokholm-Bjerregaard; Krüger A/S
Kasper Lindholm; Krüger A/S
Artur Tomasz Mielczarek; BIOFOS
Dines Thornberg; BIOFOS

Graphics:
Explicit ApS
DTU Sustain

Photos:
Explicit ApS
DTU Sustain

ISBN: 978-87-7038-619-7

Miljøteknologisk Udviklings- og Demonstrations-program

Projektet, som er beskrevet i denne rapport, er støttet af Miljøteknologisk Udviklings- og Demonstrationsprogram (MUDP) under Miljøministeriet, der støtter udvikling, test og demonstration af miljøteknologi.

MUDP investerer i udvikling af fremtidens miljøteknologi til gavn for klima og miljø i Danmark og globalt, samtidig med at dansk vækst og beskæftigelse styrkes. Programmet understøtter dels den bredere miljødagsorden, herunder rent vand, ren luft og sikker kemi, men understøtter også regeringens målsætninger inden for klima, biodiversitet og cirkulær økonomi.

Det er MUDP's bestyrelse, som beslutter, hvilke projekter der skal modtage tilskud. Bestyrelsen betjenes af MUDP-sekretariatet i Miljøstyrelsen.

MUDP-sekretariatet i Miljøstyrelsen
Tolderlundsvej 5, 5000 Odense| Tlf. +45 72 54 40 00

Mail: ecoinnovation@mst.dk
Web: www.mudp.dk

Contents

Sammenfatning

Lattergas (N_2O) emissioner fra biologisk kvælstoffjernelse er en betydelig bidragyder til den samlede klimapåvirkning forbundet med spildevandsbehandling. Derfor har der været øget fokus på at mindske N_2O-emissioner i de seneste år, hvilket har ført til udvikling og test af innovative måleteknologier i AWAIRE-projektet. Specifikt, er to nye målemetoder blevet evalueret med henblik på måling af N_2O-emissioner fra renseanlæg: Drone Flux Measurement (DFM) metoden og Eddy Covariance (EC) metoden.

I dette projekt blev effektiviteten af disse nye teknologier vurderet i forhold til etablerede metoder som sporgasdispersionsmetoden (TDM) og væskefase N_2O sensorer (LPS). Den sidstnævnte, der er bredt anvendt på adskillige renseanlæg i Danmark og andre steder, fungerer som en kontinuerlig målemetode ved at måle N_2O-koncentrationen i de biologiske proceslinjer på et renseanlæg. Anvendelsen af LPS giver driftspersonale indsigt i N_2O-dannelsen i procestanke, hvilket muliggør justering af driften af disse for at reducere N_2O-emissioner.

Sammen med andre parametre, herunder luftstrøm under iltning, vandtemperatur, tankdimensioner og luftningsparameteren (kLa), kan N_2O-koncentrationerne målt af LPS bruges til at give modelberegnede emissionsrater - dvs. hvor meget N_2O der udledes til atmosfæren rapporteret i masseenheder som kg N_2O time-1. Sammen med data om kvælstofbelastningen til anlægget kan disse værdier bruges til at beregne emissionsfaktorer - dvs. procent kvælstof (% N) udledt som N_2O.

På grund af Danmarks mål om reduktion af drivhusgasemissioner, herunder et mål om at reducere emissionerne med 70% inden 2030 sammenlignet med niveauet i 1990, kan det være relevant at give nødvendige incitamenter eller anden form for regulering af spildevandssektoren for at reducere N_2O-emissioner. For at kunne gøre dette er det vigtigt at levere ensartede, alment accepterede metoder til at måle N_2O-emissioner fra renseanlæg.

Metoder til N_2O-måling

Hovedmålet med AWAIRE-projektet var at sammenligne de førnævnte målemetoder (DFM, TDM, EC og LPS) for at kvantificere N_2O-emissioner. DFM- og TDM-metoderne er remote sensing metoder, der omfatter bestemmelse af N_2O-niveauer (koncentrationer over baggrundsniveauet) i fanen nedvinds kilden. Begge metoder giver øjebliksmålinger, hvor en operatør skal være på stedet for at udføre målingerne. Dette er ikke tilfældet for LPS og EC, hvor måleudstyr kan opsættes til at levere måledata over længere perioder - dog kræves der vedligeholdelse for begge metoder under måleperioderne.

DFM-metoden tilpasset N_2O, er udviklet af Explicit ApS og testet i AWAIRE-projektet. DFM blev oprindeligt udviklet primært til kvantificering af metanemissioner fra forskellige industrier.

TDM-metoden er udviklet af DTU og er i tidligere studier blevet anvendt til at kvantificere N_2O-emissioner fra forskellige kilder, herunder spildevandsrensningsanlæg i Danmark og andre steder. Disse studier har ligeledes inkluderet validering og usikkerhedsvurdering af målemetoden.

EC er blevet brugt til at overvåge gasfluxe fra økosystemer, men anvendelsen af EC til kvantificering af N_2O fra spildevandsbehandling er os bekendt ikke blevet testet før.

Sensorerne til måling af N_2O i væskefasen (LPS), der blev brugt i denne undersøgelse, er udviklet af Unisense. Deres output er integreret i STAR^2 og Hubgrade Performance Plant, der er udviklet af Krüger.

DFM-metoden anvender en UAV (drone), hvor en letvægts-gassensor er monteret for at bestemme atmosfæriske N_2O-koncentrationer. På den samme drone er der monteret to vindmålere, som bestemmer vindvektorer på det sted, hvor N_2O målingen foretages. DFM-målinger består af enkeltflyvninger (eller målemure), hvor dronen flyver i fanen nedvinds kilden i flere højder, hvilket giver et sæt fluxdensiteter for hver målemur. For at reducere usikkerheden udføres flere målemure, hvorfra en gennemsnitlig emissionsrate beregnes.

Ved TDM-metoden anvendes en kontinuerlig, kontrolleret frigivelse af en sporgas på kilden kombineret med nedvinds atmosfæriske målinger af N_2O og sporgaskoncentrationer. Brugen af sporgas eliminerer behovet for måling af vind for at bestemme dispersion af N_2O i atmosfæren. Hver TDM-måling består af et antal (>10) traverser af nedvindsfanen med et køretøj, hvor udstyr er installeret til at måle atmosfæriske koncentrationer af N_2O og sporgas. N_2O-emissionsrater beregnes for hver fanegennemkørsel, hvorfra en gennemsnitlig rate beregnes.

EC består af instrumenter monteret i et tårn, der med høj målefrekvens giver målinger af atmosfæriske gaskoncentrationer og vindvektorer. Modsat TDM og DFM er placeringen af luftprøvetagning og vindmåling stationær, hvilket betyder, at metoden er afhængig af vindtransport af gasser til prøvetagningsstedet. For EC bestemmes fluxrater for et område nær tårnet. Dimensionerne og placeringen af dette område afhænger af vindretningen, tårnhøjden og andre faktorer.

Projektaktiviteter
AWAIRE-projektet omfattede følgende aktiviteter:
• Kalibrering og laboratorietest af N_2O-gasanalyser til DFM-applikation
• Kontrolleret N_2O-frigivelsestest til DFM-emissionskvantificering
• Test af DFM-applikation på forskellige renseanlæg
• Udvikling af DFM-måleprotokol til kvantificering af N_2O-emissioner
• Videreudvikling af LPS-afledt N_2O-emissionsbestemmelse hos BIOFOS Avedøre
• Sammenlignende målinger af N_2O-emissioner hos BIOFOS Avedøre ved hjælp af DFM, TDM og LPS
• Anvendelse af EC hos BIOFOS Avedøre for at studere N_2O-emissionsdynamik og sammenligning med LPS
• Yderligere TDM-målinger for at kvantificere sæsonvariation af N_2O-emissionsrater fra BIOFOS Avedøre
• Udkast til måleprotokol i forhold til måling af N_2O-emissioner fra renseanlæg

Hovedresultatet af de første fire nævnte aktiviteter var oprettelsen af en DFM-måleprotokol, der skal følges for at kvantificere N_2O-emissionsrater fra renseanlæg. DFM-metoden blev brugt til at kvantificere N_2O-emissioner fra BIOFOS Avedøre i sammenlignende målinger med TDM og LPS. TDM-målinger blev brugt til at kvantificere N_2O-emission i yderligere målekampagner for at studere sæsonmæssig emissionsvariation - og sammenligne disse med LPS-afledte emissionsrater. Baseret på observationerne i dette projekt og pågående, relateret arbejde blev der udarbejdet et udkast til måleprotokol med anbefalinger til fremtidigt arbejde.

Resultater og diskussion
DFM-metoden, tilpasset kvantificering af N_2O fra renseanlæg, blev succesfuldt udviklet og testet under AWAIRE-projektet. DFM blev sammenlignet med TDM-målinger, hvor der i alt blev udført 24 samtidige DFM/TDM-målinger, hvor N_2O-emissioner fra beluftningstanke på BIOFOS Avedøre blev kvantificeret. Hver observation bestod af en flyvning svarende til en målevæg og en samtidig serie TDM-traverser (i gennemsnit 6,3). Af de samtidige målinger var varierede emissionsraten for DFM mellem 0,18 og 99,8 kg N_2O time-1, og emissionsraten målt med TDM mellem 0,27 og 106,0 kg N_2O time-1. De højeste emissionsrater for begge metoder var på en dag, hvor unormale driftsbetingelser forårsagede unormalt høje N_2O-emissioner fra anlægget. Der blev ikke observeret nogen generel tendens til, at den ene metode konsekvent målte en højere

emissionsrate end den anden. Den gennemsnitlige emissionsrate fra alle 24 observationer var sammenlignelig mellem DFM (16,8 kg N_2O time-1) og TDM (15,7 kg N_2O time-1).

TDM- og DFM-målinger blev sammenlignet med samtidige LPS-afledte N_2O-emissionsrater. Her var antallet af observationer højere end for sammenligningen af DFM med TDM: 38 TDM-målinger bestående af 400 traverser og 38 DFM-målinger, hver bestående af en flyvning/måle-væg. I gennemsnit var både DFM og TDM daglige emissionsrater højere end LPS-emissionsrater fra de samme perioder (47% og 77% for henholdsvis DFM og TDM). For DFM-kampagnerne varierede de daglige gennemsnitlige emissionsrater mellem 0,30 og 10,20 kg N_2O time-1, med en gennemsnitlig værdi på 4,28 kg N_2O time-1, mens den gennemsnitlige samtidige LPS-emission var 2,91 kg N_2O time-1. For TDM varierede de daglige gennemsnitlige emissionsrater mellem 0,38 og 13,35 kg N_2O time-1, med en gennemsnitlig værdi på 4,96 kg N_2O time-1. LPS-værdierne svarende til TDM-målinger varierede mellem 0,13 og 9,55 kg N_2O time-1, med en gennemsnitlig værdi på 2,80 kg N_2O time-1. Mulige årsager til de højere remote-sensing-værdier sammenlignet med LPS inkluderer usikkerhed i luftstrømshastigheden, der bruges i emissionsberegningen, LPS-sensordrift og til opskalering af emissioner fra de fire procestanke udstyret med LPS til alle otte procestanke på anlægget.

Under AWAIRE blev LPS N_2O-emissionsberegningerne videreudviklet, hvor styringssystemet blev ændret fra STAR-systemet til Hubgrade Performance Plant. Til brug for sammenligning med TDM- og DFM-målinger blev der implementeret korrektion i forhold til negativ sensordrift for LPS. Negativ drift af LPS-sensorerne kan resultere i negative koncentrationsmålinger og en undervurdering af N_2O-emissionen til luften. Hvis dette blev observeret, blev der tilføjet en korrektion til alle N_2O-koncentrationsværdier i væskefasen for måledagene, der svarer til den negative koncentration for hver sensor.

EC blev brugt til at måle N_2O-fluxer fra dele af iltningstanke ved BIOFOS Avedøre i to perioder i 2022 og 2023. EC-metoden var i stand til at måle den dynamiske N_2O-flux og illustrere både den sæsonmæssige og daglige variabilitet fra beluftningstanke. Resultaterne for den sæsonmæssige variabilitet matchede med resultaterne fra remote-sensing-metoder er anvendt i denne undersøgelse. Den høje tidsmæssige opløsning af N_2O-fluxe målt med EC-metoden tillod sammenligning af emissionens dynamik med de modellerede emissioner baseret på LPS. Resultaterne viste en stærk overensstemmelse mellem de to metoder, især for 2023, efter at N_2O-sensoren i væskefasen blev flyttet indenfor EC-tårnets flux-område.

Overordnet set var emissionsfaktorer (% N udledt som N_2O til luften normaliseret til kvælstofbelastningen til den biologiske proceslinje) for de to remote-sensing-metoder (TDM og DFM) højere end dem, der er afledt fra LPS-målinger. For remote sensingmetoderne var emissionsfaktoren 2,2% og 2.8% for henholdsvis TDM og DFM., hvor emissionsfaktoren beregnet ud fra LPS-værdier for de samme måledage var 1,2%.

På grund af den meget dynamiske korttids- og sæsonmæssigekarakter af N_2O-emission fra spildevandsbehandling kan kontinuerlige målinger som LPS være det mest nøjagtige værktøj til at opgøre N_2O-emissioner fra disse anlæg. Imidlertid kan flere faktorer forårsage usikkerhed i beregningerne af emissionsraten baseret på LPS, herunder den anvendte luftningsparameter (kLa), sensorplacering, ekstrapolation til tanke uden LPS, sensordrift med mere. Målingerne af direkte emissioner foretaget i AWAIRE-projektet ved hjælp af TDM og DFM antyder, at LPS-emissionssatser undervurderer N_2O-emissioner fra BIOFOS Avedøre. Remote sensing-metoder som TDM og DFM kan give mulighed for at kvalificere LPS-emissionssatser og afgøre, om der er behov for justeringer af parametrene i emissionsmodellen.

Konklusion

To nye metoder til måling af N_2O-emission fra spildevandsbehandling (DFM og EC) blev testet og sammenlignet med eksisterende metoder (TDM og LPS). Remote sensing metoderne (TDM

og DFM) målte konsekvent højere N_2O-emissionssatser (i gennemsnit 47-77%) sammenlignet med LPS på BIOFOS Avedøre over 15 måledage. Årsagen til denne forskel i emissionsrater er ikke fastlagt, men kan være en effekt af den unøjagtige bestemmelse af luftstrøm i procestanke, negativ LPS-sensordrift, utilstrækkelig kalibrering af LPS-sensorer eller unøjagtighed forårsaget af ekstrapolation af emissionsraten fra procestanke med LPS sensorer til øvrige tanke. De højopløselige N_2O-fluxe fra EC-metoden viste en stærk overensstemmelse med hensyn til emissionsdynamikken ved sammenligning med LPS-modellerede emissioner.

N_2O-emissioner fra renseanlæg er meget dynamiske, hvor kontinuerlige målemetoder som LPS kan være værdifulde til bestemmelse af årlige emissionssatser og anlægsspecifikke N_2O-emissionsfaktorer. De remote sensing målinger, der er rapporteret i denne rapport, antyder dog, at validering af N_2O-emissioner baseret på LPS-målinger - måske for hvert anlæg - er nødvendig for at sikre nøjagtig opgørelse af N_2O-emissioner fra spildevandsbehandling.

1. Summary

Nitrous oxide (N_2O) emissions stemming from biological nitrogen removal are a significant contributor to the overall climate footprint associated with wastewater treatment. Consequently, there has been a heightened focus on mitigating N_2O emissions in recent years, leading to the development and testing of innovative emission measurement technologies within the AWAIRE project. Specifically, two novel approaches have been evaluated for targeting N_2O emissions from wastewater treatment plants: the Drone Flux Measurement (DFM) method and the Eddy Covariance (EC) method.

In this project, the effectiveness of these new technologies was assessed in comparison to established methods such as the Tracer gas Dispersion Method (TDM) and Liquid Phase Sensors (LPS). The latter, widely employed at numerous wastewater treatment plants in Denmark and elsewhere, operates as a continuous measurement method by measuring N_2O concentration in the biological process lines of a wastewater treatment plant. The application of LPS allows operators to gain insights into N_2O formation within the lines, thereby enabling adjustments to the operation of the lines to reduce N_2O emissions.

Coupled with other parameters, which include airflow during aeration, water temperature, tank dimensions and mass transfer coefficients, the N_2O concentrations measured by LPS can be used to provide calculated emission rates – i.e. how much N_2O is emitted to the atmosphere reported in mass rate units, such as kg N_2O h^{-1}. Coupled with data on nitrogen load to the plant, these values can be used to calculate emission factors – i.e. percentage nitrogen (% N) emitted as N_2O.

Due to Denmark's targets for reduction of greenhouse gas emissions, which include a near term goal to reduce emissions by 70% by 2030 compared to 1990 level, it may be relevant to provide the necessary incentives or other form of regulation for the wastewater sector to reduce N_2O emissions. To do that, it is important to provide uniform, generally accepted means to account for N_2O emissions from wastewater treatment plants.

N_2O measurement methods

The main goal of the AWAIRE project was to compare the aforementioned measurement methods (DFM, TDM, EC and LPS) to quantify N_2O emissions. The DFM and TDM methods are remote sensing methods, which include determination of N_2O levels (concentrations above background level) in the plume downwind from the source. Both methods are discrete (e.g. measures the emission at a single point in time), where an operator needs to be at the site to perform the measurements. This is not the case for LPS and EC, where measurement equipment can be set up to provide measurement data over longer periods – though maintenance is required for both methods during the measurement periods.

The DFM method adapted for targeting N_2O was developed by Explicit and tested during the AWAIRE project. DFM was initially developed, and is still applied, for the quantification of methane emissions from various industries.

TDM was developed by DTU and has been used to quantify N_2O emissions from various sources including wastewater treatment plants in Denmark and elsewhere in previous studies, which have included validation and error assessment of this measurement method.

DTU has used EC to monitor gas fluxes from ecosystems for more than 25 years, but the application of EC for quantifying N_2O from wastewater treatment has not, to our knowledge, been

tested before. The liquid phase sensors utilized in this study were developed by Unisense. Their output is integrated into the STAR^2 and Hubgrade Performance Plant, developed by Krüger.

The DFM relies on an unmanned aerial vehicle (or drone), on which a low weight, gas analyser is mounted to determine atmospheric N_2O concentrations. On the same drone, two wind sensors are also mounted, which determine wind vectors at the location where air is sampled during measurement. DFM measurements consists of single flights (or "flux walls"), where the drone traverses the plume downwind from the source at several heights, leading to a set of flux densities for each flux wall. To reduce uncertainty, several flux walls are performed, from where an average emission rate is calculated.

TDM relies on a continuous, controlled release of a gaseous tracer at the source combined with downwind atmospheric measurements of N_2O and tracer gas concentrations. The use of the gaseous tracer eliminates the need for measurement of wind to determine the dispersion of N_2O in the atmosphere. Each TDM measurement consists of a number (>10) of traverses of the plume with a vehicle, wherein equipment is installed to sample and measure atmospheric concentrations of N_2O and tracer gases. N_2O emission rates are calculated for each plume traverse, from where an average rate is calculated.

EC consists of a tower-mounted set of instruments, which provide high frequency measurements of atmospheric gas concentrations and wind vectors. Opposed to TDM and DFM, the location of air sampling and wind measurement is stationary, whereby the method relies on wind transport of gases to the sampling location. For EC, flux rates are determined for an area or "footprint" near the tower. The dimensions and location of this area depend on wind direction, tower height and other factors.

Project activities

The AWAIRE project included the following activities:

- Calibration and laboratory test of N_2O gas analyser for DFM application
- Controlled N_2O release test of DFM emission quantification
- Test of DFM application at different wastewater treatment plants
- Development of DFM measurement protocol to quantify N_2O emissions
- Refinement of LPS derived N_2O emission quantification at BIOFOS Avedøre
- Comparative measurements of N_2O emissions at BIOFOS Avedøre using DFM, TDM and LPS
- Application of EC at BIOFOS Avedøre to study N_2O emission dynamics and comparison to LPS
- Additional TDM measurements to quantify seasonal variation in emission rates at BIOFOS Avedøre
- Draft of measurement protocol to provide accurate N_2O emission estimates from wastewater treatment plants

The main result of the first four listed activities was the establishment of a DFM measurement protocol to be followed to quantify N_2O emission rates from wastewater treatment plants. In turn, the established methodology of DFM was used to quantify N_2O emissions from BIOFOS Avedøre in comparative measurements with TDM and LPS. TDM measurements were used to quantify N_2O emission in additional measurement campaigns to study seasonal emission variation – and compare those to LPS derived emission rates. Informed by the observations in this project and on-going, related work, a draft measurement protocol was outlined with recommendations for further work.

Results and discussion

The DFM method adaption for the quantification of N_2O from wastewater treatment plants was successfully developed and tested during the AWAIRE project. DFM was compared to TDM

measurements, where in total 24 simultaneous DFM/TDM measurements were performed where N_2O emissions from the biological process tanks at BIOFOS Avedøre were quantified. Each observation consisted of one flight corresponding to one flux wall and a simultaneous set of TDM transects (6.3 on average). Of the simultaneous measurements, the emission rate for DFM varied between 0.18 and 99.8 kg N_2O h^{-1}, and the emission rate measured by TDM varied between 0.27 and 106.0 kg N_2O h^{-1}. The highest emission rates for both methods were on a day where unusual operating conditions caused higher than normal N_2O emissions at the plant. No overall tendency of one method consistently measuring higher emission rate than the other was observed. The average emission rate from all 24 observations was comparable between DFM (16.8 kg N_2O h^{-1}) and TDM (15.7 kg N_2O h^{-1}).

TDM and DFM measurements were compared to simultaneous LPS-derived N_2O emission rates. Here, the numbers of observations were higher than for the comparison of DFM to TDM: 38 TDM measurements consisting of 400 transects and 38 DFM measurements each consisting of one flight/flux wall. On average, both DFM and TDM daily emission rates were higher than LPS emission rates from the same periods (47% and 77% for DFM and TDM, respectively). For the DFM campaigns, daily average emission rates varied between 0.30 to 10.20 kg N_2O h^{-1}, with the average of those being 4.28 kg N_2O h^{-1}, while the average simultaneous LPS emission was 2.91 kg N_2O h^{-1}. For TDM, daily average emission rates varied between 0.38 and 13.35 kg N_2O h^{-1}, with the average of those being 4.96 kg N_2O h^{-1}. The LPS values corresponding to TDM measurements varied between 0.13 and 9.55 kg N_2O h^{-1}, with the average being 2.80 kg N_2O h^{-1}. Possible reasons behind the higher remote sensing values compared to LPS include uncertainty in the airflow rate used to calculate LPS emission, LPS sensor drift, LPS sensor placement and upscaling of emissions from four process tanks equipped with LPS to all eight process tanks at the plant.

During AWAIRE, LPS N_2O emission calculations were refined, where the control system was changed from the STAR^2 system to Hubgrade Performance Plant. For comparison to TDM and DFM measurements, correction to negative sensor drift was implemented. Negative drift of the LPS sensors can result in negative concentration readings and an underestimation of the N_2O emission to air. If this was observed, we added a correction to all liquid N_2O concentration values of the measurement days, corresponding to the negative concentration for each sensor.

EC was used to measure N_2O fluxes from parts of the aeration tanks at BIOFOS Avedøre in two periods in 2022 and 2023. The EC method was able to address the dynamic behaviour of N_2O fluxes and to illustrate both the seasonal and diurnal variability from the aeration tanks. Results for the seasonal variability matched with the results from the other remote sensing methods applied in this study. The high-resolution N_2O fluxes from EC method allowed us the comparison of the emission dynamics with the modelled emissions based on LPS. Results showed a strong agreement between the two methods, particularly for 2023, after the liquid phase N_2O sensor was relocated to inside the flux footprint area of the EC tower.

Overall, emission factors (%N emitted as N_2O to air normalized to the nitrogen load to the biological process line) for the two remote sensing methods (TDM and DFM) were higher than those derived from LPS measurements. For the remote sensing methods, the emission factors were 2.2 and 1.8% for the TDM and DFM, respectively. The LPS value for the same measurement days was lover – 1.2%.

Due to the highly dynamic short- and long-term nature of N_2O emission from wastewater treatment, continuous measurements such as LPS may be the most accurate tool to account for N_2O emissions from these plants. However, several factors may cause uncertainty in emission rate calculations based on LPS including the mass transfer coefficients used (during aeration and non-aeration), sensor placement, extrapolation to non-LPS tanks, sensor drift and more. The measurements of direct emissions done in the AWAIRE project using TDM and DFM suggest

that LPS emission rates underestimate N_2O emissions from BIOFOS Avedøre. Remote sensing methods such as TDM and DFM may provide opportunity to qualify LPS emission rates and determine if adjustments to the emission model parameters are needed.

Conclusion

Two novel methods for measurement of N_2O emission from wastewater treatment plants (DFM and EC) were tested and compared to existing methods (TDM and LPS). The remote sensing methods (TDM and DFM) consistently measured higher N_2O emission rates (on average 44-77%) compared to LPS at BIOFOS Avedøre at 15 measurement days. The reason for this difference in emission rates has not been established but may be an effect of the inaccurate determination of airflow, negative LPS sensor drift, insufficient calibration or error caused by extrapolation of emission rate from LPS equipped tanks to non-LPS equipped tanks. The high-resolution N_2O fluxes from the EC method showed a strong agreement with regards to emission dynamic when compared with LPS modelled emissions.

N_2O emissions from wastewater treatment plants are highly dynamic, whereby continuous measurement methods such as LPS may be valuable in determination of yearly emission rates and plant specific N_2O emission factors. The remote sensing measurements reported in this study suggest, however, that validation of N_2O emissions based on LPS measurements – perhaps for each plant – is necessary to ensure accurate accounting for N_2O emissions from wastewater treatment plants.

Preface

AWAIRE is a 2-year collaborative research and development project funded by the Danish Environmental Technology and Demonstration Program (MUDP). The project was led by Explicit ApS, a technology provider specializing in monitoring air emissions. The Technical University of Denmark's (DTU) Sustain department, a renowned research institution in air emissions, contributed as a research institution and provided expertise. Krüger A/S, a water consultancy, shared insights from the wastewater industry. BIOFOS, Denmark's largest wastewater treatment utility, facilitated the primary research site for field work and provided facility data. The collective efforts are thanks to the following noteworthy contributions:

TABLE 1. Contributions.

Partner	Contributions
Explicit ApS	DFM method development and measurements, DFM data analysis, LPS data analysis, project management, reporting (sections 2, 3, 4, 8, 9.1, 12, 13)
Technical University of Denmark	TDM measurements, EC method development and measurements, TDM and EC data analysis, controlled N_2O release, DFM/TDM/LPS comparison, reporting (sections 1, 3, 4.8.2, 5, 6, 9.2, 10, 11, 12, 13)
Krüger A/S	LPS data calculation refinement and qualification, N_2O monitoring programme, data analysis, reporting (sections 7, 12, 13)
BIOFOS Group	Hosting measurement campaigns, providing of operational data, operation of controlled aeration tests, data analysis (section 12, 13)
All	All partners agreed to the summary of the report

2. Introduction

Denmark's Climate Programme 2020 was submitted in alignment with the Paris Agreement, setting a near-term goal to reduce the country's greenhouse gas emissions by 70% by 2030 compared to the 1990 level. This ambitious target is part of a broader strategy to attain climate neutrality by 2050. The plan requires substantial emissions reduction efforts starting in 2025, particularly focusing on sectors contributing to emissions, including waste. The strategy highlights that within the waste sector, wastewater treatment plants account for 5% of the total greenhouse gas (GHG) emissions (Danish Ministry of Climate, 2020).

When assessing GHG emissions from wastewater treatment plants, nitrous oxide (N_2O) forms a substantial part of a wastewater treatment plants operational emissions, with studies showing direct N_2O emissions from biological nutrient removal (BNR) processes can account for as much as 48% to 78% of the operational carbon footprint (Daelman et al., 2013; Delre et al., 2019) . This high contribution is due to N_2O's 273-fold global warming potential (GWP100) compared to CO_2 (IPCC, 2023).

One of the key challenges in evaluating N_2O emissions lies in achieving accurate quantification. Explicit has pioneered an innovative approach called the Drone Flux Measurement (DFM) method, which has undergone successful testing and documentation in a prior MUDP project known as PLANE (Knudsen & De Rossi, 2022).

While PLANE targeted methane and primarily focused on method development, the current project, AWAIRE, extends its scope beyond the DFM method. Over a two-year duration, this study aims to assess the performance of DFMs in quantifying N_2O emissions from wastewater treatment plants. AWAIRE broadens its investigation to encompass a diverse array of N_2O quantification technologies. These include the TDM, LPS coupled with a corresponding emission model, and the novel application of an EC tower to evaluate N_2O dynamics.

The overarching goal of the AWAIRE project is to conduct a comprehensive comparison of both existing and novel measurement technologies. By doing so, it aspires to offer valuable insights and guidance on the use of best available technologies for accurate N_2O quantification.

Finally, this report outlines a proposal for a validation step in a national measurement program to quantify N_2O emissions from wastewater treatment plants. The aim is to provide guidance for future compliance with the evolving requirements of the Climate Change Act.

3. Project Objectives

The primary objective of the AWAIRE project was to develop, test, and showcase effective measurement techniques for accurately quantifying N_2O emissions from wastewater treatment plants. This involves the incorporation of innovative technologies to precisely measure the total release of N_2O into the air and validate existing emission models.

The project's overarching goal is to assess and compare commercially viable measurement solutions that assist wastewater treatment plants in better understanding and managing their N_2O emissions. Additionally, AWAIRE aims to propose a concept proposal for a national N_2O measurement program for wastewater treatment plants.

Building upon the DFM technology, validated in a previous MUDP project (PLANE), AWAIRE incorporates the DFM adapted for N_2O measurement. In addition, TDM measurements, EC tower, and N_2O sensors in the LPS are included to map total N_2O emissions, seasonal variations, and process dynamics.

The following work packages were established to fulfil the requirements:

1) Design, development, and testing of the DFM method adapted for N_2O quantification.
2) Comparison of remote sensing methods for N_2O emission quantification.
3) Validation of liquid phase sensor based N_2O emission quantification.
4) Concept for measurement program and method verification.

4. Drone Flux Measurement Method

4.1 Method

The drone flux measurement (DFM) method developed by Explicit measures fugitive methane emissions from various methane emitting sources. The method was successfully tested as part of the MUDP-Plane project and validated by comparison with the tracer dispersion method (TDM) (Knudsen & De Rossi, 2022). Equipped with a state-of-the-art N_2O sensor, the same method is now applied to quantify N_2O emissions from wastewater treatment plants.

In the DFM method, several sensors attached to an unmanned aerial vehicle (UAV) measure the following parameters downwind of an emission source (e.g. the BNR stage of a wastewater treatment plant): wind speed and direction, N_2O concentrations, GPS, temperature, air pressure and additional UAV related parameters. To obtain high quality data, the UAV flies a pre-programmed pattern (referred to as “wall”) at a specific angle to the downwind plume. Since the data is collected in time and space, this method can provide a consistent representation of the flux density.

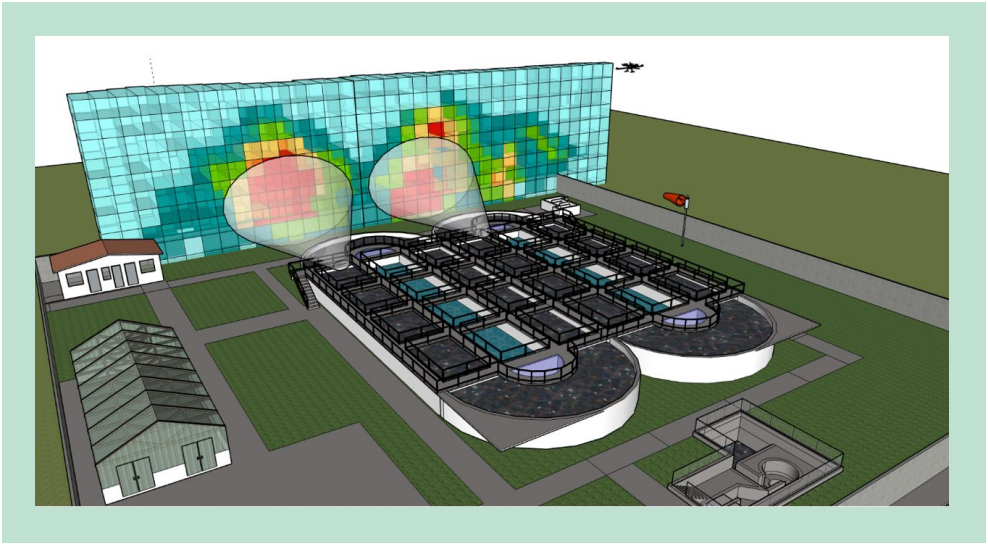


FIGURE 1. Illustration of the DFM method applied on a wastewater treatment plant.

4.2 Equipment

4.2.1 Drone

The drone system used to carry out the measurements consists of several components. The drone is equipped with a programmable flight computer to control the flight, a positioning system to measure the position of the drone itself, a gas sensor to determine the gas concentration, two wind sensors to determine the relative wind speed and the relative wind direction and a data interface to record the data during the flight.

The drone currently used by Explicit is a DJI MATRICE 300 RTK with dimensions of 810 x 670 x 430 mm (unfolded and without propeller) and a payload of 2.7 kg. Due to the sensors required

for data acquisition, the maximum flight time (without wall) is approximately 30 minutes with a wind resistance of up to 15 m/s. Any type of unmanned aerial vehicle can be used if the wind and gas sensors can be installed in a configuration that prevents the effects of the drone's air displacement on the collected data.

FIGURE 2. UAV (1) equipped with the Aeris Mira Strato N_2O (2) and Aeris wind sensor (3).

4.2.2 Wind Sensor

The wind sensor used on the drone is the TriSonica Mini sensor from Anemoment. It's the world´s smallest and lightest 3D ultrasonic anemometer. The sensor collects information regarding the wind speed along all the three directions of the air flow, together with temperature, humidity, pressure and compass data.

TABLE 2. Wind sensors specifications regarding wind speed and direction.

	WIND SPEED	WIND DIRECTION
Range	0 – 50 m/s	Horizontal plane: 0 – 360° Vertical planes: ± 30°
Resolution	0.1 m/s	1.0°
Accuracy	(0 - 10 m/s): ± 0.1 m/s (11 - 30 m/s): ± 1% (31 - 50 m/s): ± 2%	± 1.0°

4.2.3 Nitrous oxide sensor

The MIRA Strato N_2O/CO_2 sensor from Aeris Technologies is one of the most sensitive sensors on the market for its weight (N_2O: < 200ppt/s). This laser absorption analyser operates in the mid-infrared (MIR) range and has a data update rate of up to 10 Hz. These characteristics make the sensor a great fit for the DFM method.

4.3 Operational concept

In March 2023, the DFM method for targeting methane received accreditation from the Danish accreditation body DANAK (DANAK, 2023). As a consequential outcome, Explicit's IT platform

now seamlessly integrates the inspection workflow into a compliant data solution adhering to DS/EN ISO/IEC 17025:2017 standards. The identical workflow is also applicable to the target gas N_2O. Upon submission of calibration certificates from an accredited calibration laboratory, the N_2O method is anticipated to attain accreditation as well. Explicit expects the method accreditation of DFM for N_2O to be realized in the second quarter of 2024.

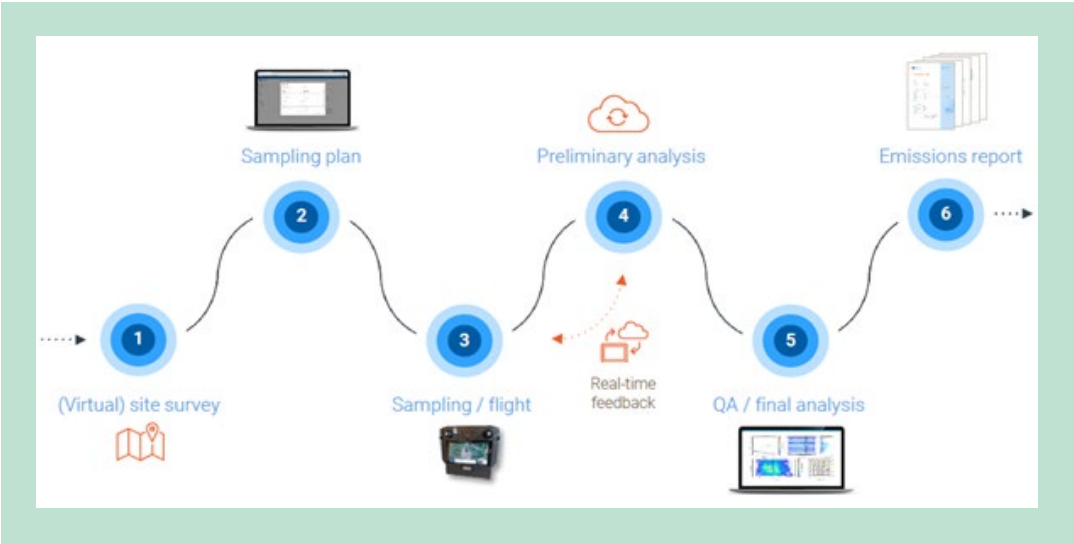


FIGURE 3. Explicit´s workflow.

4.3.1 Site survey

The first step of any measurement campaign is the site inspection. This can be done either on site or online by looking at the latest available maps of the site and surroundings. The site survey is essential to identify the feasible flight paths, avoiding possible obstacles like vegetation (i.e. high trees), topography or other buildings in the surroundings.

The pilot must be able to perform a flight path that covers the entire site downwind projection to be sure that all fugitive gas emissions from the inspected site are measured. Thus, in this step, the pilot investigates if there are any wind directions that could prevent this.
Moreover, at this stage, the presence of potential external emission sources is checked, to avoid to falsely include these in the total measurements.

4.3.2 Sampling / flight

The measurements take place if the weather conditions are favourable (e.g. no heavy rain or snow) and if the wind is substantially coming from a direction that allows the pilot to perform a flight path that covers the entire plant downwind projection. The data should preferably be collected throughout a near vertical plane downwind from the source of interest, approximately perpendicular to the mean wind. The drone flies on an open path, which can be divided into near horizontal transects, flown in alternating flight directions, and small vertical flights when changing transect.

The determination of the flight path – that can either be straight, curved or segmented - is based on information regarding the mean wind direction and the topography of the site. The pilot chooses the shape of the flight path by defining at least two points in the longitudinal direction through which the drone must navigate to: these points are known as "waypoints". Moreover, the pilot defines an "anchor point" positioned at the suspected gas emission; in case of no evidence, the anchor point is set in the middle of the site of interest. The maximum height of the flight is set depending on the plant size and vertical dispersion of the emitted gas plume and is

usually in the order of dozens of meters. Often the start minimum height is as close to the terrain as the drone obstacle sensors will allow.

The area of the wall is determined using GPS coordinates at each observation point, typically thousands of points, and in this way the uncertainty of the overall area is effectively eliminated. Usually, the pilot performs at least three walls, depending on the dynamics of the emission. After each flight, the pilot observes the magnitude of the collected gas concentrations throughout the wall. In case there are high gas concentration close to the edges of the inspected area, the wall dimension, orientation, and position of the following flight are adapted so that the highest concentrations are included and well positioned inside the inspected area. Also, the distance between transects can be adjusted, e.g. to optimise the pattern where you have high gas concentration gradients.

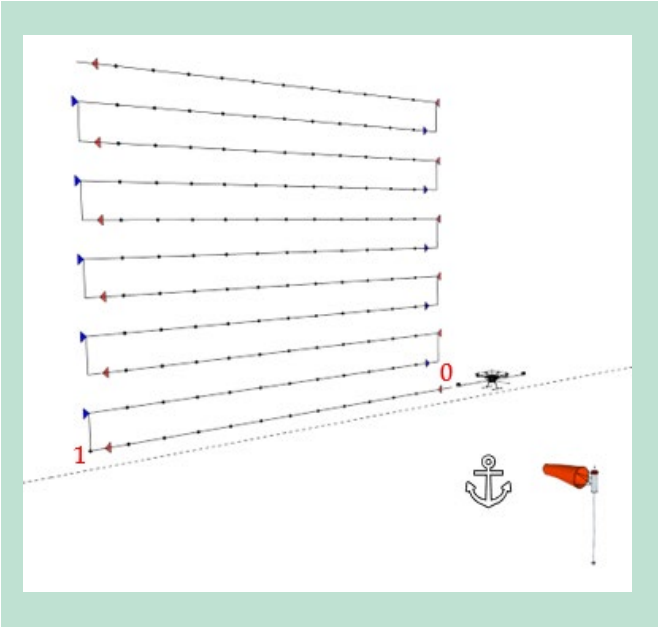


FIGURE 4. Vertical plane flight path (wall) of the DFM method.

Data types collected during a flight:

- Time
- Geographical coordinates and altitude (GPS)
- Elevation above the ground
- Target gas gross concentration
- Air pressure and temperature
- Spatial wind components: (U, V, W)
- Speed and orientation of the drone in relation to the ground (UG)
- Various parameters for the wind sensors

4.4 Quality assessment / final analysis

Before the N_2O flux can be calculated, the collected data is processed, and its quality ensured. If the quality of the data of a flight does not fulfil the quality assessment, the measurements is discarded. To evaluate the N_2O flux through a given area, it is important to know the true wind passing through the area.

The true wind $\vec{W_{Abs}}$ is defined as the wind relative to a fixed ground base point in a coordinate system (W_E,W_N,W_Z). The wind sensors mounted to the drone measure the relative wind $\vec{U_{Rel}}$ in

a (U,V,W) coordinate system. This coordinate system is transformed into the coordinate system (E,N,Z). The transformation is based on the orientation and velocity of the drone relative to the E,N,Z – coordinate system and results in $U_{Rel}^{\rightarrow}$ = (UR_E, UR_N, UR_Z).
The velocity of the drone $U_G^{\rightarrow}$ = (UG_W, UG_N, UG_Z) is continuously (every half second) measured in relation to the ground. With this measurement it is possible to calculate the true wind $W_{Abs}^{\rightarrow}$ by vector addition as expressed in equation (1) and (2).

4.4.1 True Wind:

$$W_{Abs}^{\rightarrow} = U_{Rel}^{\rightarrow} + U_G^{\rightarrow} \quad (1)$$

$$(W_E, W_N, W_Z) = (UR_E, UR_N, UR_Z) + (UG_E, UG_N, UG_Z) \quad (2)$$

The DFM method uses two wind sensors (referred to as Tool1 and Tool2) to collect the wind data. Data from one sensor is enough to perform the flux calculation. The flux calculation can be performed with the following four wind data inputs: data from Tool1, data from Tool2, average of Tool1 and Tool2 and, finally, a manual input based on wind measured with a handheld device (least preferred and applied input).

Which wind data is chosen, depends on the quality of the measured wind and is influenced by two main quality parameters. The first parameter that influences the decision on which of the above-mentioned inputs is chosen, is the true horizontal wind component. The more uniform the true horizontal wind speed and direction throughout the measurement, the higher its quality. This is illustrated in FIGURE 5 which shows two different scenarios related to the horizontal wind speed.

Tool1 shows a wind measurement with an inconsistent horizontal wind speed, whereas Tool2 shows the opposite. The two different colours represent the horizontal path the drone has flown (from left to right: red, from right to left: blue). The more overlapping the collected data, the more consistent the horizontal wind speed.

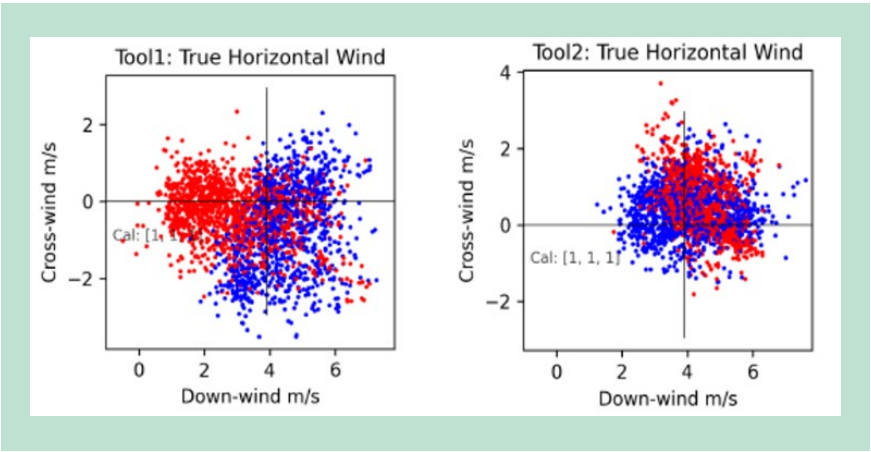


FIGURE 5. Horizontal wind speed.

FIGURE 6 shows two different scenarios related to the horizontal wind direction. The stars within the graphs depict the average horizontal wind direction obtained within each trace. The more these averages are aligned over all trajectories, the more uniform the wind direction. Here, Tool1 shows a wind measurement with an inconsistent horizontal wind direction, whereas Tool2 shows a more uniform wind direction. The two different colours represent the horizontal path the drone has flown (from left to right: red, from right to left: blue).

The second quality parameter that influences the decision making on the input is the alignment of the sensor. If a sensor is not correctly positioned (referred to as alignment), the wind generated by the drone influences the measurement of the wind.

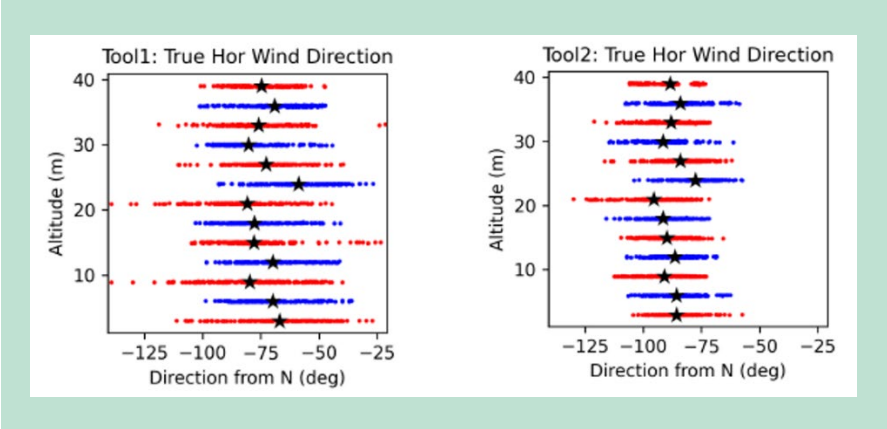


FIGURE 6. Horizontal wind speed.

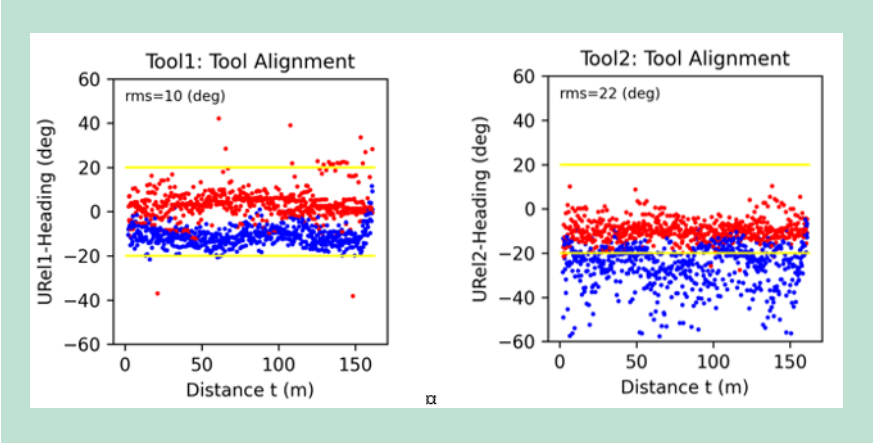


FIGURE 7. Wind Tool alignment.

The alignment can be observed in FIGURE 7. If the collected data is outside the 20% degrees threshold (yellow lines) defined by Explicit, the wind data is falsified by the wind generated by the rotors of the drone. In FIGURE 7, Tool1 is well positioned and shows a good alignment,

whereas Tool2 shows an alignment that requires adjustment. The two different colours represent the horizontal path the drone has flown (from left to right: red, from right to left: blue).

4.4.2 Background gas concentration

A statistical method is applied to assess the gas background concentration for each transect, enabling the definition of a background gas concentration profile. This profile becomes instrumental in the flux calculation process: for every transect, the defined background concentration is subtracted from the measured gas gross concentration. The entire plume of the emission source is captured when background concentrations are detected below, above, and on the sides of a flux wall. Notably, the DFM method distinguishes itself from other approaches by calculating the background concentration individually for each transect. This approach allows for the consideration of even slight variations in background concentrations associated with altitude, resulting in a more accurate evaluation of gas emissions.

FIGURE 8 visually represents how the N_2O concentration differs at 10m altitude compared to 20m altitude. Given the small signal variations in the parts per billion (ppb) range, ensuring the precise determination of the background concentration becomes crucial. Unlike methods that rely on a mean background gas concentration, the DFM method's approach proves advantageous in capturing nuanced variations and enhancing the overall precision.

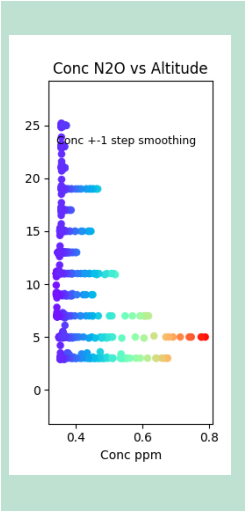


FIGURE 8. N_2O gross concentration.

4.5 Trace Flux calculation

The processed data is then used to calculate the mass flux using the equations described below. The equation that describes the flux through a given area is used as a starting point. The equation (3) forms the basis for Explicit's flux calculation.

$$Flux_{air} = U_n \cdot A \cdot \rho_{air} \quad \textbf{(3)}$$

Where:

$$U_n = true\ wind\ velocity\ to\ the\ surface\ [m \cdot s^{-1}]$$
$$A = area\ of\ the\ observerd\ surface\ [m^2]$$
$$\rho_{air} = air\ density\ [kg \cdot m^{-3}]$$

To calculate the mass flux of N_2O $Flux_{N_2O}$ $[kg \cdot s^{-1}]$, the weight fraction between N_2O and air must be considered and is calculated with the equation (4).

$$Flux_{N_2O} = U_n \cdot A \cdot \rho_{air} \cdot \%_{\omega} N_2O \quad \textbf{(4)}$$

Where:

$$\%_{\omega} N_2O = weight\ fraction\ of\ nitrous\ oxide$$

To elaborate the weight fraction $\%_{\omega} N_2O$, following equation (5) is used in combination with the measured N_2O concentration C [ppm] by the N_2O analyser:

$$\%_{\omega} N_2O = \frac{10^{-6} \cdot C}{V_{molar}} \cdot \frac{MW_{N_2O}}{MW_{air}} \cdot 100 \quad \textbf{(5)}$$

Where:

$$10^{-6} = ppm\ to\ \frac{m^3_{N_2O}}{m^3_{air}} conversion\ factor$$

$$C = N_2O\ concentraion\ [ppm]$$

$$V_{molar} = Volume\ of\ 1\ mol\ at\ STP\ [22.414L]$$

$$\frac{MW_{N_2O}}{MW_{air}} = Molecular\ weight\ fraction\ [\frac{44.01}{28.95}]$$

The N_2O sensor does not distinguish between background N_2O or N_2O emitted by the source. Therefore, the term C_{net} is introduced, which accounts for the background concentration and results from $C_{gross} - C_{background}$. The background is calculated for each trace with a statistical method developed by Explicit. Additionally, to obtain the flux emissions in $[kg \cdot h^{-1}]$, the conversion factor of 3600 is added which finalizes equation (6).

$$Flux_{N_2O} = U_n \cdot A \cdot \rho_{air} \cdot 10^{-6} \cdot C_{net} \cdot \frac{MW_{N_2O}}{MW_{air}} \cdot 3600 \quad \textbf{(6)}$$

To determine the present air density ρ_{air}, the atmospheric pressure p $[mbar]$ and ambient temperature T $[°C]$ are measured by the wind sensors and incorporated in the equation (7) below. Explicit assumes the air to be dry.

$$\rho_{air} = \rho_0 \cdot \frac{p}{p_0} \cdot \frac{T_0}{T_0 + T} \quad \textbf{(7)}$$

Where:

$$\rho_0 = air\ density\ at\ 273.15\ K\ on\ sea\ level\ [1.293\ kg \cdot m^{-3}]$$

$$p_0 = atmospheric\ pressure\ on\ sea\ level\ [1013\ mbar]$$

$$T_0 = Temperature\ at\ 0°C\ [273.15\ K]$$

Finally, the flux equation can be summarised as follows:

$$Flux_{N_2O} = U_n \cdot A \cdot C_{net} \cdot cons \quad \textbf{(8)}$$

Where:

$$cons = 10^{-6} \cdot \frac{MW_{N_2O}}{MW_{air}} \cdot \rho_0 \cdot \frac{p}{p_0} \cdot \frac{T_0}{T_0 + T} \cdot 3600$$

With the use of the equation (8), the N_2O flux is calculated through multiplying C_{net} by the area of the underlying element and the corresponding normal wind projection of the absolute wind. The normal wind projection is a dot product out of absolute wind (W_E, W_N, W_Z) and the normal vector (N_E, N_N, N_Z) to the underlying area element. The normal vector is determined by the geometry of a flown wall. This normalisation needed to process the wind data perpendicular to the wall.

Following equation (9) summarizes the flux calculation through a single trace. The resulting graphical output is shown in FIGURE 9.Each trace receives its own flux value, and the total net flux equals the sum of all fluxes from each trace.

$$Flux_{N_2O} = cons \cdot \sum_{i=1}^{N} \left(C_i - C_{bkg,i}\right) \cdot A_i \cdot (W_E, W_N, W_Z)_i \cdot (N_E, N_N, N_Z)_i \quad \textbf{(9)}$$

Where:

$$N = number\ of\ observation\ points\ in\ the\ trajectory$$

$$C = N_2O\ concentration\ measured\ [ppm]$$

$$C_{bkg} = background\ N_2O\ concentration\ measured\ [ppm]$$

$$A = area\ element\ [m^2]$$

$$(W_E, W_N, W_Z) = absolute\ wind\ components\ [m \cdot s^{-1}]$$

$$(N_E, N_N, N_Z) = vector\ normal\ to\ the\ area\ element\ in\ a\ (E, N, Z)\ system\ [unitless]$$

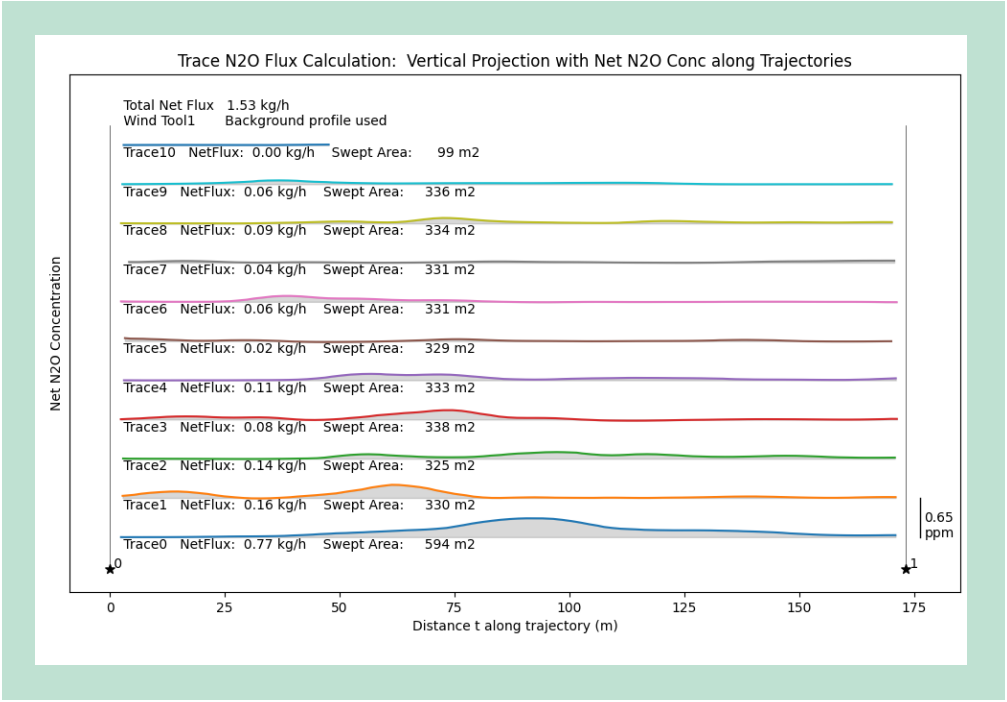


FIGURE 9. N_2O Trace Flux.

4.6 Contour Flux Calculation

The Contouring method is only used to visualize the Flux density on a flux wall and is not used to report flux rates.

For the contouring method, a lattice surface is individuated based on the drone flying path. On this surface, a regular grid of lattice points is built. The flux density at the generic lattice points are calculated by performing a weighted interpolation of the flux densities from all observation points Eq. (10). FIGURE 10 shows an example of a visualisation generated by the contouring method.

$$Flux_{N_2O} = cons \cdot \sum_{i=1}^{N} weight \cdot U_n \cdot \left(C_i - C_{bkg,i}\right) \quad \textbf{(10)}$$

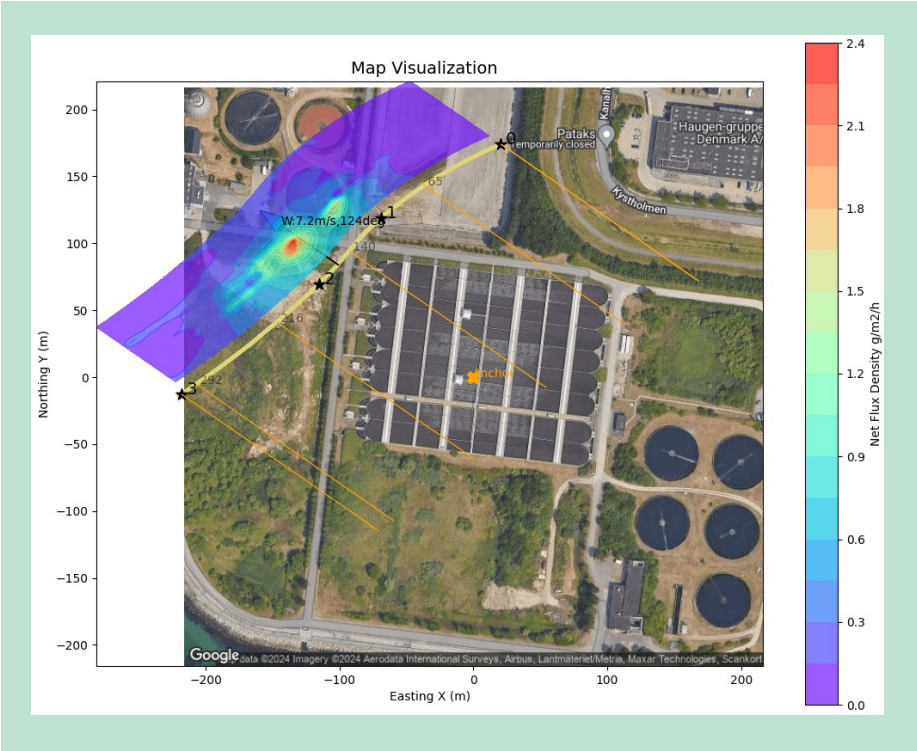


FIGURE 10. N_2O quantification at Avedøre wastewater treatment plant visualized with contour flux plot.

4.7 Uncertainty and Limitations

The uncertainty of DFM CH_4 flux results has been estimated through various approaches in previous studies and projects:

Comparison to Reference Method under Field Conditions:
The DFM results were compared to parallel investigations using a reference method, specifically the TDM, conducted by DTU Sustain or FORCE Technology. Recognized by the Environmental Agency as a reference method, TDM is associated with an uncertainty of within 20%, provided that 10 transects or more are completed (Fredenslund et al., 2019). A comparative (blind) test of CH_4 involved FORCE Technology independently evaluating the DFM method against simultaneous measurements by the TDM method as the reference method, resulting in an uncertainty of 21% (average 26 kg/h CH_4, 9 flights) (Knudsen & De Rossi, 2022).

Comparison to Controlled Release in Field Setup:
Another approach involved comparing DFM results to a controlled release of the emission gas in a field setup. One specific controlled release test of CH_4 was conducted as a blind test at the TADI test site of TotalEnergies in France. FORCE Technology independently evaluated the method uncertainty based on the TADI tests under the DS/EN ISO 20988 standard, applying the Guide to the Expression of Uncertainty in Measurement (GUM), cf. Sec. 12.6.2.1 and 12.6.2.2 (JCGM, 2008). The main conclusions indicate that for release rates larger than 2 kg/h CH_4, the uncertainty (at 95% confidence significance) of the flux determination with the DFM method is 20% when three flights are averaged and is 50% for lower release rates (between 0.3 kg/h and 2 kg/h) under similar conditions.

FORCE Technology further concluded that the uncertainty results obtained during tests of CH_4 sources are applicable to DFM measurements targeting N_2O or CO_2, provided that the N/S ratios for the detection of any of the gases are sufficiently low to be inconsequential for variations in the flux, and vice versa.

Limitations:

- The DFM method can only be applied during certain weather conditions:
  - Wind velocity between 2 and 12 m s^{-1}
  - A consistent wind direction over the time of a flux wall
  - High turbulence atmospheric conditions influence the quality of the results.
- To deliver reliable results on total emissions, the entire downwind emission plume needs to be captured by the flight path of the drone.
- A certain space for a flight path is required.

4.8 Lab results and field verification

4.8.1 Nitrous oxide sensor

The N_2O/CO_2 sensor produced by Aeris Technology called Mira Strato was tested and calibrated by FORCE Technology.

The Aeris Mira Strato sensor was calibrated using dry accredited calibration gasses consisting of either CO_2 or N_2O in nitrogen. Various concentrations of the two gasses were generated in a HOVAGAS G5 by dilution of cylinder gas with nitrogen. The CO_2 concentration varied between 0-6000 ppm and the N_2O between 0-15 ppm. TABLE 3 shows an overview of the measurement plan.

TABLE 3. Overview of the measurement plan for calibration and testing of the sensor.

Calibration			
Test	CO_2	N_2O	Temp
#	ppm	ppm	°C
1.1	0	0	20 ± 3
1.2	400	0	20 ± 3
1.3	500	0	20 ± 3
1.4	600	0	20 ± 3
1.5	1500	0	20 ± 3
1.6	3000	0	20 ± 3
1.7	4500	0	20 ± 3
1.8	6000	0	20 ± 3
1.9	0	0	20 ± 3
1.10	0	0,5	20 ± 3
1.11	0	1	20 ± 3
1.12	0	2	20 ± 3
1.13	0	5	20 ± 3
1.14	0	10	20 ± 3
1.15	0	15	20 ± 3

The main test results are shown in FIGURE 11 and FIGURE 12.

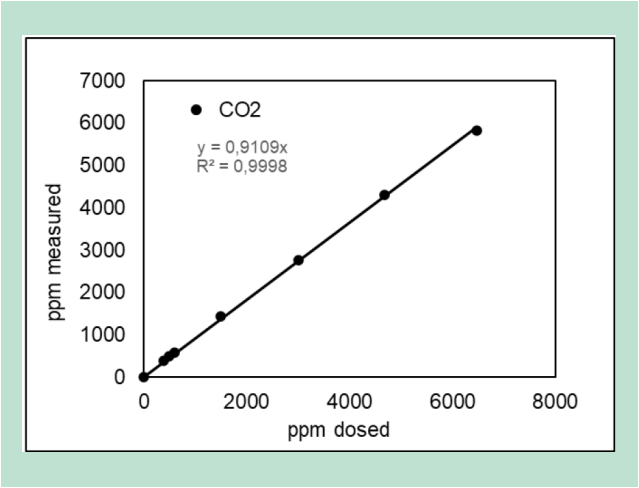


FIGURE 11. Linearity of the CO_2 sensor.

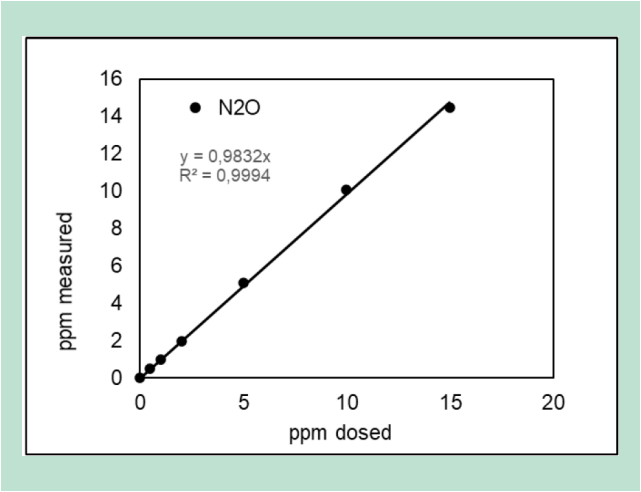


FIGURE 12. Linearity of the N_2O sensor.

The overall conclusion from the laboratory tests was that the Aeris Mira Strato N_2O/CO_2 sensor generally show good results for measurements of CO_2 and N_2O with good linearity between measured and dosed concentrations of CO_2 and N_2O.

4.8.2 Controlled N_2O release tests

The controlled release test for this study was designed and conducted by DTU and took place in an open area of a covered landfill. The controlled release test consisted of a known release of N_2O, which was then quantified by DFM and TDM.

N_2O was released at a constant flow rate by a single N_2O bottle connected by tubing to four outlet nodes about 1-1.5 m above the ground. The outlets were arranged in a 25-meter square (as visualized in FIGURE 13), to mimic the emission from a small area source. The flow rate was controlled by a two-stage regulator, with a safety valve for back flush, connected to a high precision 100 mm flow meter (Sho-rate, Brooks). To determine the flow rate released by the N_2O bottle, the bottle was weighed with a scale (precision of 0.5 g) before and after the release. In addition, time was recorded when turning the gas on and off. For verification a second determination of the release rate was done in the DTU laboratory.

The controlled release test was carried out on the 21st of April 2022, at the planned location with the planned set up, as visualized in FIGURE 13. An average wind speed of 4.7 m/s and sunny weather conditions were present.

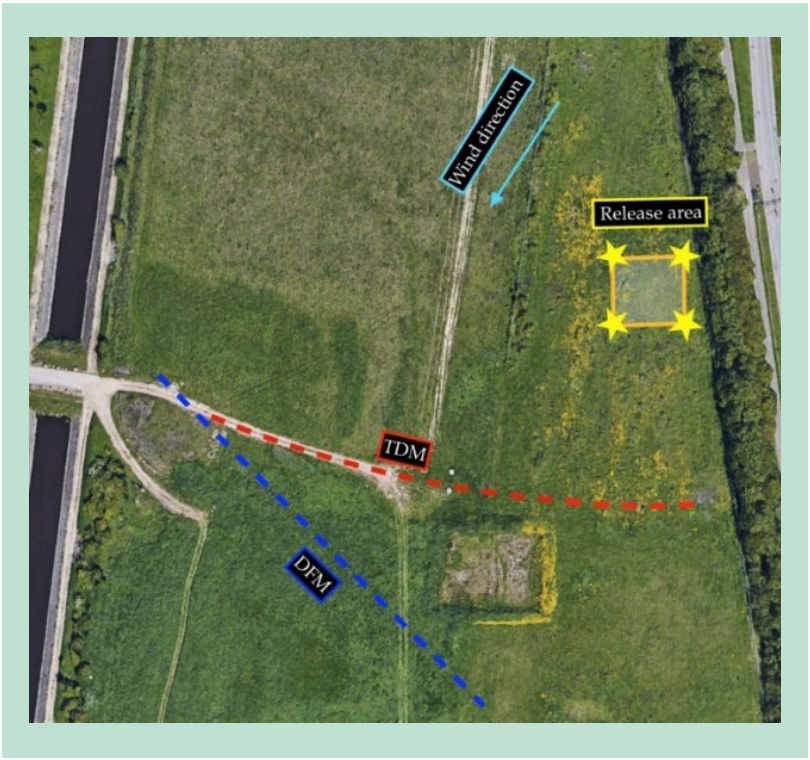


FIGURE 13. Layout of the controlled release test.

The uncertainty assessment of the DFM followed the Type A approach (DS/EN ISO 20988) where parallel measurement series using DFM and a reference method (the controlled release rate) are compared. The assessment followed the guide to the expression of uncertainty in measurements (GUM) (JCGM, 2008). Relative uncertainty, *w(y)*, for the DFM was estimated according to Eq. (11).

$$w(y) = \frac{u(y)}{y} = \sqrt{\frac{1}{N} \cdot \sum_{j=1}^{N} \left(\frac{y(j)}{y_R(j)} - 1 \right)^2 - \left(\frac{u(y_R)}{y_R} \right)^2} \qquad \textbf{(11)}$$

where w(y) is estimated relative uncertainty, u(y) is uncertainty on value y in absolute value (kg N_2O/h), y is the measurement result, y(j) is the j'th measurement results in the test series, $y_R(j)$ is the j'th reference value in the test series and $u(y_R)/y_R$ is an estimate of uncertainty on the reference values. For the controlled release test, the known release rate was considered the reference value, and it had an uncertainty of 5% (Fredenslund et al., 2019; Mønster et al., 2014). The error of the flowmeters was the manufacturers reported uncertainty and included the uncertainty in the calibration of the flow and the uncertainty when reading the flow of the individual flowmeters. The error of 5% is a conservative estimate as external calibration at a certified laboratory showed a lower uncertainty (~2.5%). Relative uncertainty w(y) from Eq. (11) is absolute uncertainty divided by the average emission and provides standard uncertainty with a confidence interval (CI) of 68%. To calculate expanded uncertainty (CI 95%), the measurement degree of freedom needed to be considered.

Results

The results from the N_2O controlled release tests are shown in TABLE 4. On average the DFM measures an emission of 1.48±0.23 kg/h. The DFM performed well, with an error ranging from -15% to +41% and an average error of 12% when compared to the controlled release rate (1.32 ±0.07 kg/h).

TABLE 4. Measured N_2O emission rates using DFM during controlled re-lease test.

Flight #	DFM (kg/h)	Error (%)[a]
1	1.5	13.6
2	1.86	40.9
3	1.4	6.1
4	1.12	-15.2
5	1.37	3.8
6	1.55	17.4
7	1.57	18.9
Average	1.48	12.0
Standard deviation	0.23	18.7

[a] Error = (Measured rate - Controlled release rate)/Controlled release rate

Based on the seven flights performed during the controlled release test the uncertainty (95% CI) was 47%. The uncertainty of a measurement will depend on the number of flights performed, as more flights are performed the uncertainty will reduce if the emission is constant. The data set was too small to assess the uncertainty of two or more flights. Theoretically, the uncertainty of an average of n measurements (n flights) is equal to the uncertainty of a single measurement (single flight) divided by the square root of n. Considering two flights (n = 2), the expected improved uncertainty reduces to 34% and to 27% for three flights (n = 3).

FIGURE 14 shows that increasing the number of flights from one to seven reduced the maximum error from 27% to about 11% for four or more flights. The error is expressed as (Measured rate - Controlled release rate)/Controlled release rate. By chance the first measurement was closer to the release rate than the following measurements, which does not mean that performing only a single flight is better than performing multiple flights. Also, the variability calculated as the standard error of the mean reduces to 0.09 kg/h as the number of flights increases to seven. An error budget propagating the error of each step of the measurements and analysis has not yet been established for the DFM method. The controlled release test was the first attempt to test the method's performance regarding N_2O emission quantification. As the test does not represent the true complexity of emissions from a wastewater treatment plant the uncertainty cannot necessarily be extrapolated to whole plant emission quantifications.

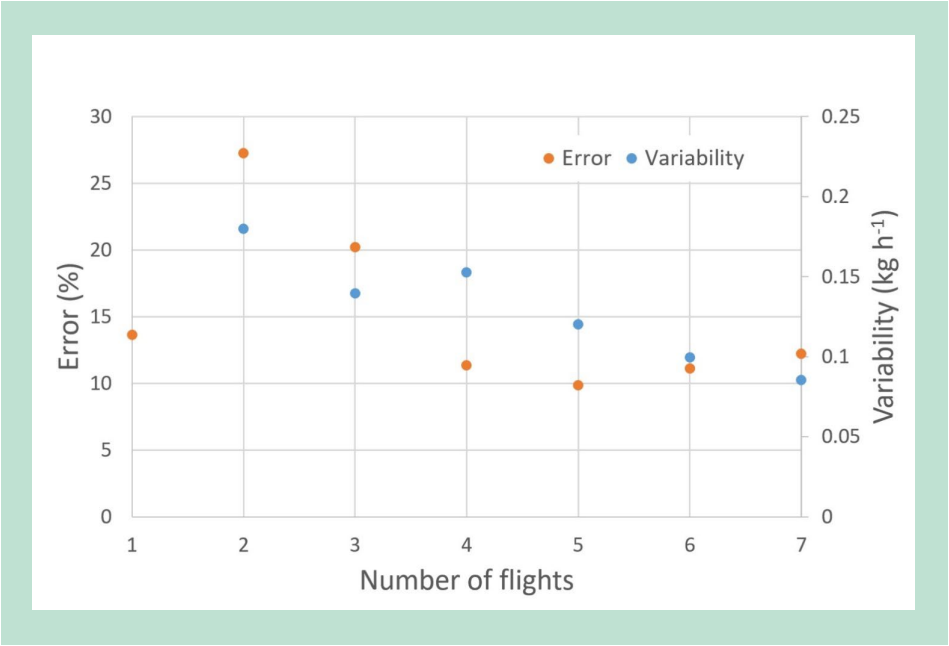


FIGURE 14. Variation in observed error and variability as a function of the number of flights, using the dataset from the controlled release test. The error is expressed as (Measured rate - Controlled release rate)/Controlled release rate and the variability is calculated as the standard error of the mean.

As per DTU findings, the TDM method could not facilitate an analysis of N_2O flux due to the presence of intense solar radiation that led to the ascent of the N_2O plume. The TDM method, as applied here, sampled atmospheric air downwind of the released gases at about 2m above ground level. Both remote sensing methods have been tested in several controlled release test as reported in section 4.7 (DFM) and 5.1 (TDM).

5. Tracer gas dispersion method

The tracer gas dispersion method (TDM) developed by DTU has been used to measure CH_4 and N_2O from various sources such as landfills, wastewater treatment plants, biogas plants, composting plants and oil and gas facilities.

Related to the AWAIRE project, TDM was used to quantify N_2O emissions from a number of Danish and Swedish wastewater treatment plants reported in (Delre et al., 2017, 2018), as well as BIOFOS Avedøre reported in (Yoshida et al., 2014).

This section provides a short description of the measurement principle, instrumentation used in this study and application of TDM at BIOFOS Avedøre as done here. For a more detailed description of the TDM measurement principle, validation and error assessment, we refer to (Mønster et al., 2014; Yoshida et al., 2014), and (Fredenslund et al., 2019).

5.1 Measurement principle, general practise and sources of error

TDM relies on continuous, controlled release of a tracer gas (here acetylene – C_2H_2) at the source of emission combined with downwind measurements of the target gas (here N_2O), where measurements are done using analytical instruments installed in a vehicle.

The general principle of TDM is that the tracer gas released at the source of emission will disperse the same way as the target gas, and that the emission rate of the target gas (E_{target}) can be calculated from measured, downwind concentrations of target and tracer gases and the known release rate of tracer gas (Mønster et al., 2014; Scheutz et al., 2011) :

$$E_{target} = Q_{tracer} \cdot \frac{C_{target} - C_{target,background}}{C_{tracer} - C_{tracer,background}} \cdot \frac{MW_{target}}{MW_{tracer}} \quad \textbf{(12)}$$

where E_{target} is the emission of the target gas (kg h^{-1}), Q_{tracer} is the tracer gas release rate (kg h^{-1}), C_{target} and C_{tracer} are measured downwind concentrations (ppb), and MW_{target} and MW_{tracer} are the molecular weights of target and the tracer gases. Background concentrations of target and tracer gases may be determined upwind from the source or outside of the downwind plume. The target to tracer gas ratio in Eq. (12) is determined by integration of the measured concentrations during traversing of the plume, plotted as a function of either time or distance. The emission rate is calculated using the following equation (13):

$$E_{target} = Q_{tracer} \cdot \frac{\int_{Plume\ start}^{Plume\ end} (C_{target} - C_{target,background})dx}{\int_{Plume\ start}^{Plume\ end} (C_{tracer} - C_{tracer,background})dx} \cdot \frac{MW_{target}}{MW_{tracer}} \quad \textbf{(13)}$$

where Q_{tracer} is the release rate of the tracer gas (kg h^{-1}), C_{target} and C_{tracer} are concentrations of target and tracer gas (ppb) above background level, MW_{target} and MW_{tracer} are the molecular weights of target and tracer gas.

The target and tracer gas plumes are traversed several times (often >10) to reduce measurement variability. Tracer is released at multiple points to mimic the emission of the target gas as well as practically possible. The further downwind measurements are performed, the less it is important to simulate the emission pattern of the source by tracer gas placement. Plots of measured concentration of target and tracer gases are used to evaluate measurement quality – both concerning mixing of gases, interference of other emission sources and determination of signal to noise ratio. Simultaneous rise, peak and fall times of target and tracer gases indicate adequate mixing of the gases.

The TDM method has been validated in several studies (Delre et al., 2018; Fredenslund et al., 2019; Mønster et al., 2014). (Mønster et al., 2014) and (Fredenslund, et al., 2019) describes validation and error assessment of TDM based on error budgets and controlled release tests. Sources of error include measurement uncertainty of the analytical instruments, uncertainty of tracer gas release rate, tracer gas placement (source simulation) and calculation uncertainty. It was concluded that the method uncertainty is 15% (Fredenslund et al., 2019; Mønster et al., 2014). Including variability, which is specific to the individual measurement, the overall uncertainty of TDM a measurement is often less than 20%, when the measurements are done in accordance with protocol (Scheutz & Kjeldsen, 2019).

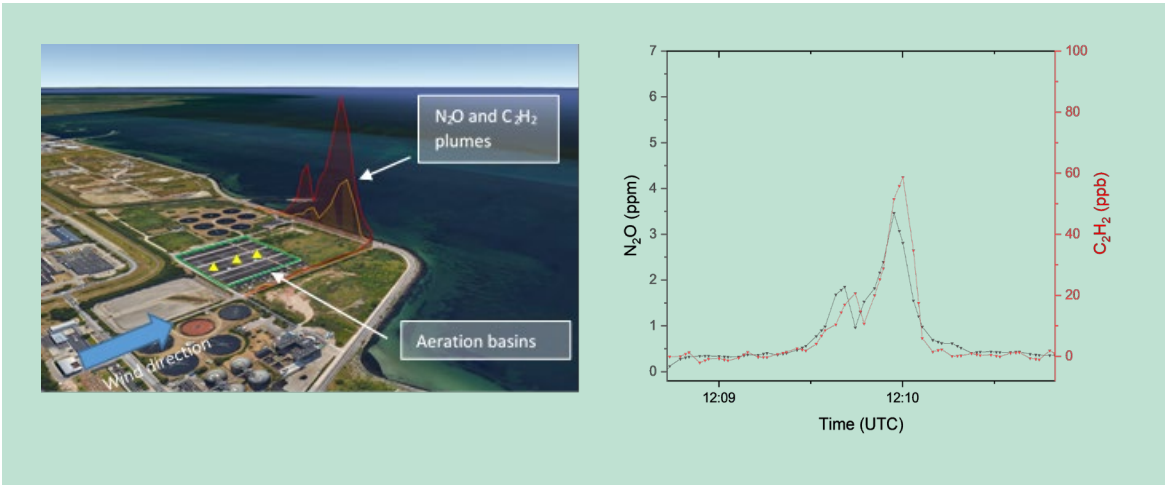


FIGURE 15. Example of a TDM measurement of N_2O emission from aeration tanks at BIOFOS Avedøre. The left graph shows measured N_2O and C_2H_2 tracer gas downwind the aeration tanks (single transect). The right figure illustrates the measurement data on location. The height of the red curve is proportional to measured N_2O concentration above background level (0.34 ppm), while the yellow curve is proportional to measured C_2H_2 concentration. Yellow triangles show locations of C_2H_2 release.

5.2 Application at BIOFOS Avedøre

TDM was used to measure total N_2O emission from the aeration tanks at BIOFOS Avedøre. Tracer gas release was done on a bridge located in the centre of the aerated zone of the aeration tanks with three release points distributed evenly on the bridge (see FIGURE 23). Tracer gas release rates were about 1 kg/h C_2H_2, where the release was distributed evenly between the release points. Measurements of downwind N_2O and tracer gas concentration were done on drivable roads at or near the plant according to wind direction.

5.3 Instrumentation

Measurements of N_2O and C_2H_2 concentrations were done using two analytical instruments: a cavity ring-down spectrometer to measure N_2O and C_2H_2 (Picarro Inc., custom-made $N_2O/C_2H_2/CO_2$ analyser), and a mid-infrared laser absorption spectrometer to measure N_2O (Aeris MIRA Ultra N_2O/CO_2 analyser) during low emission periods. The precision of N_2O measurements from the two instruments were 13 ppb (σ, 3 sec.,(Yoshida et al., 2014)), while the similar value for the Aeris instrument was about 1 ppb according to manufacturer specification. Measurement frequencies were ~0.5 Hz (Picarro) and 1 Hz (Aeris).

The instruments were installed in a vehicle, where atmospheric air was sampled through an air intake on the roof about 2 m above ground level. A GPS receiver and antenna (Hemisphere R330) was used to record position of the measurements, where coordinates were logged for each record of concentrations. Monitors inside the drivers' cabin showed concentrations in near real time (few seconds between sampling and readout), enabling evaluation of measurement quality as described in the previous section during the campaigns.

6. Eddy covariance method

Eddy covariance (EC) is a micrometeorological method measuring the turbulent fluxes of temperature, and trace gases between the land surface and the atmosphere (Baldocchi et al., 2018; Mauder et al., 2021). The method has been used widely in micrometeorology for over 40 years to determine CO_2 and H_2O exchange rates over natural ecosystems (Baldocchi et al., 2018). More recently, with the development of fast-response optical sensors, the method has been also used to measure CH_4 and N_2O fluxes both natural ecosystem e.g. peatlands and forests (Rinne et al., 2005; Tang et al., 2018; Yu et al., 2017), and anthropogenic settings, e.g. rice paddies, feedlots and landfills (Kissas et al., 2022; Prajapati & Santos, 2017; Reba et al., 2020; Xie et al., 2022).

Related to the AWAIRE project, EC was used to measure N_2O fluxes from the aeration tanks of BIOFOS Avedøre. The aim was to compare these flux measurements with emission estimates obtained from liquid phase N_2O sensors and to deduce seasonal and diurnal emission patterns.

6.1 Measurement principle, general practise and sources of error

The EC method relies on the principle of turbulent transport in the atmospheric surface layer and calculates the surface gas fluxes from the covariance between a vertical wind speed component, measured with a 3-D sonic anemometer, and a gas concentration from a gas analyser that can capture the high-frequency fluctuations. Typically, vertical wind speed and gas concentration are both continuously measured at 10 Hz and their covariance is calculated over a suitable time interval, typically between 30 minutes and 2 hours. The measured fluxes are attributed to an area upwind of the station with the use of a flux footprint model. The extent of the source area contributing to the flux (flux footprint) depends on the wind direction, relative measurement height, ground-surface characteristics, and atmospheric stability (Heidbach et al., 2017).

The method has the advantage of continuous, automated measurements over long periods, providing insights regarding both the short temporal and seasonal variability. It provides representative fluxes for a surface area in line with changing wind speed and direction. In general, most of the measured flux will come from an oval-shaped area stretching from near the tower up to 50–100 times the instrument height (Burba, 2022).

6.2 Application at BIOFOS Avedøre

An eddy covariance tower was installed by DTU at BIOFOS Avedøre. The station was situated in the eastern bridge of the aeration tanks, responsible for the biological nitrogen removal (FIGURE 16).

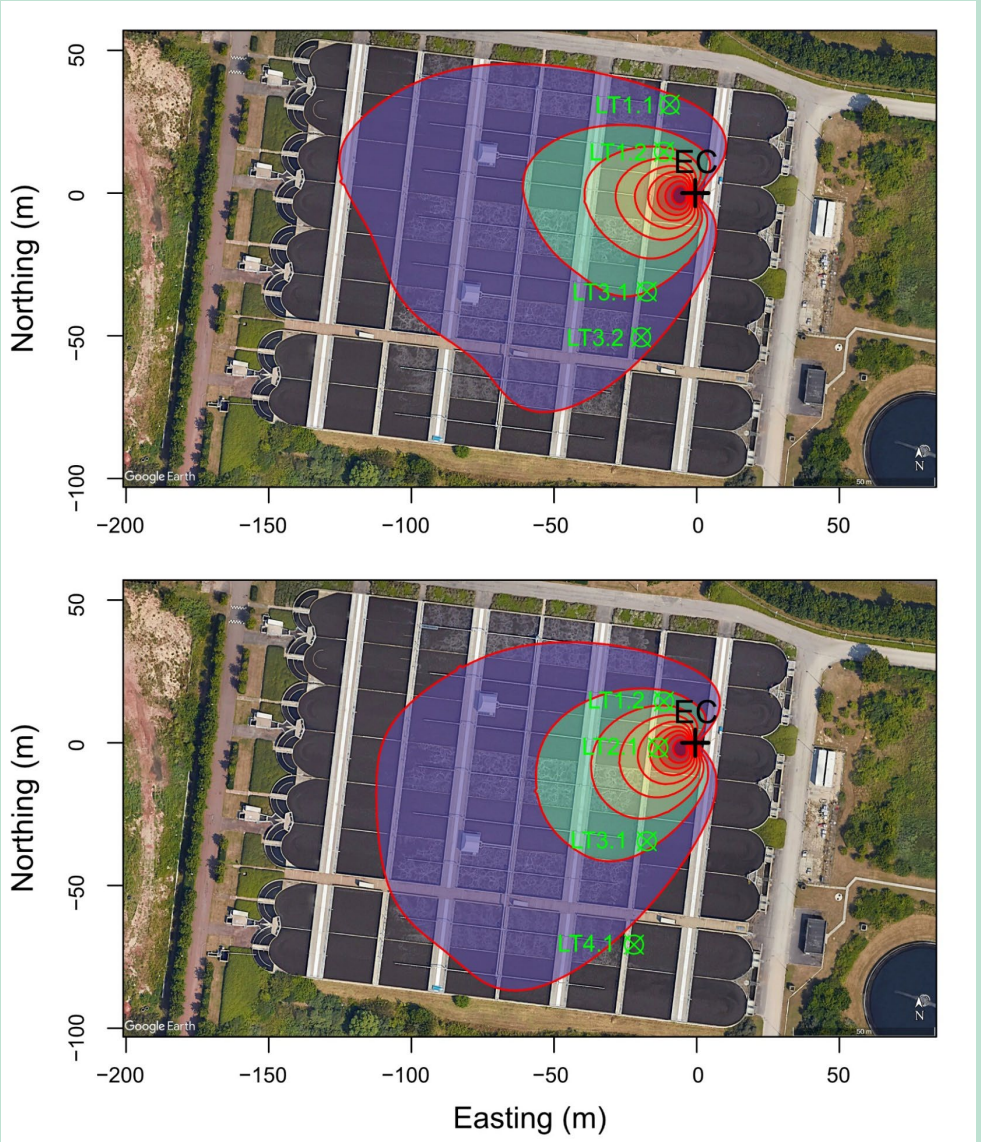


FIGURE 16. Location of the EC station and liquid phase N_2O sensors (LT1.1 – LT4.1) as well as the climatology footprints for 2022 (top panel) and 2023 (bottom panel). Only data within the wind direction sector 205° to 325° were used for calculating the footprints, to prevent any contribution from outside the aeration tanks. Footprint contour lines denote equal percentages of the flux contribution in steps of 10% from 10% to 90%. The flux footprint was calculated according to the 'simple two-dimensional footprint parameterization' described (Kljun et al., 2015) (Background image: Google Earth, Image © 2024).

6.3 Instrumentation

N_2O fluxes were recorded continuously in two separate periods spanning two consecutive years, from June to August 2022 and from June to September 2023, monitored via remote connection. The system consisted of a 3-D ultrasonic anemometer (USA-1, Metek GmbH) measuring the wind speed components and the temperature and a closed-path $N_2O/CO/H_2O$ fast-response analyser (LGR model N_2O/CO-23d, Los Gatos Research Inc.) measuring N_2O and H_2O concentrations. Turbulent flux data were recorded at 10 Hz. The fast-response $N_2O/CO/H_2O$ analyser was located at ground level connected with a 15 m long PA inlet tube (8mm inner diameter). The air was drawn through the inlet tube at a nominal flow rate of 35 L min^{-1} at STP by a vacuum

pump (model XDS-35i, Edwards Ltd., West Sussex, UK). A stainless-steel particle filter (2 µm pore size, Swagelok) was installed inline to protect the gas analyser from sea salt. The ultrasonic anemometer and the air inlet were mounted at the end of a 3m long boom in the direction of 275° at a height of 3 m above the wastewater level. The air inlet was located at the same height as the anemometer 30 cm from the centre of the anemometer's path (FIGURE 17).

FIGURE 17. Description of the EC system. Photos of the EC mast with the ultrasonic anemometer and the gas inlet above the aeration tanks (left panel) and the containers housing the closed-path $N_2O/CO/H_2O$ analyser and the vacuum pump (right panel).

N_2O fluxes, integrated over 15-min averages, were computed using EddyPro software (version 7.0.9 LI-COR Biosciences, Lincoln, NE, USA). This comparably short averaging time appeared to capture most accurately the rapid temporal variations in N_2O fluxes induced by the continuous alternations between aerobic/anoxic conditions every approximately 30 minutes. Post-processing corrections were applied to the raw data, namely (1) a double rotation method for anemometer tilt correction, (2) block averaging for extracting turbulent fluctuations, (3) time lag compensation, (4) raw data statistical tests (Vickers & Mahrt, 1997), (5) compensation for air density fluctuations (Webb et al., 1980), and (6) spectral corrections (Moncrieff et al., 1997, 2005). The flux data were filtered according to an overall quality flag system (0-1-2 system), used to identify periods of low flux quality system (Mauder & Foken, 2015). Periods that did not meet “Class 0” quality standards were discarded from the results. An additional quality control step was performed by omitting all observations with friction velocity values lower than 0.1 m s-1.

7. Liquid phase measurement method

7.1 Introduction and measurement principle

The only commercially available online sensor for measuring dissolved N_2O has been developed by Unisense Environment A/S. The sensor is made up of 3 components: The sensor body (1), the sensor head (2) and the sensor protection tube (3), see FIGURE 18.

FIGURE 18. The three components of the Unisense Environment A/S N_2O wastewater sensor, showing: (1) the sensor body, (2) the sensor head and (3) the sensor protection tube. The sensor body also contains a temperature sensor. (Unisense Environment A/S, 2023).

The sensor head is a Clark-type sensor with an internal reference, a cathode, a guard cathode and a front oxygen trap with reducing medium. It removes oxygen so that this does not interfere with the N_2O measurements. N_2O enters the sensor through a silicone rubber membrane in the centre of the 0.5 mm diameter glass sensor tip. Inside the sensor, N_2O is reduced to N_2 which generates an electrical current. This is the sensor signal which is sent to the controller for processing (*Unisense Environment A/S*, 2023). FIGURE 19 shows an illustration of the sensor tip and the measurement principle.

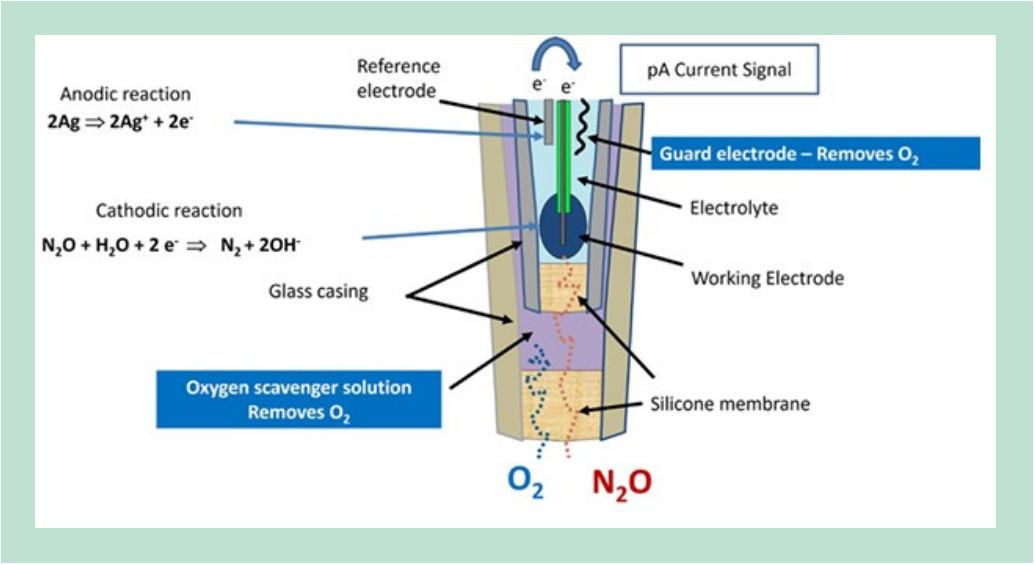


FIGURE 19. Illustration of the tip of the sensor head and the measurement principle (Unisense Environment A/S, 2023).

The N_2O sensors respond linearly to N_2O within their dedicated working range. Therefore, only a two-point calibration is needed. This is done by exposing the sensor to two concentrations of N_2O, zero, and one known concentration of N_2O. The sensor signal for N_2O is dependent on temperature. Therefore, the calibration should be performed at a temperature close to the measurement temperature. By default, the concentration value is compensated for a temperature ± 3 °C from the calibration temperature.

Unisense Environment A/S offers a standard N_2O wastewater sensor and a high temperature N_2O wastewater sensor. The sensors are available with:

- Standard Range (0-1.5 mg N_2O-N/L)
- Medium Range (0 – 9 mg N_2O-N/L)
- High Range (0 – 110 mg N_2O-N/L).

The standard N_2O Wastewater Sensors are designed to operate at temperatures between 0-30°C. The High Temperature N_2O Wastewater Sensor are designed to operate at temperatures between 30-40°C.

7.2 N_2O emissions estimation from liquid phase measurements

The dissolved N_2O wastewater sensor has the advantage that it can measure N_2O in the liquid phase before it is emitted to the atmosphere. This offers the possibility to initiate counteractions and potentially prevent actual emissions. A consequence is that the N_2O emission must be estimated/calculated based on an empirical relationship between the mass transfer coefficient $k_L a_{N_2O\ 20°C}$ and the superficial gas velocity V_g.

The superficial gas velocity of the aerated tank is calculated by dividing the total air flow with the aeration field size Eq. (14):

$$V_g \cong \frac{Q_{A\ 20°C}}{Aeration\ field\ size} \quad \textbf{(14)}$$

Where:

$$Q_A = total\ air\ flow\ [m^3 \cdot s^{-1}]$$
$$Aeration\ field\ size = total\ aerated\ field\ [m^2]$$

From the superficial gas velocity of the aerated tank the N_2O mass transfer coefficient $k_L a_{N_2O\ 20°C}$ can be calculated using the empirical equation (15) or (16).

$$k_L a_{N_2O\ 20°C} = \left\{\frac{D_R}{D_L}\right\}^{-0.49} \times 34500 \times \left(V_{g\ 20°C}\right)^{0.86} \quad \textbf{(15)}$$

$$k_L a_{N_2O\ 20°C} = \left\{\frac{D_R}{0.815}\right\}^{-0.49} \times 34500 \times \left(V_{g\ 20°C}\right)^{0.86} \quad \textbf{(16)}$$

Where:

$$V_g = Superficial\ gas\ velocity\ of\ the\ reactor\ [m^3 \cdot m^{-2} \cdot s^{-1}]$$
$$D_R = Depth\ over\ the\ diffuser\ of\ the\ reactor\ [m]$$
$$D_L = Depth\ over\ the\ laboratory\ reactor\ [0.815\ m]$$
$$k_L a_{N_2O\ 20°C} = N_2O\ mass\ transfer\ coefficient\ [d^{-1}]$$

The temperature corrected N_2O mass transfer coefficient $k_L a_{N_2O\ T_{Process}}\ [d^{-1}]$ is finally calculated with equation (17) and the help of the measured process temperature $T_{Process}\ [°C]$ as well as standard θ factor of 1.024.

$$k_L a_{N_2O\ T_{Process}} = k_L a_{N_2O\ 20°C} \times (1.024)^{T_{Process}-20°C} \quad \textbf{(17)}$$

With the $k_L a_{N2O}$ calculated using Eq. (17) and the total air flow as input the N_2O emission rate can be calculated. Following two equations are used to determine the final N_2O emission rate. The first equation (18) is being used when the aeration system is on.
Whereas equation (19) is used during the denitrification stage when aeration is switched off.

$$r_{N_2O,T_{Process}} = H_{N_2O,T_{Process}} \times S_{N_2O} \times \left[1 - e^{-\frac{k_L a_{N_2O\ T_{Process}}}{H_{N_2O}} \times \frac{V_R}{Q_A}}\right] \times \frac{Q_A}{V_R} \quad \textbf{(18)}$$

$$r_{N_2O,T_{Process}} = k_L a^{Non-aerated}_{N_2O\ T_{Process}} \times \left[S_{N_2O} - \frac{C_{N_2O,air}}{H_{N_2O,T_{Process}}}\right] \quad \textbf{(19)}$$

Where:

$$r_{N_2O,T_{Process}} = N_2O\ emission\ rate\ [g-N\ N_2O\cdot m^{-3}\cdot d^{-1}]$$
$$H_{N_2O,T_{Process}} = Henrys\ constant$$
$$S_{N_2O} = measured\ N_2O\ concentration\ [g-N\ N_2O\cdot m^{-3}]$$
$$V_R = Volume\ of\ aerated\ part\ of\ reactor\ [m^3]$$
$$C_{N_2O,air} = N_2O\ concentration\ in\ air\ equilibrium\ [g-N\ \cdot m^{-3}]$$

The dimensionless Henrys constant $H_{N_2O,T_{Process}}$ is also dependent on the process temperature and the temperature correction can be calculated as per Eq.(20) and Eq.(21):

$$H_{N_2O,T_{Process}} = \frac{1}{k_H \times R \times (T_{Process}+273.15) \times 10^3 \frac{L}{m^3}} \quad \textbf{(20)}$$

$$k_H = k_H^{\theta} \times e^{\left(\frac{-\Delta solnH}{R}\times\left(\frac{1}{T_{Process}+273.15}-\frac{1}{T^{\theta}+273.15}\right)\right)} \quad \textbf{(21)}$$

Where:

$$k_H^{\theta} = Henrys\ constant\ at\ the\ std.temp.\ [mol\cdot L^{-1}\cdot bar^{-1}]$$
$$T^{\theta} = Standart\ temperature\ [°C]$$
$$T_{Process} = Mixed\ liquor\ temperature\ [°C]$$
$$\frac{-\Delta solnH}{R} = The\ enthalpy\ of\ the\ solution\ [K]$$

Unisense Environment A/S supply the following N_2O mean values for $\boldsymbol{k_H^{\theta}}$,$\frac{-\Delta solnH}{R}$ and supporting numbers as given in TABLE 5.

TABLE 5. Literature values used for the emission model Literature values used for the emission model (Unisense Environment A/S, 2023).

Parametre	k_H^{θ}	$\frac{-\Delta solnH}{R}$	$C_{N_2O,air}$	R	$k_L a_{N_2O\,T_{Process}}^{Non-aerated}$
Unit	$[mol\cdot L^{-1}\cdot bar^{-1}]$	$[K]$	$[g-N\cdot m^{-3}]$	$[m^3\cdot bar\cdot mol^{-1}\cdot K^{-1}]$	$[d^{-1}]$
Value	0.0247	2675	0.0003	8.314×10^{-5}	2 – 4

Studies have shown that the N_2O emission calculations based on N_2O concentration measurements are consistent with off-gas measurements (Baeten et al., 2020; Baresel et al., 2016) but other studies have shown that a calibration is sometimes needed (Myers et al., 2021).

The formulas for calculating emissions during aeration as shown in Eq. (14) – (21) can be used in wastewater treatment plants with bottom aeration and for systems without aeration (ex. during denitrification). Another set of formulas (not included here but offered by Unisense Environment A/S on request) can be used to approximate (less accurate) emissions from systems with surface aeration.

The measuring range of the sensor is extended into the negative, giving a maximum sensitivity at very low concentrations. If the sensor reads steady values between 0.00 and -0.05 N_2O-N mg/L for 15 min, the Autozero feature of the Controller (If this option is activated/added) will set this as new baseline. If the values are continuously lower than -0.05, Autozero will raise an alarm indicating the need to perform a new 2-point calibration. Autozero is standard on all controller boxes after 1 October 2023 (This is a new feature not available during the execution of the project). If negative values occur in older controllers, a zero-point calibration should be done.

7.2.1 Calculating emissions in Hubgrade Performance Plant

During the project the advanced online control system used to optimize the operation of Avedøre wastewater treatment plant has gone through several developments. This also included the N_2O emission calculations. Initially STAR^2 was applied until it was upgraded to Hubgrade Performance Plant. In Hubgrade, the original LAB version of the emission calculation feature has been extended to a new standard feature available to all Hubgrade users. The calculation uses the formulas supplied by Unisense Environment A/S.

The upgraded standard feature of the emission calculation depends on the following online input:

- N_2O signal from the sensor [mg N_2O-N/l]
- Airflow [Nm^3/h]
- Temperature [°C]

In addition, the following settings are needed for configuration (see FIGURE 20):

- Total tank volume [m^3]
- Tank depth [m]
- Aeration available (Yes/No)
- Diffuser hight (above bottom) [m]
- Diffuser coverage [%]

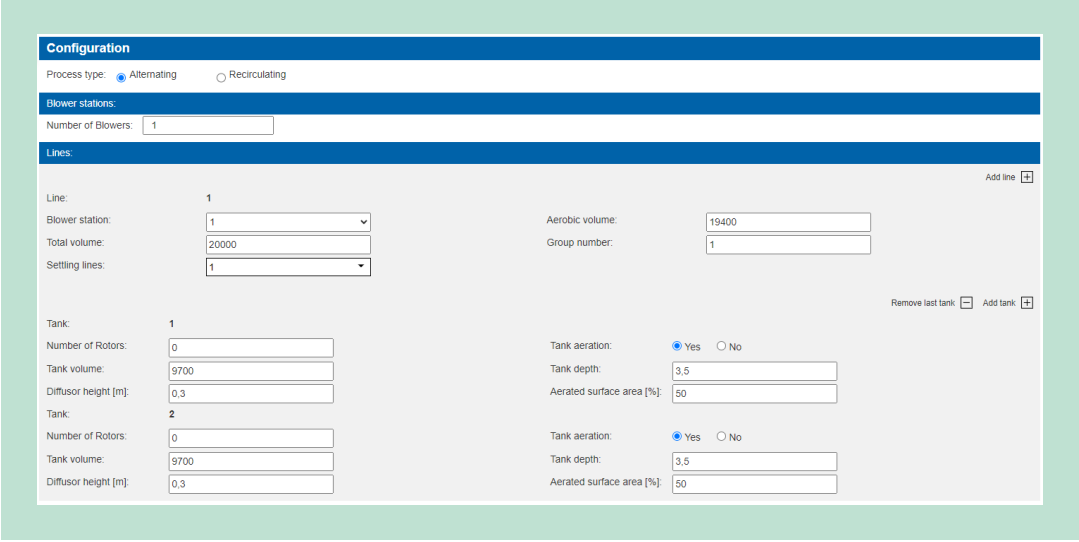


FIGURE 20. The configuration settings in Hubgrade for one process line at Avedøre wastewater treatment plant.

The following filtering settings is available (see FIGURE 21):
General settings:
Filter time for N_2O (default 10 min)
Filter time for airflow (default 10 min)

Filter time for temperature (default 10 min)

7.2.1.1 Handling of baseline drift and negative values

The emission calculation is sensitive to sensor drift and negative values (especially due to changes in wastewater temperatures) and must be calibrated when the temperature changes ± 3 °C. Hence, it is common to have periods with negative N_2O concentration measurements – which is incorrect. There are several approaches to handle this. The best is to do frequent calibration. As post-processing it is possible to overwrite small negative values with zero or to do a baseline correction. In STAR[2], no post processing was performed, in the LAB version of the Hubgrade emission feature, small negative values were replaced with zero and in the new standard Hubgrade version an automated baseline correction has been implemented.

In Hubgrade, if the sensor data shows stable measurements (difference between minimum and maximum values is less than 10^{-6} mg N_2O-N/l) for a specified time period (default 2h) the baseline is shifted/corrected by the average value during the time period. The maximum allowed correction is specified by the user (default 0.05 mg N_2O-N/l). The user settings are shown in FIGURE 21.

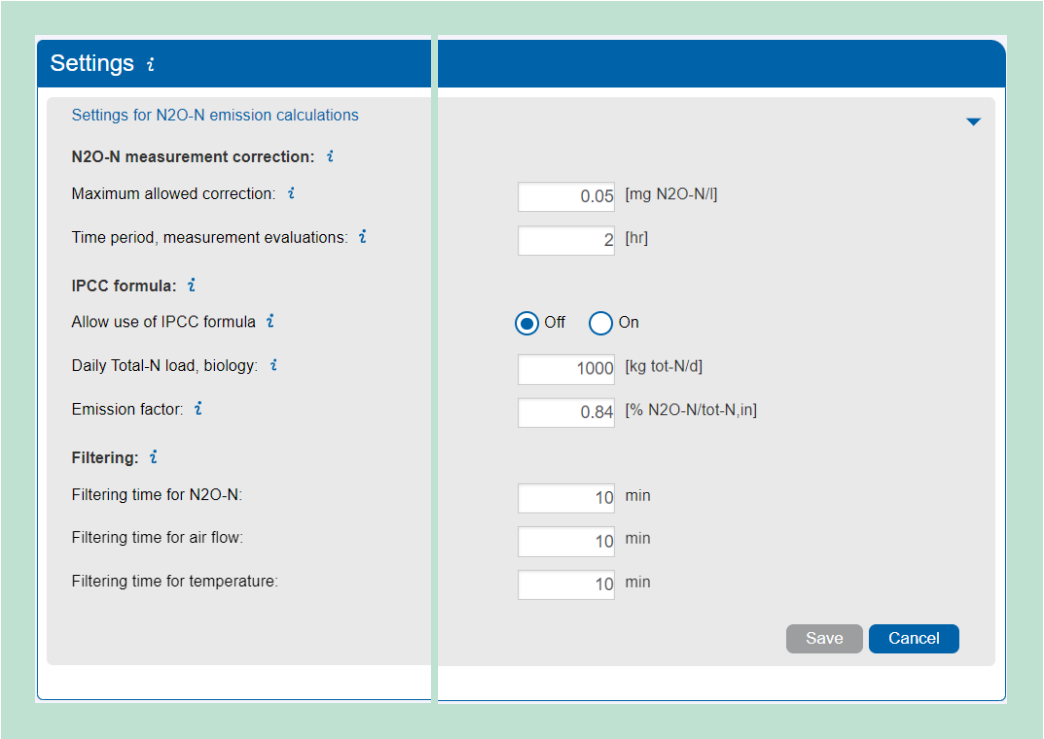


FIGURE 21. The user interface of the standard N_2O emission calculation feature of Hubgrade Performance Plant, with the maximum allowed baseline correction and time period used for measurement evaluation. Additionally, settings for estimating emission factors and the settings used for filtering (smoothing) data are shown.

In FIGURE 22 an example of a baseline adjustment is shown, using the method and settings mentioned above.

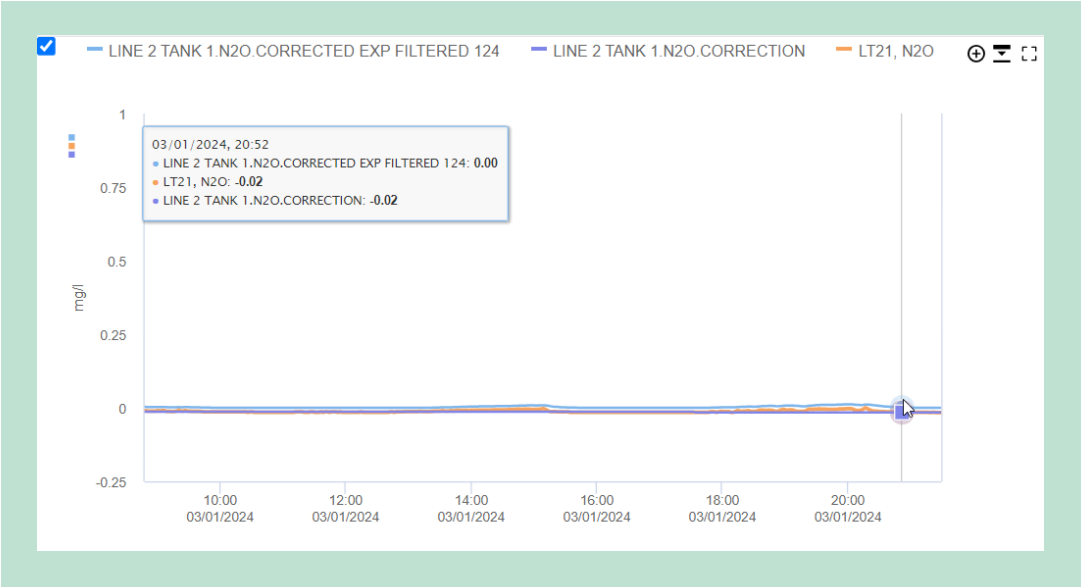


FIGURE 22. An example from Avedøre wastewater treatment plant Hubgrade, where the raw data input is shown (orange), the true baseline is estimated (purple) and the corrected data is shown (blue). Here the data inputs are shifted 0.02 mg N_2O-N/l up the y-axis with a corrected baseline value of 0 mg N_2O-N/l.

7.3 Extrapolating liquid phase measurements to whole plant emissions

Measuring N_2O concentration in the liquid phase requires a conversion to N_2O emission to the atmosphere, and thus depends on both the flow rate of aeration in the process tank and the mass transport coefficient for N_2O. The conversion depends on whether the process tank is bottom aerated or surface aerated and is associated with greater uncertainty, especially in surface aerated facilities. The use of process-specific sensors has a number of general limitations.

First, a sensor only measures at one location, which will rarely be representative of the total N_2O emission from a process unit or a facility. Therefore, there may be a need to use several representative locations.

Second, the accuracy of the sensors can be discussed because measurements are based on the assumption that the bioline is under steady state conditions, which may not be valid - that is, the "right" location is not the same when the dynamics change in the process. However, this applies as a general limitation for all types of process-specific measurements.

Third, changes in wastewater content such as increased salt content can lead to stripping of N_2O from the liquid phase, which can affect the uncertainty of the emission calculation (Kosse et al., 2017). Mass transport from water to air (and thus the emission) is dynamic and depends on aeration and environmental factors such as temperature, so the use of a single value to calculate the mass transfer coefficient, k_La, can be problematic (Liu Ye et al., 2022).

Measurement uncertainties

The measurement is sensitive to temperature changes and should therefore be calibrated at temperature changes of ±3°C. In addition, the sensor heads become worn over time and need to be replaced every 4-6 months to guarantee valid measurements. If routine maintenance is not performed, it can be a source of measurement uncertainty. In 2022, the calibration of the

LPS was conducted in compliance with the provided instructions. However, in 2023, the calibration of the LPS did not consistently follow the manufacturer's specified guidelines.

The measurement of the liquid concentration itself has high precision with ±5% uncertainty (Unisense Environment A/S, personal communication, January 26, 2024).
The "larges" uncertainty is associated with the emission model calculations.
Unisense estimates a total uncertainty on the emission calculation of less than ±20% (Andersen, M.H., personal communication, November 2, 2023).

This depends, among other things, on the correct determination of air flow and mass transport coefficient (k_La) for N_2O.

Studies have shown that this emission calculation can determine N_2O emissions in accordance with control measurements in the gas phase with > 87% agreement (Baresel et al., 2016; Marques et al., 2016). In addition, (Myers et al., 2021) showed that the method for determining k_La affects the emission calculation and confirms that a calibrated k_La is important for the emission calculation. They further estimated that the effect of a direct error on the N_2O measurement alone of ±10 % would cause a similar error on the emission calculation of ±10 %. Similarly, the effect of a ±50 % error of the k_La_{N2O} would cause a ±25 % error on the calculated emission. An airflow error of ±10 % was estimated to cause a 7-8 % difference in calculated emissions.

Extrapolation to whole plant emissions

The current method for estimating the whole plant emission rate based on a reduced number of LPS measuring points is based on a volume ratio. The measured emission rates are multiplied by the ratio between total volume of the process tanks divided by the volume of the process tanks with a sensor. In Avedøre wastewater treatment plant the 8 process tanks each have the same volume and 4 tanks have sensors. The total emission from the plant was calculated as the sum of modelled emissions from the four process tanks multiplied by two to get the total emission from all 8 process tanks.

It is known from previous studies (the VARGA project) that the emission rate between tanks and between process lines are not identical (Miljøstyrelsen, 2023). During reference years (with apparent similar conditions in the tanks, the emission factor varied by a factor of approx. 1.5-2 while differential operation (i.e. mitigation efforts) resulted in even higher difference between tanks (up to a factor of 3.8).

Besides the actual N_2O concentration and the k_La_{N2O} value, Q_A is very important to the actual and calculated emission rate. When assuming that the whole plant emission rate depends on the process volumes it is indirectly also assumed that the N_2O concentration and Q_A are also identical between tanks. This is not the case. Q_A changes dynamically in intensity (m^3/h) and duration (h with aeration), influencing the flux and overall emission of the different tanks.

8. Method functionalities

The main properties and characteristics of the methods described in this chapter are summarised in TABLE 6 including their key benefits and limitations.

TABLE 6. Summary of key properties and characteristics of N_2O measurement methods.

Property	LPS	DFM	TDM	EC
N_2O Gas sensor type (technology)	Amperometric	Laser-based	Laser-based	Laser-based
Direct/ indirect gas measurement	Indirect (sensor measures in the liquid phase)	Direct	Direct	Direct
Sensor medium	Liquid	Gas	Gas	Gas
Output unit	Mass rate per process tank (kg/tank/h)	Mass rate (kg/h)	Mass rate (kg/h)	Mass rate per unit area (kg/m^2/h)
Upscaling to plant level	Extrapolation of emission rates to non-LPS tanks (if any)	None - total plant emission is measured	None - total plant emission is measured	Extrapolation of emission rates to total tank area
Continuous /discrete	Continuous	Discrete	Discrete	Continuous
Measurement scope	Individual process tanks	Site-level (all process tanks)	Site-level (all process tanks)	Individual process tanks
Measurement uncertainty	Unknown	20% (with three or more walls)	<20% (with ten or more transects)	Unknown
Cost	One-time cost (+ maintenance)	Cost per measurement	Cost per measurement	One-time cost (+ maintenance)
Key benefits	- Continuous monitoring. - Real-time. - Can be integrated with other online sensor data, giving insight to interlinking operational parameters and process dynamics.	- Direct gas measurement. - Plant-wide and/or asset-specific quantification. - Can identify sources of emissions (site-level). - Wind measured at each observation point. - Visualisations assist with pinpointing high emission zones - Accredited method.	- Direct gas measurement. - Plant-wide quantification. - Stationary measurements can be used on smaller sources. - Can identify sources of emissions (site-level). - Wind measurements not needed. - Visualisations assist with pinpointing high emission zones. - Accredited method.	- Continuous monitoring. - Real-time. - Observation of emission dynamics. - Low sensor drift.

Key limitations	- Indirect emission quantification. - Relies on accuracy of model input parameters, such as airflow. - Calibration requirements (can also be source of error). - Negative sensor drift can lead to underestimation of N_2O emission. - Maintenance requirements ('clogging' can be source of error)	- Requires certain weather conditions (essentially, wind speeds between 2 m/s and 10 m/s, site-specific wind direction, and no rain or snow). - Obstructions can restrict possible flight paths. - Entire emission plume must be captured. - Not suitable for long term and continuous monitoring. - Requires post-measurement analysis.	- Requires certain weather conditions (preferably overcast, wind speed > 1 m/s). - Relies on access to appropriate paths/roads. - Not suitable for long term and continuous monitoring. - Requires post-measurement analysis.	- Limited knowledge on application on wastewater treatment plants. - It requires complex calculations and must fulfil assumptions regarding uniform terrains and homogeneous emissions. - Stationary approach (uncertainty around representation of total emissions).

9. Field campaigns

9.1 Plant description Avedøre

Avedøre wastewater treatment plant is located in the Greater Copenhagen Region, in Denmark. The plant is operated by the BIOFOS group, the biggest wastewater treatment company in Denmark. Annually, the Avedøre wastewater treatment plant treats wastewater from approximately 350,000 Person Equivalents (PE), corresponding to an annual wastewater volume of 22.9 million m^3 (BIOFOS, 2021).

The biological nitrogen removal (BNR) stage at the Avedøre wastewater treatment plant is a BioDeNitro configuration and represents the most important section of the treatment plant in terms of N_2O emissions, as this is where both formation and emissions occur during nitrogen removal. In total, the BioDeNitro configuration consists of four biological lines (marked yellow) with two process tanks each, as shown in FIGURE 23.

FIGURE 23. Overview of the biological nitrogen removal (BNR) at Avedøre wastewater treatment plant show four biological lines each consisting of two process tanks. (Background image: Google Maps, Image © 2022).

The two process tanks of each of the four lines operate together with a wastewater retention time of around 24 hours. The lines operate in varying configurations, which expose the wastewater to several nitrification and denitrification phases. The configuration is dictated by ammonia and nitrate concentrations, which also dictate into which tank the inflow and outflow of wastewater will be to/from at any time. The configuration at a given time is decided by the system with the goal of optimising nitrogen removal.

Several process parameters are continuously monitored by a central information system, which is used to optimise process dynamics. Collected data, by numerous different sensors, includes feed, airflow, NH_4^+, NO_3^-, N_2O, dissolved oxygen (DO) and temperature. These data are fed into a data management and optimisation system, called Hubgrade. Under normal operations, the mechanisms, which control the process dynamics of the plant are automated by the system, relative to desired 'set-points' of adjacent parameters. For example, in the case of airflow into

the tanks, the pipe valves adjust how much they open to maintain set points of desired DO levels in the water phase. The main airflow at Avedøre is pumped by two pairs of compressors to a pipe positioned across all 8 process tanks. Airflow into each tank is estimated as a proportion of the airflow from the main air inlet, relative to the extent each valve is open.

Several research studies regarding N_2O have been carried out at Avedøre wastewater treatment plant. A study in 2014 used TDM to examine N_2O emissions from the plant (Yoshida et al., 2014). Emissions ranged from 0.37 kg/h to 10.5 kg/h, which correspond to emissions factors of 0.0015 kg N_2O-N/kg T-N_{inlet} and 0.042 kg N_2O-N/kg T-N_{inlet}, respectively (or 0.15% and 4.2%, respectively). A longer-term study in 2019 gave insight into the seasonal variability of N_2O emissions from the site and concluded an average EF of 0.0105 kg N_2O-N/kg T-N_{inlet} (or 1.05%) (Chen et al., 2019). A study in 2021, which used mass flow analysis ascertained a theoretical EF of 0.026 kg N_2O-N/kg T-N_{inlet} (subsequently adjusted to 0.016 kg N_2O-N/kg T-N_{inlet}) (Faragò et al., 2021).

9.2 Overview of campaigns

Several types of field campaigns were performed to meet the project objectives listed in section 3. Those campaigns were:

- Initial testing of DFM at different wastewater treatment plants: BIOFOS Avedøre, Esbjerg Renseanlæg Vest and Ejby Mølle Renseanlæg
- Controlled, off-site N_2O release test to evaluate DFM (procedure and results are described in section 4.8.2)
- Comparative DFM/TDM/LPS measurements at BIOFOS Avedøre and Nivå Renseanlæg
- Additional TDM/LPS measurements at BIOFOS Avedøre for a better coverage of seasonal variation in N_2O emission
- Comparative LPC/EC continuous monitoring at BIOFOS Avedøre to assess short term N_2O emission dynamics

The initial testing of DFM was done to develop the measurement protocol of DFM for the application (quantification of N_2O emission from wastewater treatment plants), which has led to the methodology described in section 4. The results of those initial tests are not included in the comparison to TDM and LPS measurement in section 10, as they were performed before the methodology was established.

TABLE 7. Overview of comparative DFM/TDM/LPS measurement campaigns at wastewater treatment plants in the project. Number of DFM and TDM measurements indicate those which passed quality assurance and could therefore be compared to LPS derived values.

BIOFOS Avedøre				
Date (dd-mm-yyyy)	**DFM - # measurements**	**TDM - # measurements (# transects)**	**Simultaneous DFM and TDM - # measurements (# TDM transects)**	**Comments**
29-03-2022	5	4 (40)	0 (0)	
26-04-2022	3	5 (53)	3 (21)	Plant maintenance – high N_2O emission
29-06-2022	-	2 (18)	-	
08-07-2022	1	2 (18)	1 (5)	
26-08-2022	6	2 (21)	3 (11)	

BIOFOS Avedøre				
Date (dd-mm-yyyy)	**DFM - # measurements**	**TDM - # measurements (# transects)**	**Simultaneous DFM and TDM - # measurements (# TDM transects)**	**Comments**
29-03-2022	5	4 (40)	0 (0)	
26-04-2022	3	5 (53)	3 (21)	Plant maintenance – high N_2O emission
29-06-2022	-	2 (18)	-	
12-10-2022	3	2 (28)	1 (6)	
10-01-2023	6	6 (69)	4 (27)	Controlled operation
11-01-2023	-	3 (38)	-	
04-05-2023	-	1 (10)	-	
08-05-2023	8	5 (54)	6 (36)	Controlled operation
26-06-2023	4	4 (43)	4 (23)	
28-06-2023	5	4 (41)	2 (13)	
28-08-2023	-	1 (10	-	
14-09-2023	-	1 (10)	-	
19-12-2023	-	1 (12)	-	
SUM	41	43 (453)	24 (152)	
Nivå Renseanlæg				
Date (dd-mm-yyyy)	**DFM - # measurements**	**TDM - # measurements**	**Simultaneous DFM and TDM - # measurements**	**Comments**
03-05-2022	2	0	0	Very low N_2O emission

[a] For DFM, one measurement consists of one flight/flux wall

Most of the comparative measurement campaigns were done at BIOFOS Avedøre (15 measurement days), while one comparative measurement campaign was done at Nivå Renseanlæg. DFM covered 9 measurement days and TDM 15.

Each DFM measurement comprised of one flight/flux wall, and each TDM measurement comprised of approximately 10 transects (10.5 in average). 41 DFM measurements consisting of 41 flights and 43 TDM measurements consisting of 453 transects were performed at BIOFOS Avedøre during the comparative measurement campaigns. In addition, some DFM and TDM measurements were performed during the comparative measurements, which were not considered valid (DFM) or were below detection limit (TDM). In all, 12 DFM flights were excluded (23%), of which 8 were during the first 3 measurement days. For TDM the emissions were below detection (about 0.1 to 0.2 kg/h) at one campaign at Avedøre and at the Nivå campaign.

Due to the high N_2O emission dynamics at the plant, only emission rates obtained during simultaneous DFM and TDM measurements were compared. For TDM, emission rates were calculated based on transects performed during the same time interval as it took to perform one flight. During the 12-28 minutes flights, on average 6.3 TDM transects were performed. Often more

TDM transects were performed either prior or after the flight has ended. However, these TDM transects were excluded to obtain a more accurate emission comparison with DFM.

LPS was operational at BIOFOS Avedøre at all 15 measurement days for the comparative tests. This enabled comparison of the remote sensing measurement to simultaneous LPS derived values of N_2O emission. One of the LPSs in Nivå Renseanlæg was not calibrated correctly, and the second produced a result that was not suitable for comparison.

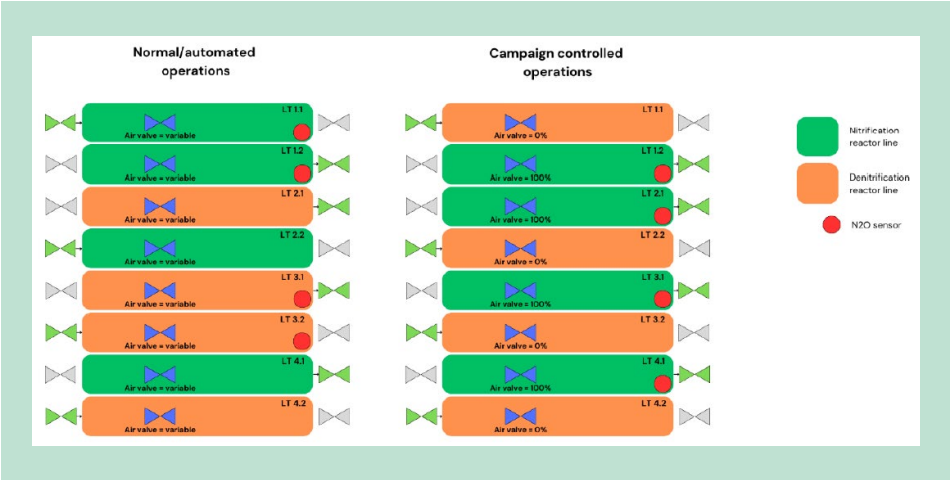


FIGURE 24. Left figure illustrates line configuration under normal/automated operation, where LPS equipped process tanks may be aerated or not, and with varying air supply. Right figure shows configuration under controlled operation, where LPS equipped tanks were aerated at maximum rate, while non-LPS equipped tanks were not aerated (Lewis Lallana, 2023).

During two measurement days at BIOFOS Avedøre (10-01-2023 and 08-05-2023), aeration was altered to provide an improved basis for comparison of DFM and TDM to the LPS emission rates. This is referred to as “controlled operation” in TABLE 7. At both dates, aeration was manually adjusted to be continuously at constant, equal rates (valves at 100%) in the four out of eight tanks equipped with LPS, while the remaining four tanks were not aerated (FIGURE 24). This was done in two 1-hour periods for both dates. The N_2O emission determined based on the four LPS equipped tanks were compared with the N_2O emission rates measured by DFM and TDM.

The EC measurements were performed during two periods: 02-06-2022 to 20-08-2022 and 08-06-2023 to 29-09-2023.

10. Emission results comparisons

In the AWAIRE project, four methods were used to measure N_2O emissions: eddy covariance method (EC), drone flux method (DFM), liquid phase sensors (LPS) and tracer gas dispersion method (TDM). In this section of the report, simultaneously measured emission rates determined using these methods are compared.

10.1 Comparison of remote sensing methods – DFM to TDM

24 individual measurements were performed, where both TDM and DFM were measuring N_2O emission rates simultaneously, and the measured emission rates were above detection limit and passed quality control. All these measurements were performed at BIOFOS Avedøre, where the 24 simultaneous measurements were done on 8 different days (see section 9.2). At the comparative measurement campaign performed at Nivå Renseanlæg, N_2O emissions were very low (< 0.1 kg N_2O h^{-1}), and the measurements of the TDM were not usable for comparison because emissions were below detection and associated with high uncertainty. Two valid measurements were obtained by the DFM method however, due to the extremely low emission rate, the uncertainty on these measurements is very high (91 % for each measurement and 73 % for the average of the two measurements). The LPS at Nivå Renseanlæg were not functioning properly, and their output could not be used for comparison.

The simultaneous measurements consisted of one DFM flight, and several TDM transects (6.3 on average) collected during the time interval of DFM. FIGURE 25 shows N_2O emission rates measured from the aeration tanks at BIOFOS Avedøre, where emission rates measured using DFM is plotted as function of measured emission rate using TDM. Of the simultaneous measurements, the emission rate for DFM varied between 0.18 and 99.8 kg N_2O h^{-1}, whereas the emission rate measured by TDM varied between 0.27 and 106.0 kg N_2O h^{-1}. The highest emission rates for both methods were at the day, where unusual operating condition caused higher than normal N_2O emission at the plant.

No overall tendency of one method measuring higher emission rate than the other was observed. The average emission rate from all 24 observations was slightly higher for DFM (16.8 kg N_2O h^{-1}) than TDM (15.7 kg N_2O h^{-1}). However, discarding a single measurement (26-04-2022, 3rd measurement) out of the 24, causes the average emission rate of TDM to be higher compared to DFM. Out of the 24 observations, TDM measured higher emission compared to DFM 11 times, whereas the opposite was true for 13 measurements.

Apart from the various causes of measurement uncertainty described for both methods, short term (minute to minute) variation of the true N_2O emission rate may partly explain differences in DFM and TDM emission rates. Both TDM and DFM traverses the plume, where air is sampled at background level for parts of each measurement at either side of the plume (TDM), or at either side, above, or below the plume (DFM). Thus, both methods measure emission for parts of the period from start to finish of a DFM flight (15-20 minutes one flight) or set of TDM transects (where one transect takes 3-4 minutes).

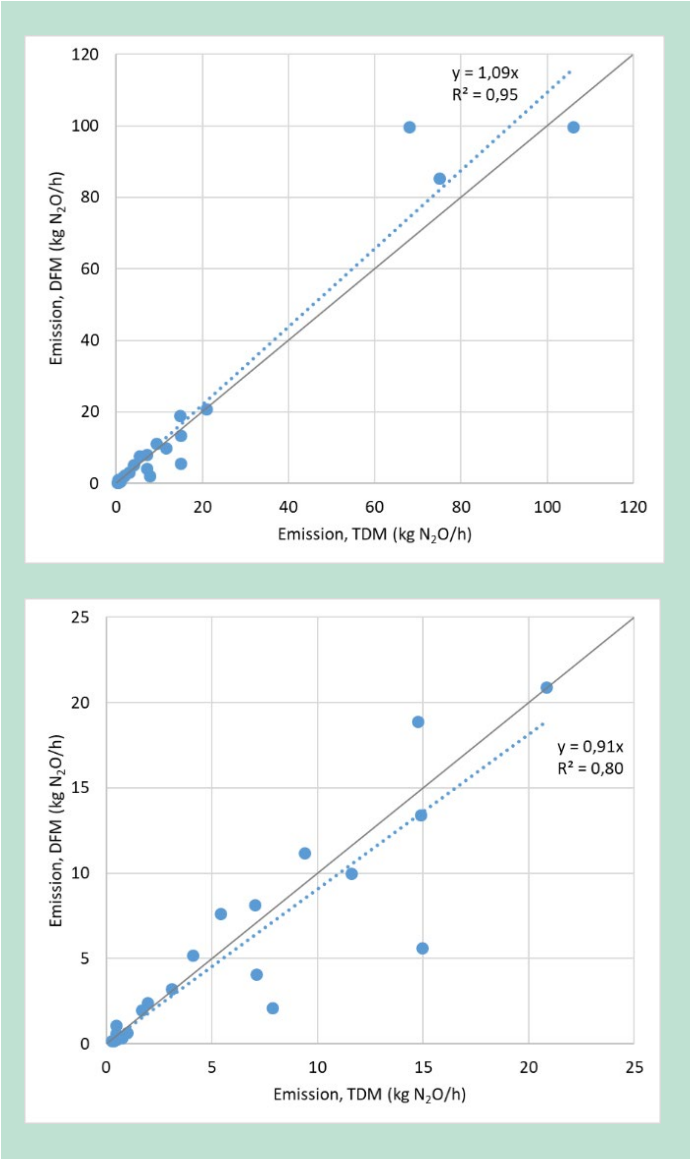


FIGURE 25. Comparison of measured N_2O emission rates by DFM and TDM. Simultaneous flights and transects only. Top graph shows all simultaneous measurements, while lower graph omits high emission day (26-04-2022).

At one measurement (not included in FIGURE 25), aeration was started in one of the tanks during the DFM flight (half-way to end of flight). Since the drone was mostly above the plume after start of the aeration, it is likely that the DFM derived emission rate was lower than the actual, average N_2O emission for the flight period. Since TDM was primarily measuring at the end of the flight (only two transects), this measurement was considered not usable for comparison.

At each of the eight days, where simultaneous TDM and DFM measurements were performed, the numbers of measurements varied between 1 and 6 per day, where one measurement is a DFM flight/flux wall and several TDM transects done during the DFM flight. Daily, average N_2O emission rates are listed in TABLE 8. The largest difference between emission rates was 73%, where the number of measurements were lowest (1 DFM flight, 5 simultaneous TDM transects). The average, daily emission rates of the two methods were similar – 15.5 and 15.8 kg N_2O h^{-1} for TDM and DFM, respectively. This average was based on 24 DFM flights and 152 TDM transects done during 8 measurement days.

TABLE 8. Average N_2O emission for each measurement days – simultaneous DFM and TDM measurements.

Date	# Simultaneous measurements (# TDM tran-sects)	N_2O emission, TDM (kg N_2O h^{-1})	N_2O emission, DFM (kg N_2O h^{-1})	Difference in emission rate (E_{TDM}-E_{DFM} / E_{TDM})*
26-04-022	3 (21)	83.0	94.9	-14%
08-07-2022	1 (5)	7.9	2.1	73%
26-08-2022	3 (11)	1.0	1.1	-20%
12-10-2022	1 (6)	3.1	3.2	-5%
10-01-2023	4 (37)	0.40	0.31	22%
08-05-2023	6 (36)	11.9	12.3	-4%
26-06-2023	4 (23)	3.8	4.7	-23%
28-06-2023	2 (13)	13.3	7.8	41%
Average	**3.0 (16.9)**	**15.5**	**15.8**	**-2%**

* E_{TDM}: N_2O emission rate measured by TDM, E_{DFM}: N_2O Emission rate measured by DFM

10.2 Comparison of remote sensing methods to liquid phase sensors – DFM/TDM to LPS

10.2.1 All campaigns

Based on LPS data, N_2O emission rates were calculated corresponding to the time intervals covered by DFM (time slot for one flight) or by TDM (time slot for groups of approximately 10 TDM transects). LPS sensors were operational at all 15 measurement days during the comparative TDM and DFM measurements. However, at one of the measurement days (26-04-2022), maintenance caused unusual high N_2O emission at the plant, where the liquid phase sensors were saturated, and thus did not provide valid results (significant underestimation of the N_2O emission). The LPS data from this day are therefore left out of this comparison. As mentioned in section 7, refinements to the calculation of LPS emission rates were performed during the project period. The comparison of TDM and DFM emission rates to LPS values shown here is done using the final refined LPS emission rates.

The TDM and DFM data reported in this section includes measurements, which were not simultaneous, meaning that for some data, only one of the two remote sensing methods were being used. Therefore, the data for comparison of TDM to LPS and DFM to LPS is larger than the comparison between DFM and TDM described in the previous section: 38 TDM measurements consisting of 400 transects and 38 DFM measurements each consisting of one flight/flux wall.

FIGURE 25 shows emission rates measured by TDM and DFM, plotted as function of LPS emission rates for each measurement. We note that this figure includes TDM and DFM measurements, which were not done simultaneously.

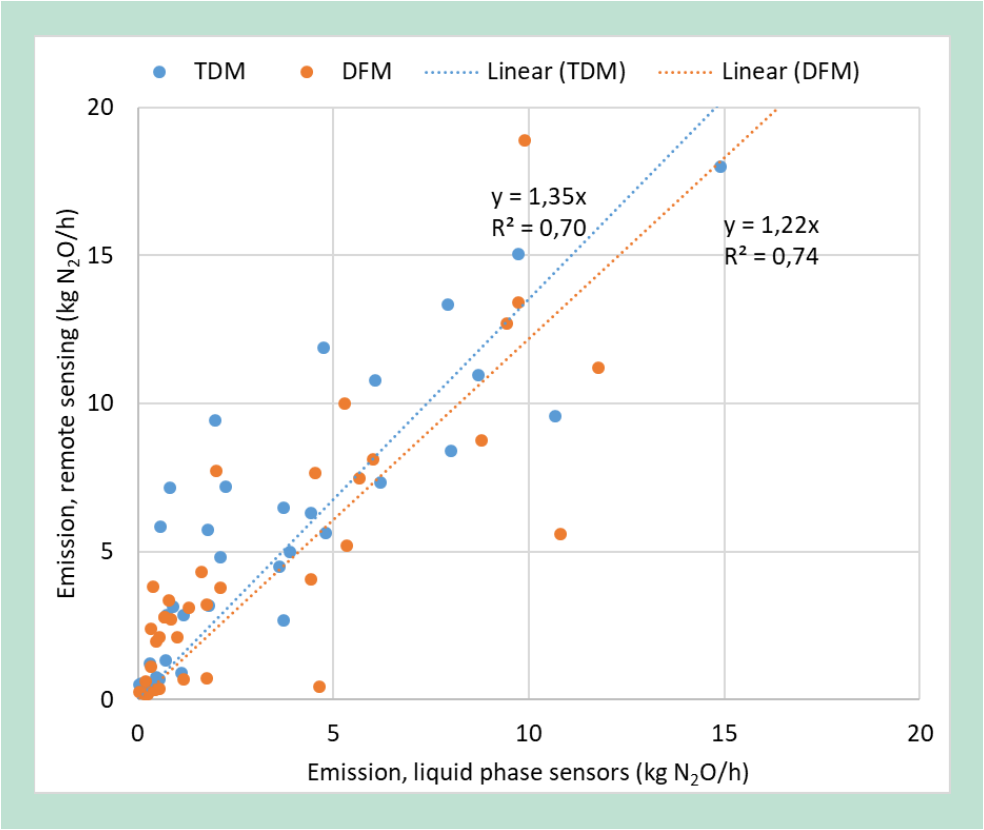


FIGURE 26. Comparison of TDM to LPS and DFM to LPS measured N_2O emission rates. The plot includes single DFM flights/flux walls and single TDM measurements (sets of approximately 10 transects), which are compared to LPS values of the corresponding periods.

TABLE 9 shows average emission rates for each day of comparative measurements. On average, both DFM and TDM daily emission rates are higher than LPS emission rates from the same time periods (TABLE 9). There are, however, measurements where LPS derived emission rates are higher than the corresponding DFM and TDM values. Apart from measurement uncertainties, some of the difference between DFM and LPS, and TDM and LPS rates, may be explained by the fact that only 50% of the process tanks at BIOFOS Avedøre were equipped with LPS. It is plausible that for some of the measurements, where the differences are highest, the extrapolation of emission rates to non-LPS equipped tanks is a significant source of uncertainty regarding the LPS emission rates.

Daily average emission rates varied between 0.38 and 13.35 kg N_2O h^{-1} for TDM, where the corresponding LPS values varied between 0.13 and 9.55 kg N_2O h^{-1} (TABLE 9). Average daily emission rates were almost always higher for TDM compared to LPS for the same periods. The only exception was 29-06-2022, where the LPS emission rates were slightly higher (LPS: 3.68, TDM: 3.59 kg N_2O h^{-1}) (TABLE 10). Average emission for the measurement days for TDM was 4.96 kg N_2O h^{-1}, which was about 77% higher than the corresponding LPS value (2.80 kg N_2O h^{-1}).

For the DFM campaigns, daily average emission rates varied between 0.30 to 10.20 kg N_2O h^{-1}, where the average of those being 4.28 kg N_2O h^{-1}. As for TDM, the DFM measured emission rates were similar or higher than the average LPS derived emission rates from the same periods. On average, daily DFM emission rates were 47% higher than simultaneous LPS emission rates (DFM: 4.28 kg N_2O h^{-1}, LPS 2.91 kg N_2O h^{-1}). Possible reasons behind these differences are discussed in section 11.

TABLE 9. Average emission rates for each day of comparative measurements. LPS emission rates listed are those, which corresponded to the periods of either TDM or DFM.

Date	Average N_2O emission, TDM (# measurements) [a]	Average N_2O emission, LPS during TDM	Average N_2O emission, DFM (# measurements) [b]	Average N_2O emission, LPS during DFM
(dd-mm-yyyy)	kg N_2O h^{-1}			
29-03-2022	6.79 (4)	2.02	2.94 (5)	0.88
29-06-2022	3.59 (5)	3.68		
08-07-2022	6.50 (2)	0.69	2.10 (1)	1.01
26-08-2022	1.00 (2)	0.62	3.06 (6)	0.75
12-10-2022	4.83 (2)	2.77	3.37 (3)	1.72
10-01-2023	0.38 (6)	0.13	0.30 (6)	0.25
11-01-2023	0.63 (3)	0.46		
04-05-2023	13.35 (1)	7.94		
08-05-2023	11.47 (5)	9.55	10.20 (8)	8.48
26-06-2023	4.25 (4)	3.25	4.71 (4)	3.00
28-06-2023	9.66 (4)	5.85	7.56 (5)	7.21
28-08-2023	2.85 (1)	0.74		
14-09-2023	2.86 (1)	1.18		
19-12-2023	1.22 (1)	0.31		
Average	**4.96**	**2.80**	**4.28**	**2.91**
Difference, remote sensing to LPS*	TDM: 77%		DFM: 47%	

* $(E_{REMOTE\ SENSING}-E_{LPS})/E_{LPS}$. [a] Each TDM measurement consisted for 10 plume transects lasting about 30-60 minutes. [b] Each DFM measurement consisted of one flight lasting 15-20 minutes.

The LPS sensor configuration was changed 07-01-2023 from having the four sensors in process tanks 1.1,1.2,3.1 and 3.2 to having the four sensors in process tanks 1.2, 2.1, 3.1 and 4.1. The latter represented a more evenly distribution of the sensors between the four lines. This change may have caused an improvement in the calculated LPS emission rates. The largest discrepancies between LPS and DFM/TDM were observed before sensor reconfiguration. The single largest difference in daily average emission rate was 08-07-2023, where the average emission measured using TDM (2 measurements) was 6.50 kg N_2O h^{-1}, while the average LPS emission rate during TDM measurements was 0.69 kg N_2O h^{-1} – nearly an order of magnitude lower.

10.2.2 Controlled operation

During two measurement days at BIOFOS Avedøre (10-01-2023 and 08-05-2023), the aeration schedule was altered to provide an improved basis for comparison of DFM and TDM to the LPS-derived emission rates. At each day, aeration was activated solely in the LPS-equipped tanks for two one-hour periods, at constant, similar airflow to each LPS tank.

FIGURE 27 shows emission rates and airflows recorded for each LPS-equipped process tank from one of the days of controlled operation (08-05-2023). The two periods of controlled operation are marked on the figure. In the remaining time depicted, operation of the aeration tanks was automated. During the periods of controlled operation, airflows to each of the four tanks

were constant, and emission rates were less varying compared to automated operation according to this data.

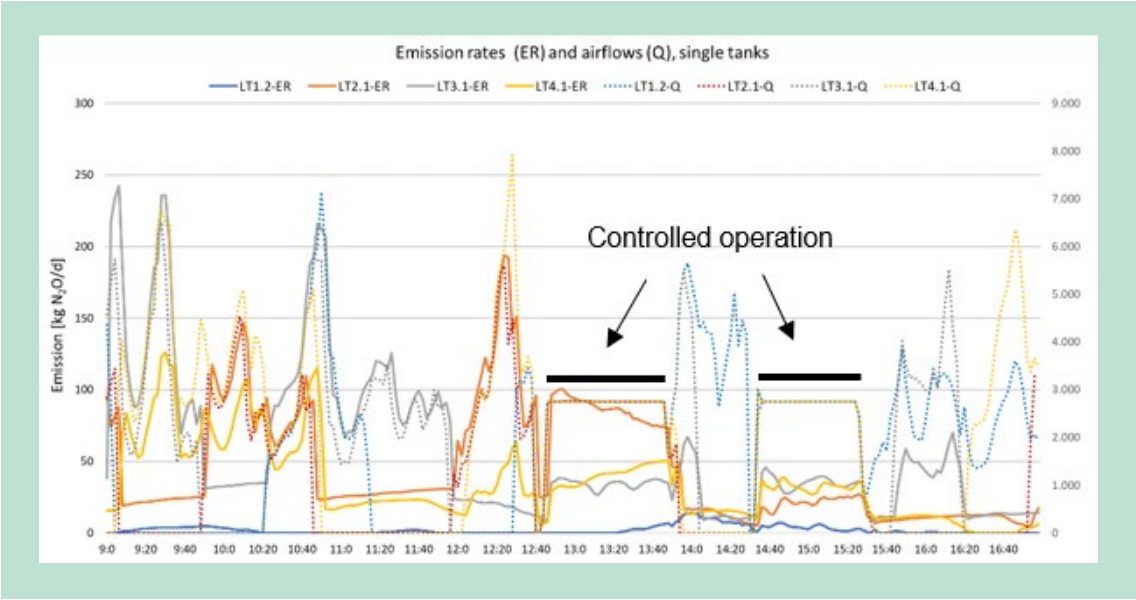


FIGURE 27. LPS data (N_2O emission to the air and airflow) from each of the four LPS-equipped tank on 08-05-2023.

Average N_2O emission rates derived from the LPS were calculated for each of the four tanks for the aerated periods. The total emission from the aerated tanks was determined by taking the sum of the emissions from the four tanks. N_2O emissions from four non-aerated tanks were unknown due to the lack of sensors in these tanks. For comparison to remote sensing measurements (DFM and TDM), the N_2O emissions from non-aerated tanks were derived from an estimate, where we assumed 15% N_2O emission rates from the four non-aerated tanks compared to the aerated ones.

TABLE 10 lists average emission rates from the LPS-equipped process tanks during controlled operation according to LPS measurements. As expected, the emission rate from the January campaign was relatively low (sum, 4 tanks: 0.10-0.17 kg N_2O h^{-1}), whereas the emission rate from the May campaign was relatively high (sum, 4 tanks: 3.81-6.63 kg N_2O h^{-1}). At both campaigns, the average emission rate from tank 1.2 was significantly lower than the other three LPS-equipped tanks (TABLE 10). However, emissions rates also varied between the other tree tanks (2.1, 3.1, and 4.1).

DFM and TDM measurements were done during each of the four, one-hour periods of controlled operation. In all, 8 DFM measurements, each consisting of one flight/flux wall, and 9 TDM measurements, consisting of 72 transects in total, were performed. FIGURE 28 shows DFM and TDM emission rates from single measurements plotted as function of LPS rates, where N_2O emissions from non-aerated tanks are assumed to be 15% of the sum of emission rates from aerated tanks. Compared to the campaigns described in the previous section, which included campaigns under normal operation, the emission rates obtained by LPS and DFM/TDM are more strongly correlated (higher R^2). However, there are also in these data clear tendencies towards remote sensing measurements resulting in higher emission rates compared to LPS values.

TABLE 10. Average N_2O emission determined by LPS during controlled operation at 10-01-2023 and 08-05-2023. "SUM of aerated/LPS-equipped tanks + 15%" is the assumed total emission from all lines, including non-aerated process tanks w/o LPS.

10-01-2023	Average emission aerated tanks, period 1 (12:12–13:12) (kg N_2O h^{-1})	Average emission aerated tanks, period 2 (14:08-15:08) (kg N_2O h^{-1})
Tank 1.2	0.000	0.000
Tank 2.1	0.034	0.033
Tank 3.1	0.000	0.000
Tank 4.1	0.066	0.136
SUM	**0.100**	**0.169**
SUM + 15%	**0.115**	**0.195**
8-5-2023	**Average emission aerated tanks, period 1 (12:46-13:44) (kg N_2O h^{-1})**	**Average emission aerated tanks, period 2 (14:34-15:24) (kg N_2O h^{-1})**
Tank 1.2	0.048	0.164
Tank 2.1	3.546	0.878
Tank 3.1	1.402	1.446
Tank 4.1	1.631	1.320
SUM	**6.628**	**3.808**
SUM + 15%	**7.622**	**4.380**

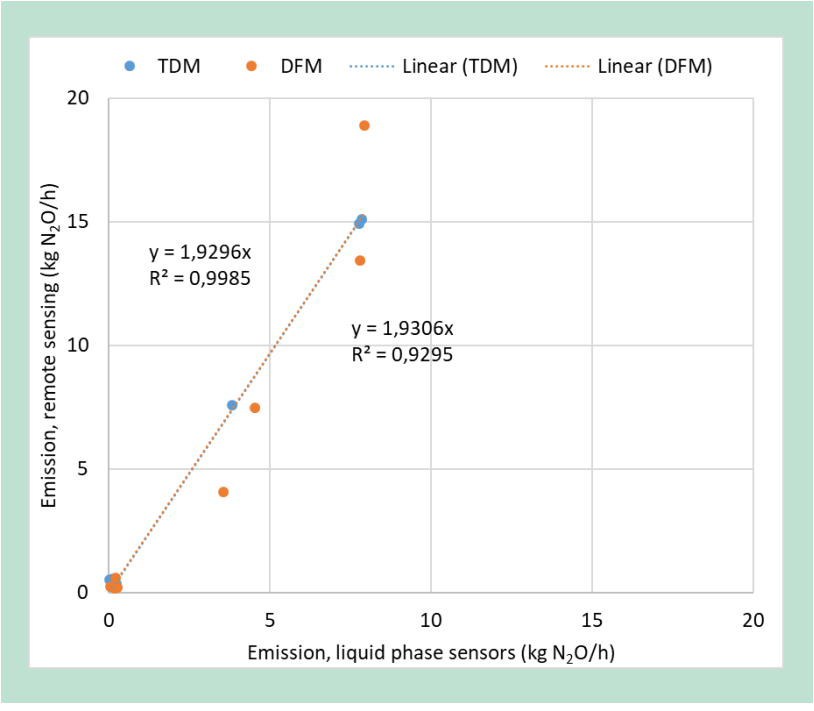


FIGURE 28. Comparison of DFM and TDM N_2O emission rates (single measurements) to simultaneous LPS values.

The average emission rates determined by remote sensing during 10-01-2023 were 0.44 and 0.31 kg N_2O h^{-1} for TDM and DFM, respectively. The average LPS rates during remote sensing

measurements were 0.14 and 0.17 kg N_2O h^{-1}, during TDM and DFM measurements, respectively (TABLE 11), whereby LPS emission rates were about half of remote sensing values.

Similarly, remote sensing N_2O emission rates for 08-05-2023 were 12.53 and 10.97 kg N_2O h^{-1} for TDM and DFM respectively, while the corresponding LPS rates were 6.48 and 5.95 kg N_2O h^{-1}. Both campaigns thus showed that LPS-derived emissions were about half of the remote sensing measurements, which is in line with the comparison results obtained during normal plant operations, see section 10.2.1. Reasons behind discrepancy in emission rates determined by LPS compared to remote sensing are discussed in section 11. In addition, the change in operation may have caused a change in relation to emission from non-aerated tanks compared to aerated ones.

TABLE 11. Daily average N_2O emission rates during controlled operation.

Date	Average N_2O emission, TDM (# measurements)[a]	Average N_2O emission, LPS during TDM	Average N_2O emission, DFM (# measurements)[b]	Average N_2O emission, LPS during DFM
(dd-mm-yyyy)	(kg N_2O h^{-1})			
10-01-2023	0.44 (6)	0.14	0.31 (4)	0.17
08-05-2023	12.53 (3)	6.48	10.97 (4)	5.95

[a] Each TDM measurement consisted of 7-9 transects lasting about 15-25 minutes. During the 9 TDM measurements 72 transects were performed in total. [b] Each DFM measurement consisted of one flight lasting 15-20 minutes. Eight DFM measurements were performed consisting of 8 flights.

10.3 Seasonal and diurnal emission variability from EC method

FIGURE 29 shows 15-min averaged N_2O fluxes for the two monitoring periods (June to August 2022 and June to September 2023). The emission pattern exhibits noticeable variations, both on the long term (seasonal variability) and on the short term (hourly variability). Fluxes varied widely throughout the duration of the experiment from zero to almost 30 µmol m^{-2} s^{-1}. The short-term variability arises from the fluctuation in wind direction, causing the system to sample from an area outside the aeration tanks, and the consistent alternations between the aeration (high fluxes) and non-aeration (low fluxes) phases. In the subsequent analysis of the seasonal and diurnal patterns using EC data, the range of wind direction was limited between 205° and 325° based on the location of the EC system in respect to the aeration tanks (FIGURE 16).

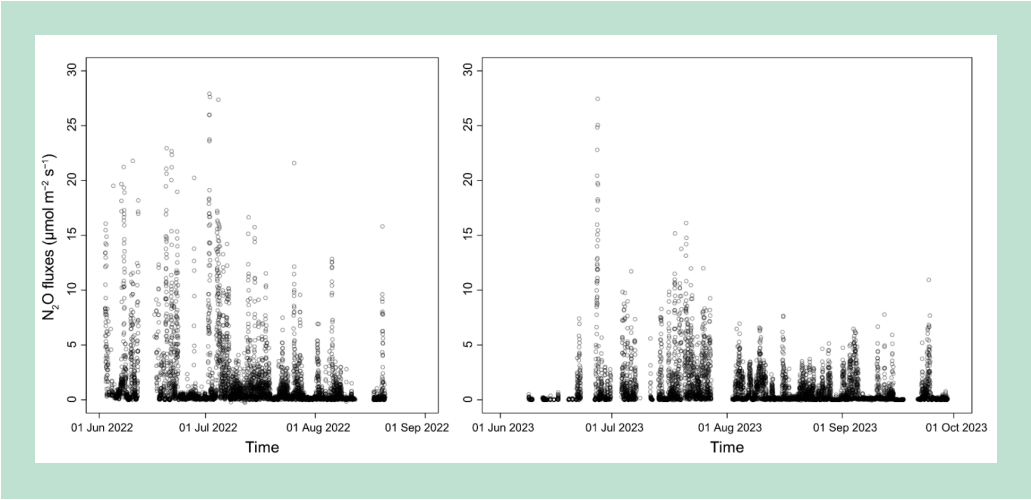


FIGURE 29. Time-series of 15-min averaged N_2O fluxes for the two monitoring periods, June to August 2022 (left panel) and June to September 2023 (right panel). Any gaps observed in the time-series result from equipment or power failures.

Despite the study's duration not being sufficient to fully capture the annual N_2O emission variation and identify its peak period, results showed a pronounced seasonal variation with a decreasing trend as summer months progressed (FIGURE 30 – left panel). The highest N_2O fluxes were measured in June with a monthly mean of 3.81 µmol m^{-2} s^{-1}, followed by subsequent decrease by half in the next two months. The mean N_2O flux estimates for September were slightly higher than those of the preceding month, aligning with the results obtained from the TDM and DFM methods (FIGURE 33). Overall, the observed seasonal variability is in accordance with the findings reported by (Daelman et al., 2013), performing a 16-month monitoring campaign measuring the N_2O emissions from the entire liquid surface of covered activated sludge tanks.

Diurnal variability was also investigated using the EC data, taking advantage of the method's high sampling frequency. FIGURE 30 – right panel shows that emission peaks around midnight and reaches its lowest value between 8 and 9 in the morning. A comparable diurnal pattern was demonstrated by (Daelman et al., 2015), who associated it with the characteristic nitrogen loading pattern to the wastewater treatment plant, influenced by a lag time. This lag time corresponds to the hydraulic retention time of the lines preceding the aeration tanks.

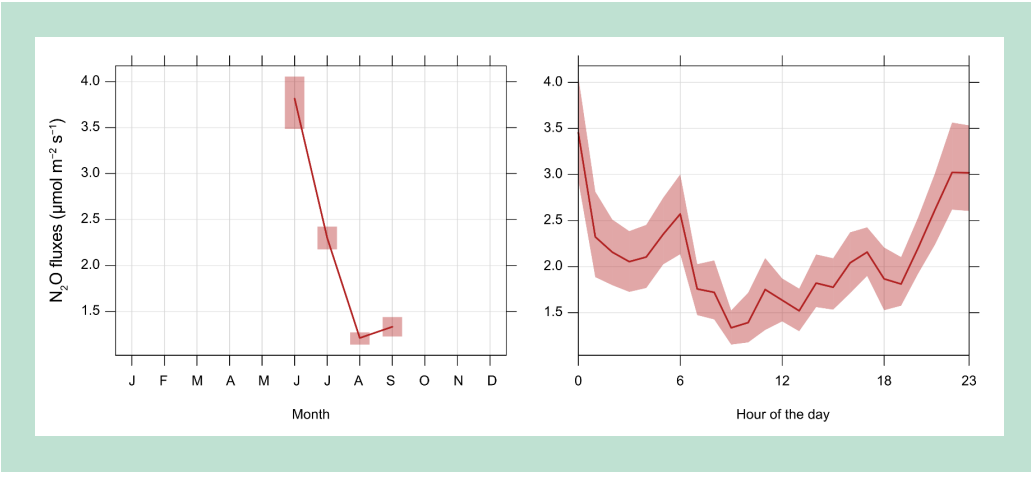


FIGURE 30. Monthly (left panel) and diurnal (right panel) pattern of 15-min averaged N_2O fluxes from the two monitoring periods combined. Solid lines represent mean N_2O flux estimates and shaded areas indicate the 95% confidence interval. For this analysis, the range of

wind direction was limited between 205° and 325° effectively creating flux footprint confined within the boundaries of the aeration tanks.

10.4 Comparison of measured emission dynamics – EC to LPS

N_2O emissions estimated by using models with liquid-phase N_2O concentrations as input parameters, were tested against EC fluxes for the two different measuring periods. The aim was to determine the ability of EC method to accurately capture the N_2O temporal variability from a wastewater treatment plant by comparing with an independent dataset. However, a restriction on this analysis is that the model estimates and EC results cannot be compared directly, due to differences in spatial resolution and the measuring unit. EC fluxes are expressed in μmol m^{-2} s^{-1} and represent spatially averaged emissions over a footprint area upwind the EC mast. Model's output is expressed in kg h^{-1} and represent only the tank in which the model inputs were measured (air flow, N_2O_w concentration, biological line's temperature).

During both measuring periods, we identified representative instances when the wind direction was approximately 275º and the fluxes could be attributed to a footprint area mainly from the tanks 1.2 and 2.1 (FIGURE 31a and FIGURE 32a).

For the first measuring period, flux estimates were compared with model's estimates from tank 1.2; the only tank with a liquid phase N_2O sensor in the vicinity of the flux footprint (FIGURE 31a). Both methods showed a good match regarding the emission dynamics, with the only exceptions occurring during periods with non-aeration for the tank 1.2 but with aeration from the tank 2.1 (e.g. July 14th 01:00-04:00, July 24th 01:00-02:00). On such occasions, EC method would detect N_2O fluxes, whereas model's estimates would be almost zero.

Prior to the start of the 2nd measuring period, two liquid phase N_2O sensors were relocated from tanks 1.1 and 3.2 to tanks 2.1 and 4.1, respectively. Therefore, flux estimates were compared with the sum of model's estimates from the tanks 1.2 and 2.1 (FIGURE 32a). Results revealed an even stronger agreement between the two methods than from the first measuring period. This is attributed to the fact that the 80% source area was located within tanks 1.2 and 2.1, where we obtained data from the liquid phase N_2O sensors. Yet, the ratio of N_2O emissions between the two methods differed in the different instances, most likely due to negative drift in the liquid phase N_2O sensors.

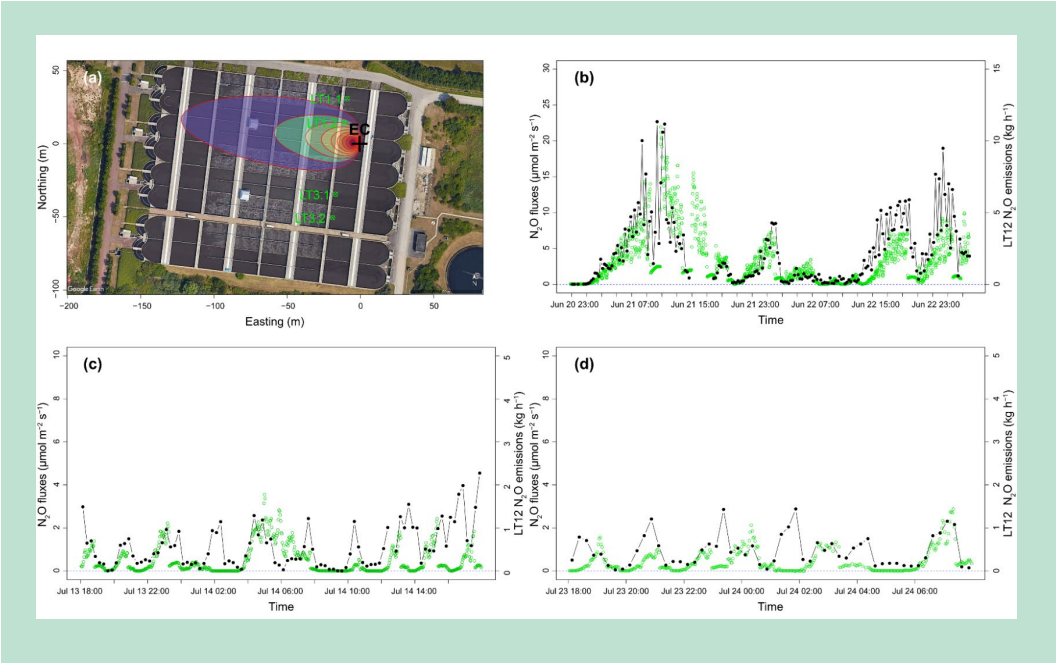


FIGURE 31. (a) Footprint climatology derived from the investigated time-series of the first measuring period. (b - d) Illustrative time-series of the modelled N_2O estimates (green points) alongside 15-min averaged EC fluxes (black lines and points). (Background image: Google Earth, Image © 2024).

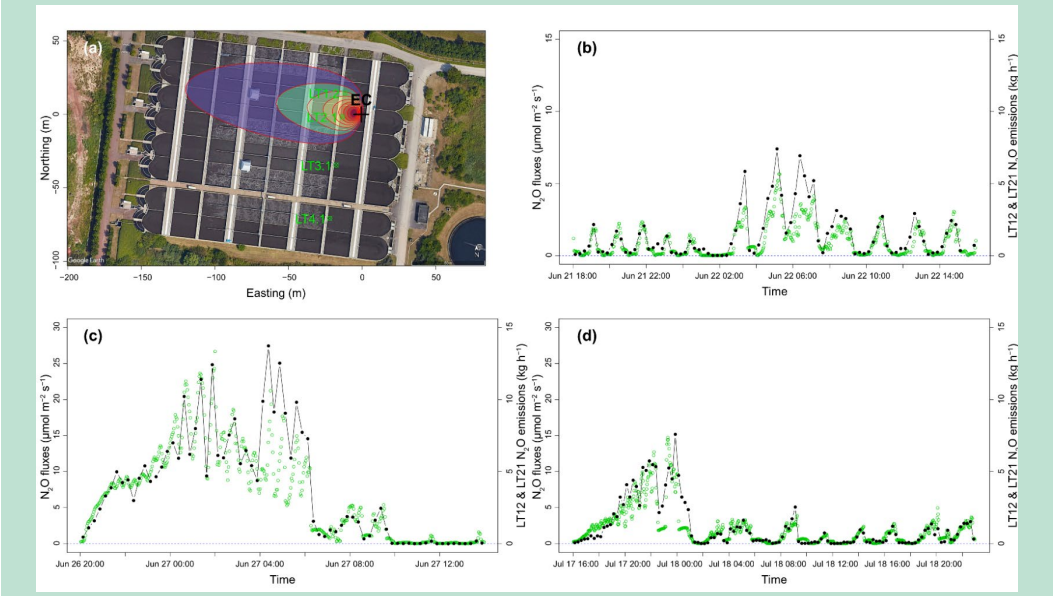


FIGURE 32. (a) Footprint climatology derived from the investigated time-series of the second measuring period. (b - d) Illustrative time-series of the modelled N_2O estimates (green points) alongside 15-min averaged EC fluxes (black lines and points). (Background image: Google Earth, Image © 2024).

11. Emission factors

In general, emission factors normalise emission rates to other parameters, which enables comparison of emission under varying operational conditions, comparison between different facilities and technologies, etc. In national reporting of greenhouse gases, emission factors (including country specific emission factors) are multiplied by activity data to account greenhouse gas emissions.

In this study, the measured N_2O emission rates and records of total nitrogen load to the aeration tanks were utilised to calculate N_2O emission factors for BIOFOS Avedøre, where N_2O emission is normalised to nitrogen load to the aeration tanks:

$$EF_{N2O} = \frac{E_{N2O}}{Nload}$$

Where, EF_{N2O} is the N_2O emission factor (% N to aeration tanks emitted as N_2O), E_{N2O} is the N_2O emission measured by either TDM, DFM or LPS (kg N_2O-N d^{-1}) and N load is the amount of total nitrogen in the pre-clarified wastewater pr. day (kg total-N d^{-1}).

The N load was calculated from measured, total water flows to the aeration tanks, where daily average values were considered, and measured total-N concentrations in the inlet water led to treatment in aeration tanks. Total-N concentration values were retrieved from laboratory analysis results, which are performed at intervals of approximately two weeks at BIOFOS Avedøre. The analysis interval meant that the dates of comparative TDM/DFM/LPS measurements were often not the same as the date of lab analysis of total-N. Instead, we used the data nearest in time to calculate N load, where the time difference varied between 0 and 7 days. The average N load for the 15 measurement days was 3300 kg total-N d^{-1} with maximum and minimum values of about 4100 kg and 2700 total-N d^{-1}.

Measurements done on the day of unusual high N_2O emission (26-04-2022) due to maintenance were excluded. The rationale behind leaving out this result is that the circumstances that led to the high measured emission rates occur infrequently (less than once pr. year), while measurements on that day comprise of 7% of the measurement days. Furthermore, the unusual high N_2O emission was outside the LPS measurement range.

Four sets of measured values of N_2O emission (daily averages) were used to calculate N_2O emission: TDM, DFM, LPS (all) and LPS (TDM/DFM) (FIGURE 33). LPS (all) is the daily average (midnight to midnight) LPS derived N_2O emission and LPS (TDM/DMF) is the LPS daily average emission factors for the times of day, where either TDM, DFM or both remote sensing methods were in use.

The emission factors followed the same seasonal trend as the emission rates with peak emission factors in May-June and a smaller peak emission factor in October, 2022, where after the emission factors remained low during the winter months.

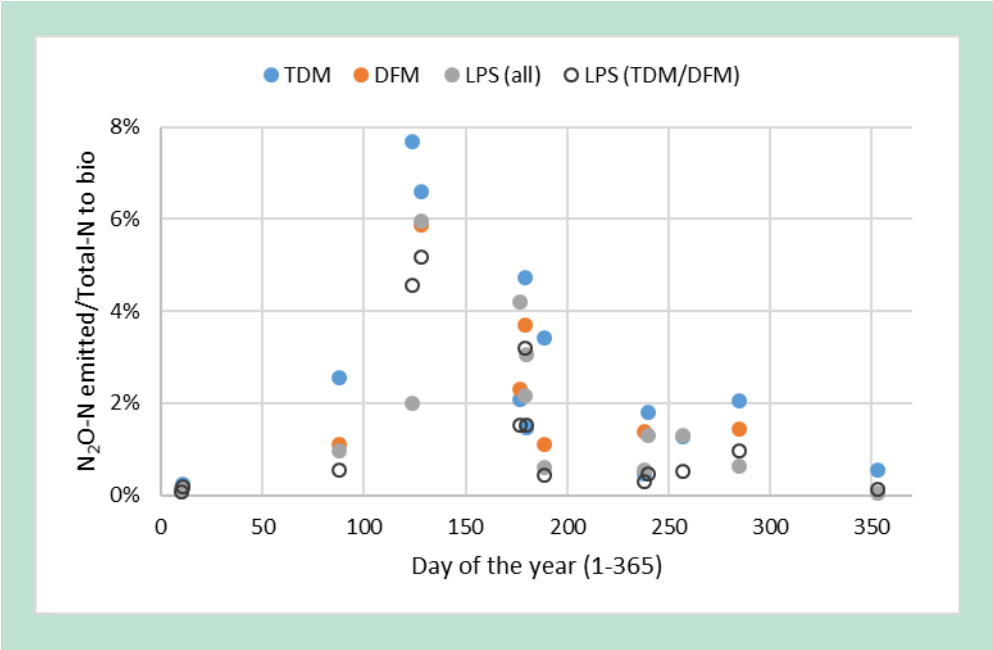


FIGURE 33. Emission factors (daily values) based on daily averages of N_2O emission from TDM, DFM and LPS measurements.

The average emission factors based on the different measurement data varied between 1.4 and 2.5% (TABLE 12), where the lowest were the LPS derived emission factors. Those were 1.4 and 1.6% for LPS (all) and LPS (TDM/DFM), respectively. Both remote sensing methods resulted in higher emission factors – 2.2 and 2.5 % for DFM and TDM, respectively. DFM was not utilised at all measurement days, whereby the basis for calculating these averages with regards to emission factors is different than for TDM and LPS.

TABLE 12. N_2O emission factors based on TDM, DFM and LPS measurements.

Date (dd-mm-yyyy)	EF - TDM	EF - DFM	EF - LPS (mid-night to mid-night)	EF - LPS (simultaneous TDM/DFM)
29-03-2022	2.6%	1.1%	1.0%	0.5%
29-06-2022	1.5%		3.1%	1.5%
08-07-2022	3.4%	1.1%	0.6%	0.4%
26-08-2022	0.5%	1.4%	0.6%	0.3%
12-10-2022	2.1%	1.4%	0.6%	1.0%
10-01-2023	0.1%	0.3%	0.1%	0.1%
11-01-2023	0.3%		0.2%	0.2%
04-05-2023	7.7%		2.0%	4.6%
08-05-2023	6.6%	5.9%	6.0%	5.2%
26-06-2023	2.1%	2.3%	4.2%	1.5%
28-06-2023	4.7%	3.7%	2.2%	3.2%
28-08-2023	1.8%		1.3%	0.5%
14-09-2023	1.3%		1.3%	0.5%
19-12-2023	0.5%		0.1%	0.1%
Simple average	**2.5%**	**2.2%**	**1.6%**	**1.4%**

Date (dd-mm-yyyy)	EF - TDM	EF - DFM	EF - LPS (mid-night to mid-night)	EF - LPS (simultaneous TDM/DFM)
29-03-2022	2.6%	1.1%	1.0%	0.5%
29-06-2022	1.5%		3.1%	1.5%
08-07-2022	3.4%	1.1%	0.6%	0.4%
26-08-2022	0.5%	1.4%	0.6%	0.3%
Time weighted average	**2.2%**	**1.8%**	**1.3%**	**1.2%**

Two averages of EF were calculated – "simple average" and "time weighted average". Simple average applies equal weighting to all observations, whereas "time weighted average" takes into account the differences in intervals between observations. For the time weighted average, each observation is presumed to account for the time interval equal to halfway between the previous measurement to halfway until the following measurement. Since measurements during the project were more frequent during high emission periods, the time weighted average EF's are lower than simple average EF's.

The average emission factors are in-line with previously reported N_2O emission factors from BIOFOS Avedøre. (Yoshida et al., 2014) reported emission factors varying between 0.2 and 4.3% at different measurement days (4 in all), based on TDM measurements.

DEPA, 2023 reported average, annual emission factors varying between 0.58 and 3.85% in the years 2019-2022, and between two different operational strategies of the aeration tanks and a test, where several modifications to reduce N_2O emission were applied to the operation). (Miljøstyrelsen, 2023).

In general, DFM and TDM derived emission factors from simultaneous measurements are higher compared to LPS values (on average, a factor of about 60% higher). The same is the case when comparing TDM and DFM emission factors to LPS daily averages. At two days (29-06-2022 and 26-06-2022), LPS daily average emission factors were higher than the remote sensing methods. The reason for this may be that the remote sensing measurement were done in periods of those two days, where the N_2O emission was low.

It is not surprising that the emission rates, and thereby emission factors varied somewhat between the methods, as all of them have their biases and uncertainties. As explained in sections 4, 6 and 7, several factors are cause of measurement uncertainties for three methods applied, which is also the case for measurements more broadly. It is, however, unlikely that random error is the cause of 15 daily average values of LPS derived emission rates (at same time periods as DFM/TDM) are equal or lower than that of the two remote sensing methods. This suggest a bias, which has not been identified during this project. Two, known factors regarding LPS may provide some explanation. The sensors need calibration due to drift. The drift is towards reduced sensitivity, which can explain that LPS emission rates are somewhat lower than DFM and TDM. More frequent calibration would mitigate this effect. At BIOFOS Avedøre, the airflow rates used in the LPS calculation model are not measured but derived from valve settings. This is suspected to be a cause of uncertainty, and may also be a cause of bias, where actual flow rates are higher than those considered in the N_2O emission model. k_La values are higher than 2 for the non-aerated periods and in parts of the biological lines. Finally, the upscaling of emissions based on four LPS sensors to 8 tanks is associated with uncertainty.

12. Monitoring programme

In the effort to reduce the greenhouse gas effect associated to the treatment of wastewater it is essential and fundamental to first accurately measure the direct N_2O emissions. However, this is not straight forward. The emissions are highly dynamic and have both temporal and spatial variation. Remote sensing plant-wide measurement technologies, like the TDM and DFM offer the opportunity to quantify the whole plant emission rate and thus cover the entire spatial variation but fails to cover the temporal variation.

The LPS method offers continuous measuring and thus covers the temporal variance but is challenged with regards to spatial coverage and the fact that the LPSs do not measure the emission directly but depends on the calculation of a mass transfer coefficient and determination of a correct airflow stripping from the surface of the process tank volume.

The calculations of the emission rate from LPS measurements in the present study showed an apparent consistent underestimation of the emission rate compared to the DFM and TDM ranging from a factor of 1.5 to 3.1. This highlights the need for validation and calibration of the emission calculation and extrapolation method when using the LPS method.

The installation of LPSs in every process tank and a correct measurement of air flow would help to reduce the uncertainty of the whole plant emission estimation. Still, the emission calculation needs to be validated, and additionally the k_La_{N2O} values of the aerobic and anoxic N_2O mass transfer may need calibration. Furthermore, the k_La_{N2O} has been shown to change with changes in air flow and cannot necessarily be considered a constant (Domingo-Félez et al., 2014).

Since the cost of installing and maintaining LPSs and performing TDM or DFMs depends strongly on number of sensors and measurements, it is beneficial to keep these at an optimal level. It is, however, not possible to determine an optimal sensor coverage (sensors per tank) or optimal frequency of plant-wide campaigns (number per year) based on the available data.

When performed simultaneously the present project has shown that the plant-wide methods (DFM and TDM) can be used to evaluate the calculation and extrapolation method based on the LPS method. Below we propose a method for a qualitative validation protocol.

Qualitative validation protocol for evaluation of the extrapolation of process specific LPS emission calculations to whole plant emissions

In a scenario with LPS in every biological process tank and known (and accurate) air flow to each tank, the DFM and TDM can be used to validate the calculation of the emissions and to calibrate the k_La_{N2O}. It is however, not known how frequently this must be done, and this requires further studies.

In a scenario without LPSs in every biological process tank the overall plant emission is estimated based on a reduced number of sensors. Therefore, it is assumed that the conditions and emission rates are comparable/similar in tanks with and without sensors. To minimize uncertainties during a validation campaign two modes (aerated and non-aerated mode) of operation should be applied for the process tanks:

- Generally during both campaign modes
  - Ensure the performance and calibration of the LPSs
  - Concentration levels of NH_4 and NO_3 should be comparable between all tanks
  - SS concentration should be comparable between all tanks

    - Wastewater flow distribution should be equal
    - Return sludge, side-stream return and reject water should be mixed with influent prior to tank distribution or distributed equally between tanks
    - The mixers should be turned on and tanks completely mixed
- Specifically for the non-aerated campaign mode
    - During this campaign the aeration is turned off in all tanks during the validation campaign
- Specifically for the aerated campaign mode
    - During this campaign the aeration is turned on in the tanks with a sensor
    - The airflow is kept constant during the validation campaign
    - The airflow is distributed equally between tanks

The N_2O emission obtained based on the LPS is validated against a second methods, which measures the plant-wide N_2O emission such as TDM or DFM. If the value of the calculated N_2O emission based on the LPS method falls is comparable to emission value of the applied plant-wide method (considering the uncertainty of the method) the LPS method is considered acceptable. Higher difference between methods should disqualify the validation and promote additional validation campaigns and trigger initiatives to improve the similarity.
These could be:

- Repeat the campaigns and determine if the difference is consistent or fluctuating
- Control the validity and precision of the airflow data
- Identify if the difference primarily originates from the aerated of non-aerated tanks
- Increase the number of LPS to get better tank coverage of the wastewater treatment plant.

13. Conclusions

Based on the work described in this report, we conclude the following:

- Based on previous development of a drone-based method to measure methane emissions, the drone flux method (DFM) was successfully designed, tested and adapted to quantify N_2O emission from wastewater treatment plants.
- Quantification using the DFM was done at a wastewater treatment simultaneously with tracer gas dispersion measurements (TDM) during several comparative campaigns. N_2O emission rates were comparable between the two methods, and no tendency of one method leading to higher emission rates than the other was observed.
- Measured TDM and DFM N_2O emission rates were compared to liquid phase sensor (LPS) based N_2O emission rates at BIOFOS Avedøre. TDM and DFM emission rates were proportional to LPS values, but a tendency of higher TDM and DFM emission rates compared to LPS was observed.
- Extrapolation of N_2O emission from non-sensor equipped aeration tanks may be a significant source of error in LPS determination of N_2O emission. Distribution of LPS sensors is important, where (ideally) each aeration tank should be equipped with a LPS sensor.
- The cause(s) of difference between TDM/DFM compared to LPS rates was not identified, but several possible explanations were identified.
- To provide accurate assessments of N_2O emission rates based on LPS, remote sensing methods may be used to qualify LPS emission rates at plant level, where parameters in the emission calculation may need to be adjusted.
- The eddy covariance method was found to be able to address the dynamic behaviour of N_2O fluxes, and to illustrate both the seasonal and diurnal variability from the aeration tanks. Results for the seasonal variability matched the results from the other remote sensing methods applied in this study.
- The high-resolution N_2O fluxes from EC method allowed us the comparison with the LPS modelled emissions. Results showed a strong agreement with regards to emission dynamic between the two methods.
- Plant-wide methods like TDM and DFM provide spatial coverage but lack temporal resolution, whereas the LPS method offers continuous monitoring but encounters challenges in spatial coverage and direct emission measurement. Despite these challenges, LPS measurements can actively contribute to N_2O formation mitigation. Therefore, it is recommended to employ a method that enables continuous N_2O monitoring to capture temporal variations, facilitating a comprehensive assessment of yearly emissions.
- To enhance the accuracy of the LPS emissions extrapolation, it is recommended to install an LPS in each process tank and validate the emission calculations against remote sensor methods (DFM or TDM) to improve the whole-plant emissions estimation. This approach allows for adjustments in sensor coverage, airflow calibration, and emission extrapolation, leading to a more reliable estimation of plant-wide emissions.

14. References

Baeten, J. E., van Loosdrecht, M. C. M., & Volcke, E. I. P. (2020). When and why do gradients of the gas phase composition and pressure affect liquid-gas transfer? *Water Research*, *178*, 115844. https://doi.org/10.1016/J.WATRES.2020.115844

Baldocchi, D., Chu, H., & Reichstein, M. (2018). Inter-annual variability of net and gross ecosystem carbon fluxes: A review. *Agricultural and Forest Meteorology*, *249*, 520–533. https://doi.org/10.1016/J.AGRFORMET.2017.05.015

Baresel, C., Andersson, S., Yang, J., & Andersen, M. H. (2016). Comparison of nitrous oxide (N2O) emissions calculations at a Swedish wastewater treatment plant based on water concentrations versus off-gas concentrations. *Advances in Climate Change Research*, *7*(3), 185–191. https://doi.org/10.1016/J.ACCRE.2016.09.001

BIOFOS. (2021). *Miljøberetning 2020*. https://biofos.dk/media/a0tdwifp/biofos-milj-beretning-2020.pdf

Burba, G. (2022). *Eddy Covariance Method for Scientific, Regulatory, and Commercial Applications*.

Chen, X., Mielczarek, A. T., Habicht, K., Andersen, M. H., Thornberg, D., & Sin, G. (2019). Assessment of Full-Scale N2O Emission Characteristics and Testing of Control Concepts in an Activated Sludge Wastewater Treatment Plant with Alternating Aerobic and Anoxic Phases. *Environmental Science and Technology*, *53*(21), 12485–12494. https://doi.org/10.1021/acs.est.9b04889

Daelman, M. R. J., van Voorthuizen, E. M., van Dongen, L. G. J. M., Volcke, E. I. P., & van Loosdrecht, M. C. M. (2013). Methane and nitrous oxide emissions from municipal wastewater treatment – results from a long-term study. *Water Science and Technology*, *67*(10), 2350–2355. https://doi.org/10.2166/wst.2013.109

Daelman, M. R. J., van Voorthuizen, E. M., van Dongen, U. G. J. M., Volcke, E. I. P., & van Loosdrecht, M. C. M. (2015). Seasonal and diurnal variability of N2O emissions from a full-scale municipal wastewater treatment plant. *Science of the Total Environment*, *536*, 1–11. https://doi.org/10.1016/j.scitotenv.2015.06.122

DANAK . (2023). https://registry.danak.dk/19946/registry/619?lang=en

Danish Ministry of Climate, E. and U. (2020). *Climate Programme 2020 Denmark's Mid-century, Long-term Low Greenhouse Gas Emission Development Strategy*.

Delre, A., Mønster, J., Samuelsson, J., Fredenslund, A. M., & Scheutz, C. (2018). Emission quantification using the tracer gas dispersion method: The influence of instrument, tracer gas species and source simulation. *Science of The Total Environment*, *634*, 59–66. https://doi.org/10.1016/J.SCITOTENV.2018.03.289

Delre, A., Mønster, J., & Scheutz, C. (2017). Greenhouse gas emission quantification from wastewater treatment plants, using a tracer gas dispersion method. *Science of The Total Environment*, *605–606*, 258–268. https://doi.org/10.1016/J.SCITOTENV.2017.06.177

Delre, A., ten Hoeve, M., & Scheutz, C. (2019). Site-specific carbon footprints of Scandinavian wastewater treatment plants, using the life cycle assessment approach. *Journal of Cleaner Production*, *211*, 1001–1014. https://doi.org/10.1016/J.JCLEPRO.2018.11.200

Domingo-Félez, C., Mutlu, A. G., Jensen, M. M., & Smets, B. F. (2014). Aeration Strategies To Mitigate Nitrous Oxide Emissions from Single-Stage Nitritation/Anammox Reactors. *Environmental Science & Technology*, *48*(15), 8679–8687. https://doi.org/10.1021/es501819n

Faragò, M., Damgaard, A., Madsen, J. A., Andersen, J. K., Thornberg, D., Andersen, M. H., & Rygaard, M. (2021). From wastewater treatment to water resource recovery: Environmental and economic impacts of full-scale implementation. *Water Research*, *204*, 117554. https://doi.org/10.1016/J.WATRES.2021.117554

Fredenslund, A. M., Rees-White, T. C., Beaven, R. P., Delre, A., Finlayson, A., Helmore, J., Allen, G., & Scheutz, C. (2019). Validation and error assessment of the mobile tracer gas dispersion method for measurement of fugitive emissions from area sources. *Waste Management*, *83*, 68–78. https://doi.org/10.1016/J.WASMAN.2018.10.036

Heidbach, K., Schmid, H. P., & Mauder, M. (2017). Experimental evaluation of flux footprint models. *Agricultural and Forest Meteorology*, *246*, 142–153. https://doi.org/10.1016/J.AGRFORMET.2017.06.008

IPCC, I. P. on C. C. (2023). *Climate Change 2021 – The Physical Science Basis: Working Group I Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press. https://doi.org/DOI: 10.1017/9781009157896

JCGM. (2008). *Evaluation of measurement data-Guide to the expression of uncertainty in measurement Évaluation des données de mesure-Guide pour l'expression de l'incertitude de mesure*. www.bipm.org

Kissas, K., Ibrom, A., Kjeldsen, P., & Scheutz, C. (2022). Annual upscaling of methane emission field measurements from two Danish landfills, using empirical emission models. *Waste Management*, *150*, 191–201. https://doi.org/10.1016/J.WASMAN.2022.07.005

Kljun, N., Calanca, P., Rotach, M. W., & Schmid, H. P. (2015). A simple two-dimensional parameterisation for Flux Footprint Prediction (FFP). *Geoscientific Model Development*, *8*(11), 3695–3713. https://doi.org/10.5194/gmd-8-3695-2015

Knudsen, J., De Rossi, L., Knudsen (Ed), B., Scheutz (Ed), C., & Fredenslund (Ed), A. (2022). *The Plane Project : napping and quantification of GHGs from diffuse emission sources using drone technology and vertical measuring walls*. Environmental Protection Agency.

Kosse, P., Lübken, M., Schmidt, T. C., & Wichern, M. (2017). Quantification of nitrous oxide in wastewater based on salt-induced stripping. *Science of The Total Environment*, *601–602*, 83–88. https://doi.org/10.1016/J.SCITOTENV.2017.05.053

Lewis Lallana, A. (2023). *Measurement and Quantification of N2O Emissions from Wastewater Treatment Plants in Denmark*. DTU Sustain.

Liu Ye, Jose Porro, & Ingmar Nopens. (2022). Quantification and Modelling of Fugitive Greenhouse Gas Emissions from Urban Water Systems. *IWA Publishing*.

Marques, R., Rodriguez-Caballero, A., Oehmen, A., & Pijuan, M. (2016). Assessment of online monitoring strategies for measuring N2O emissions from full-scale wastewater treatment systems. *Water Research*, *99*, 171–179. https://doi.org/10.1016/J.WATRES.2016.04.052

Mauder, M., & Foken, T. (2015). Documentation and Instruction Manual of the Eddy-Covariance Software Package TK3. *Arbeitsergebnisse, Universität Bayreuth, Abt. Mikrometeorologie (ISSN 1614-8916)*, *62*, 62.

Mauder, M., Foken, T., Aubinet, M., & Ibrom, A. (2021). Eddy-Covariance Measurements. In T. Foken (Ed.), *Springer Handbook of Atmospheric Measurements* (pp. 1473–1504). Springer International Publishing. https://doi.org/10.1007/978-3-030-52171-4_55

Miljøstyrelsen. (2023). *VARGA : vandressource, genvindingsanlæg*.

Moncrieff, Clement, Finnigan, & Meyers. (2005). Averaging, Detrending, and Filtering of Eddy Covariance Time Series. In X. Lee, W. Massman, & B. Law (Eds.), *Handbook of Micrometeorology: A Guide for Surface Flux Measurement and Analysis* (pp. 7–31). Springer Netherlands. https://doi.org/10.1007/1-4020-2265-4_2

Moncrieff, Massheder, De Bruin, Elbers, Friborg, Heusinkveld, Kabat, Scott, Soegaard, & Verhoef. (1997). A system to measure surface fluxes of momentum, sensible heat, water vapour and carbon dioxide. *Journal of Hydrology*, *188–189*(1–4), 589–611. https://doi.org/10.1016/S0022-1694(96)03194-0

Mønster, J. G., Samuelsson, J., Kjeldsen, P., Rella, C. W., & Scheutz, C. (2014). Quantifying methane emission from fugitive sources by combining tracer release and downwind measurements – A sensitivity analysis based on multiple field surveys. *Waste Management*, *34*(8), 1416–1428. https://doi.org/10.1016/J.WASMAN.2014.03.025

Myers, S., Mikola, A., Blomberg, K., Kuokkanen, A., & Rosso, D. (2021). Comparison of methods for nitrous oxide emission estimation in full-scale activated sludge. *Water Science and Technology*, *83*(3), 641–651. https://doi.org/10.2166/wst.2021.033

Prajapati, P., & Santos, E. A. (2017). Measurements of methane emissions from a beef cattle feedlot using the eddy covariance technique. *Agricultural and Forest Meteorology*, *232*, 349–358. https://doi.org/10.1016/J.AGRFORMET.2016.09.001

Reba, M. L., Fong, B. N., Rijal, I., Adviento-Borbe, M. A., Chiu, Y.-L., & Massey, J. H. (2020). Methane flux measurements in rice by static flux chamber and eddy covariance. *Agrosystems, Geosciences & Environment*, *3*(1), e20119. https://doi.org/https://doi.org/10.1002/agg2.20119

Rinne, J., Pihlatie, M., Lohila, A., Thum, T., Aurela, M., Tuovinen, J.-P., Laurila, T., & Vesala, T. (2005). Nitrous Oxide Emissions from a Municipal Landfill. *Environmental Science & Technology*, *39*(20), 7790–7793. https://doi.org/10.1021/es048416q

Scheutz, C., & Kjeldsen, P. (2019). Guidelines for landfill gas emission monitoring using the tracer gas dispersion method. *Waste Management*, *85*, 351–360. https://doi.org/10.1016/J.WASMAN.2018.12.048

Scheutz, C., Samuelsson, J., Fredenslund, A. M., & Kjeldsen, P. (2011). Quantification of multiple methane emission sources at landfills using a double tracer technique. *Waste Management*, *31*(5), 1009–1017. https://doi.org/10.1016/J.WASMAN.2011.01.015

Tang, A. C. I., Stoy, P. C., Hirata, R., Musin, K. K., Aeries, E. B., Wenceslaus, J., & Melling, L. (2018). Eddy Covariance Measurements of Methane Flux at a Tropical Peat Forest in Sarawak, Malaysian Borneo. *Geophysical Research Letters*, *45*(9), 4390–4399. https://doi.org/https://doi.org/10.1029/2017GL076457

Unisense Environment A/S. (2023). https://unisense-environment.com/manuals/

Vickers, D., & Mahrt, L. (1997). Quality Control and Flux Sampling Problems for Tower and Aircraft Data. *Journal of Atmospheric and Oceanic Technology*, *14*(3), 512–526. https://doi.org/https://doi.org/10.1175/1520-0426(1997)014<0512:QCAFSP>2.0.CO;2

Webb, E. K., Pearman, G. I., & Leuning, R. (1980). Correction of flux measurements for density effects due to heat and water vapour transfer. *Quarterly Journal of the Royal Meteorological Society*, *106*(447), 85–100. https://doi.org/https://doi.org/10.1002/qj.49710644707

Xie, Y., Zhang, M., Xiao, W., Zhao, J., Huang, W., Zhang, Z., Hu, Y., Qin, Z., Jia, L., Pu, Y., Chu, H., Wang, J., Shi, J., Liu, S., & Lee, X. (2022). Nitrous oxide flux observed with tall-tower eddy covariance over a heterogeneous rice cultivation landscape. *Science of The Total Environment*, *810*, 152210. https://doi.org/10.1016/J.SCITOTENV.2021.152210

Yoshida, H., Mønster, J., & Scheutz, C. (2014). Plant-integrated measurement of greenhouse gas emissions from a municipal wastewater treatment plant. *Water Research*, *61*, 108–118. https://doi.org/10.1016/J.WATRES.2014.05.014

Yu, X., Song, C., Sun, L., Wang, X., Shi, F., Cui, Q., & Tan, W. (2017). Growing season methane emissions from a permafrost peatland of northeast China: Observations using open-path eddy covariance method. *Atmospheric Environment*, *153*, 135–149. https://doi.org/10.1016/J.ATMOSENV.2017.01.026

AWAIRE

The AWAIRE project aimed to assess and compare innovative methods for measuring nitrous oxide (N_2O) emissions from wastewater treatment plants. Two novel approaches, the Drone Flux Measurement (DFM) method adapted for targeting N_2O emissions and the Eddy Covariance (EC) method, were evaluated alongside the established Tracer gas Dispersion Method (TDM) and a widely employed Liquid Phase Sensors (LPS) method.

The project found a strong correlation between the remote sensing methods (DFM and TDM), consistently indicating higher N_2O emission rates (averaging 44-77%) in comparison to continuous measurements with LPS at BIOFOS Avedøre.

The EC method provided high-resolution insights into N_2O dynamics and showed strong agreement with the modelled emissions based on LPS.

Due to the dynamic nature of N_2O emissions, continuous measurements like LPS may still be valuable for determining yearly emission rates and plant-specific N_2O emission factors, but validation of these measurements is crucial for accurate accounting of N_2O emissions from wastewater treatment plants.

The Danish Environmental
Protection Agency
Tolderlundsvej 5
DK - 5000 Odense C

www.mst