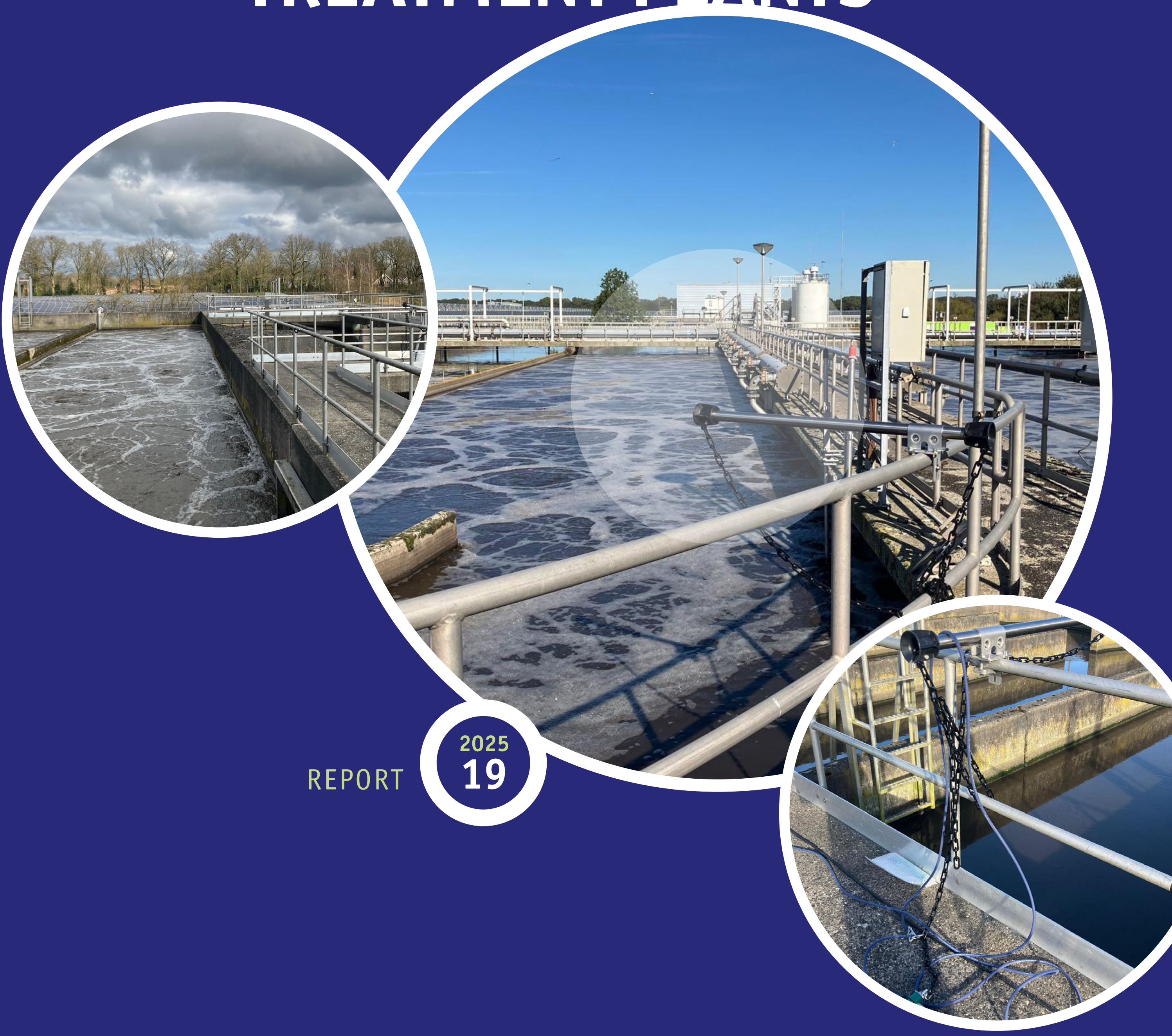
# HANDBOOK MONITORING NITROUS OXIDE EMISSIONS AT WASTEWATER TREATMENT PLANTS



REPORT

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# FOREWORD

**Ten years after the first study on nitrous oxide emissions from Dutch wastewater treatment works, a Community of Practice (CoP) Nitrous Oxide was established in 2019. The CoP has significantly contributed to accelerating nitrous oxide research in the Netherlands. The Dutch Water Authorities have the ambition to be Climate Neutral in 2030.**

With the start of the Nitrous Oxide Acceleration Program in 2024, the research into nitrous oxide emissions has gained even more momentum. By the end of 2025, it is expected that continuous nitrous oxide measurements will be conducted at approximately 60 treatment works in the Netherlands, and this will continue until the end of 2027! This will in the future and already now provide a wealth of information. The lessons on setting up a good monitoring campaign for measuring nitrous oxide emissions to achieve a reliable and uniform emission factor are shared in this report. We do this from a Dutch perspective, but the lessons learned are valuable for everyone. With the experience from the Netherlands, the lessons learned can be directly applied and contribute to accelerating nitrous oxide research that is now being set up and started worldwide.

The objectives of the acceleration program in the Netherlands are:

- Determine the actual nitrous oxide emissions per WwTW as accurately as possible, to ultimately establish emission factors for the Netherlands that are internationally recognized
- Determine a validated set of mitigation measures, that provide insight into the effect of mitigation measures on the nitrous oxide emissions

To achieve these goals, a lot of work has been done in the Netherlands over the past two years to establish a monitoring protocol that ensures a uniform method of measuring and calculating emission factors. The experiences and knowledge described in this handbook come from all 21 Water Authorities participating in the acceleration program in the Netherlands. In this handbook, we address:

- Determining the correct nitrogen load treated in the treatment work, which is essential for calculating an emission factor.
- Determining the number of sensors to be placed and where to place them, and how to perform a location determination. The next step is the purchase and installation of the sensors.
- Calibrating and replacing the sensor head at the right time is essential to achieve a reliable and as complete as possible dataset! To achieve this, it is also crucial to detect deviations in time and take the appropriate actions immediately.
- Calculating nitrous oxide emissions and presenting the data that needs to be available for this.
- Presentation of which process parameters are valuable to measure and collect to gain maximum knowledge about the level of emissions and how to reduce them!

Mark van der Werf
Director STOWA

# THE STOWA IN SHORT

### HOW WE WORK

STOWA is the knowledge and innovation hub for regional water managers in the Netherlands, serving the water authorities and provinces. We help them gain the insights and knowledge they need to tackle regional water management challenges more effectively. We do that by identifying and prioritizing key research questions through dedicated program committees. We commission our research from a range of experts, consultancies, institutions, and universities, and oversee them in their work.

Once the research is complete, we ensure that the findings are shared widely within the broader water management community. We also promote experience and knowledge sharing through events, working groups, excursions, conferences and communities of practice. We work together with ministries, Rijkswaterstaat, municipalities and water companies, among others.

### OUR RESEARCH FOCUS

STOWA's research covers all facets of water management, from flood defense and urban water management to water treatment and systems. Key themes include climate adaptation, flood protection, water quality and ecology, energy transition and circular economy.

The research questions we address span technical disciplines, the natural sciences, governance, legal frameworks and the social sciences. All our work is geared towards providing practical solutions for regional water managers. This is central to our mission as the Foundation for Applied Water Research.

### WHO WE ARE

As a knowledge organization, STOWA is independent, impartial and transparent. Users of our knowledge can trust that the findings in our reports are objective and balanced. This ensures that our knowledge provides a reliable foundation for improving water management and fostering innovations to meet today's and future challenges. The regional water managers themselves decide how to apply STOWA's insights in practice. While STOWA can serve as advisor, we do not play a role as implementors or directors.

STOWA is a non-profit foundation and follows the guidelines for non-profit organizations (RJ-640). Our annual report includes both financial statements and a detailed overview of the foundation, its activities and key statistics.

# HANDBOOK MONITORING NITROUS OXIDE EMISSIONS AT WASTEWATER TREATMENT PLANTS

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# 1

# INTRODUCTION

## 1.1 BACKGROUND

### 1.1.1 ACCELERATION PROGRAMME NETHERLANDS

The Dutch water authorities have the ambition to achieve climate neutrality by 2035. Understanding the extent of nitrous oxide emissions and how to reduce them is an important part of achieving this ambition. Over the past 15 years, a lot of insight has already been gained into the possible extent of emissions, what influences them and how they can potentially be reduced. The main observations from 15 years of nitrous oxide research in the Netherlands and abroad are:

- The internationally established IPCC emission factor (EF) for nitrous oxide (1.6 kg $N_2O$-N/ kg N-$tot_{influent}$) is not fully representative for the Dutch situation.
- The process parameters causing nitrous oxide emissions are well known, but it is still unclear how they can be controlled, i.e. what are possible measures to reduce the nitrous oxide emissions, what is the effectiveness of the implied measures and how do these measures affect effluent quality and, for example, electricity and chemical consumption?

For the water authorities to achieve climate neutrality in 2035 there is a need to accelerate the knowledge around estimating and reducing nitrous oxide emissions at Wastewater Treatment Works (WwTW's). An acceleration programme that was established in 2023 and administratively approved provides the desired acceleration. The main objectives of the program are:

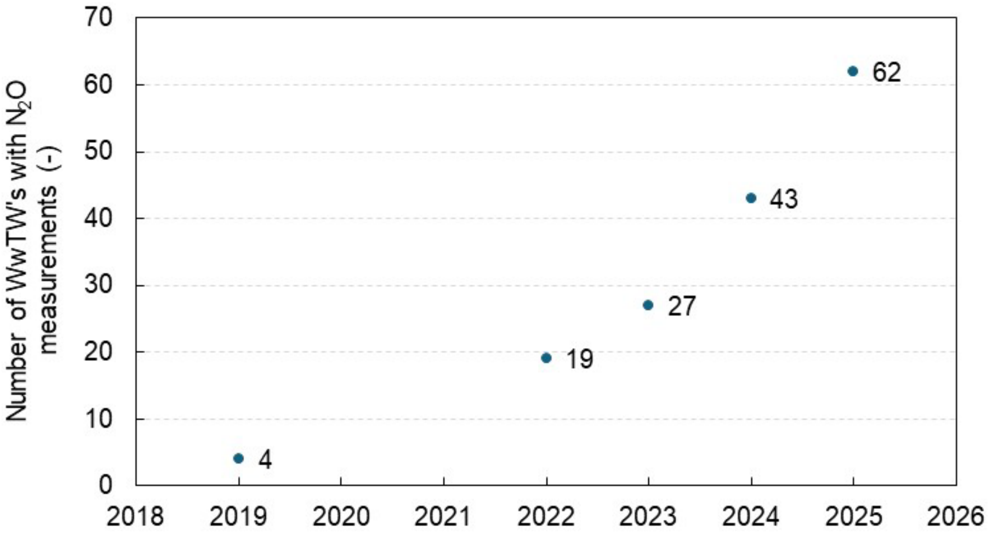
1. To determine the actual nitrous oxide emissions per WwTW as accurately as possible, to ultimately establish emission factors for the Netherlands that are internationally recognized.
2. To determine a validated set of mitigation measures, that also provide insight into the effect (percentage of reduction) of the mitigation measures on the nitrous oxide emissions.

To achieve the goals of the acceleration programme, it is **important** that the determined emission factors for nitrous oxide are expressed in kg $N_2O$-N per kg nitrogen influent. Given the time, energy and costs involved in the acceleration programme, it is important that the measurements performed, and the associated results are reliable and comparable. Therefore, it is necessary that the measurements and calculations within the acceleration programme are carried out in a consistent and reliable manner. To achieve this, a monitoring protocol has been established that prescribes the setup of an accurate measurement campaign. This monitoring protocol was created based on the knowledge and experience gained by all participating water authorities and the suppliers of the nitrous oxide sensors. For comparability, emission factors for each WwtW are expressed in kg $N_2O$-N per kg nitrogen.

### 1.1.2 ESTABLISHMENT OF ACCELERATION PROGRAMME NETHERLANDS

The acceleration programme builds on the nitrous oxide research that started in 2019 or earlier at several water utilities. At the same time, the Community of Practice (CoP) Nitrous Oxide was established. This led to an increase in the number of WwTW's that started measuring the nitrous oxide emissions prior to the start of the acceleration programme. This is illustrated in Figure 1.

**FIGURE 1** NUMBER OF WWTWS IN THE NETHERLANDS WHERE NITROUS OXIDE IS MEASURED FROM 2019 (START COP). THE ACCELERATION PROGRAMME WAS ESTABLISHED IN 2023



When the programme was established and approved (2023), measurements were already being taken at 27 WwTWs, whereas in 2019 there were four WwtW's which were measuring the emissions. The programme officially started in 2024, and by the end of that year, the number of WwTWs with nitrous oxide measurements was 43. By the end of 2025, this number will have increased to 62. This is also the total amount of WwTWs that will be monitored for the remainder of the program's duration until the end of 2027.

The process data (both online and laboratory data) are centrally collected in a national database for almost all WwTWs, which is linked to a program called "Z-info". The database stores the process data of the WwTWs and pumping stations of 19 water utilities. This database is used to collect all the raw data needed to calculate the nitrous oxide emissions and emission factor. For the acceleration programme, a special calculation module has been built that uses the data from the database to calculate nitrous oxide emissions, which can then be reported, for example, as a trend. This work will be carried out in 2025 and will result in the emission factor being calculated uniformly for all participating WwTWs, making them comparable. The method for validating the data (i.e., for the calculations) is yet to be determined.

The four-year research is funded by the 21 water boards themselves, but a contribution has also been provided by the Ministry of Climate and Green Growth.

## 1.2 THE SCOPE AND OBJECTIVE

The objective of this manual is to provide a guide, based on the knowledge and experience gained in the Netherlands, to set up and carry out a monitoring campaign for nitrous oxide emissions. The manual also aims to share and spread this knowledge outside the Netherlands and to provide practical tools for those who want to start determining and/or reducing nitrous oxide emissions from a WwTW.

It is important to note that the practical/technical feasibility of the prescribed protocol needs to be considered for each location, and a pragmatic solution should be considered. Therefore, the manual presented here is still a document that will be adjusted and supplemented during the acceleration programme.

Finally, we do realize that we are writing this manual from a Dutch perspective. In the Netherlands more than 300 WwTWs must comply with a nitrogen requirement of 10 mg/l (or lower in case of requirements from the Water Framework Directive (WFD)) and total phosphorus requirements between 1 and 2 mg/l. Because of the new urban wastewater treatment directive (UWTD), which has been in place since 2024, these requirements will become stricter. In result of the strict discharge requirements both the denitrification and nitrification process takes place at a Dutch installation. This is certainly not always the case for WwTWs outside the Netherlands, where less stringent requirements apply and, for example, only COD or ammonium needs to be removed. The presence of a denitrification tank can influence the measured nitrous oxide emissions, the denitrification is both a source and a mitigation measure to reduce nitrous oxide during nitrification. To meet the strict discharge requirements, most Dutch WwTWs are also designed as ideally mixed tanks. Outside the Netherlands, where less stringent requirements may have been set for effluent quality, treatment is often carried out in plug flow reactors. In such reactors, the concentration of components such as ammonium is higher than in ideally mixed tanks. WwTWs in the Netherlands do have a plug flow reactor, often for nitrification. The experiences of these reactors are included in this manual.

# 2

# EMISSION FACTORS AND MEASUREMENT CAMPAIGN REQUIREMENTS

## 2.1 PAST, PRESENT AND FUTURE OF EMISSION FACTORS

Since the first Foundation for Applied Water Research (STOWA) study started in 2008, the emission factor for nitrous oxide has been regularly adjusted. In the Netherlands, around 2008, an emission factor of 1% was applied based only on research into nitrogen conversion in soil. Later, the 2006 IPCC factor of 0.035% was applied, based on only one study on a WwTW not designed for nitrogen removal (Daelman, M.R.J., 2014)[1] . In 2019, the IPCC emission factor was adjusted to 1.6% based on 30 studies in which the emissions were measured at WwTWs. However, this dataset still shows a large variation where the lowest and highest emission factors differ by a factor of three (Song et al., 2024)[2]. In 2022, the results of a re-analysis on the dataset of 30 studies were published by de Haas & Andrews[3] . Based on this re-analysis, the IPCC2019 emission factor was adjusted to 1.1%, which was recognized by the IPCC as the emission factor to be used for New Zealand. Since 2024, this emission factor does also apply for the Netherlands.

Since the first studies were conducted in the Netherlands, and in many other countries, it has been made clear that one emission factor for all WwTWs is not representative. The observed variation **between** WwTWs, and **at** WwTWs, is far too big. Another important drawback is that the current emission factor assumes the input nitrogen load in the influent based on which the amount of nitrous oxide is calculated (kg $N_2O$-N/kg $N_{influent}$). This means that reductions in nitrous oxide emissions at the WwTW will never be visible in the emission factor. Understanding to what extent nitrous oxide emissions are reduced is very important, in addition to having a good understanding of the extent of emissions.

Therefore, the acceleration programme aims to develop a set of emission factors that are more representative of the Dutch situation, while also accounting for the different treatment configurations and process parameters. The research focuses on identifying treatment parameters (configuration, presence or absence of digestion, sludge load, etc.) that are distinctive for the measured nitrous oxide emissions. This should lead to a decision tree from which an emission factor per WwTW can be derived. This approach acknowledges the variations between WwTWs, but the emission factor will still be expressed as a percentage of the influent nitrogen load. This is to align with the current IPCC methodology, which is necessary for the IPCC to recognize the derived emission factors.

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[1] Daelman, M.R.J., 2014, Emissions of methane and nitrous oxide from full-scale municipal wastewater treatment works, PhD Thesis, TU Delft.

[2] Song, C. et al, 2024, Oversimplification and misestimation of nitrous oxide emissions from wastewater treatment works, Nature Sustainability, volume 7, October 2024, p. 1348 - 1358.

[3] De Haas, David, and John Andrews, 2022, Nitrous oxide emissions from wastewater treatment - Revisting the IPCC2019 refinement guidelines, Environmental Challenges 8, 100557.

## 2.2 PURPOSE OF MEASUREMENT CAMPAIGN

The way a measurement campaign for nitrous oxide emissions is set up and conducted depends on the desired goal. The goal may be to gain insight into the magnitude of the emissions (emission factor) alone, or it may be to gain insight into the conditions under which nitrous oxide is formed (formation processes) and how to prevent these conditions from occurring, thereby reducing nitrous oxide emissions.

The dataset from the second STOWA study[4] on nitrous oxide emissions at the WwTW Kralingseveer was used by Daelman et al., 2013[5] and Vasilaki et al., 2020[6] to determine how long a measurement campaign should last and what the measurement frequency should be to achieve a reliable emission factor for nitrous oxide. Both studies reached the same conclusions:

- If the goal is to gain insight into the emission factor for nitrous oxide from the WwTW, continuous measurement of nitrous oxide emissions over a year is not necessary. ‘Grab samples’ collected throughout the year on weekdays (at random times) will suffice.
- If the goal is to also gain insight into formation processes, then online measurement with a high measurement frequency is a must!

In line with these conclusions, the Dutch acceleration programme has been designed. Since the objective of the acceleration programme is to gain insight into both the emissions and the reduction of emissions, continuous monitoring of nitrous oxide emissions has been adopted. Continuous measurement over a whole year provides insight into the “baseline situation” of the WwTW, after which reduction measures are investigated. It is thereby considered that emissions at WwTWs can vary between years, for example, due to differences in ‘dry’ and ‘wet’ years. To gain insight into the amount of the emissions, the incoming nitrogen load is determined based on the regular sampling program, in which the incoming nitrogen load is measured several times per week or per month (depending on the size of the WwTW). For insight into reduction possibilities, such an approach is not sufficient because years of research in the Netherlands and abroad have shown that nitrous oxide emissions are highly variable. Not only between WwTWs, but also within the WwTW, emissions vary greatly throughout the day and at least hourly. This makes it clear that to gain a good understanding of the possibilities to reduce nitrous oxide emissions, the emission factor (kg $N_2O$-N per kg $N_{incoming}$) must be made visible per quarter hour[7]. This requires (semi) continuous measurement of the incoming nitrogen load.

## 2.3 READING GUIDE

The following parameters are then briefly required to determine the emission factor:

- Incoming nitrogen load based on 24-hour composite sample.
- Incoming nitrogen load based a measurement on at least a quarter-hourly basis.
- Nitrous oxide concentrations and air flow on at least a quarter-hourly basis, to be able to calculate emission factors on a quarter-hourly basis.

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[4] STOWA, 2012, Emissie broeikasgassen vanuit RWZI’s, rapportnummer 2012-20.

[5] Daelman, M.R.J., de Baets, B., van Loosdrecht, M.C.M., Volcke, E.I.P., 2013, Influence of sampling strategies on the estimated nitrous oxide emissions from wastewater treatment plants, Water Research, 47, p. 3120-3130.

[6] Vasilaki, V., Danishvar, S., Mousavi, A., Katsou, E., 2020, Data-driven versus conventional N2O EF quantification methods in wastewater; how can we quantify reliable annual EFs?, Computers and Chemical Engineering, 141, 106997.

[7] Without this data, it is not possible to understand the actual causes of nitrous oxide formation and how these can be eliminated through adjustments in the operation and/or design of a treatment plant. Monitoring only the nitrous oxide concentration is not sufficient to gain insight into the causes and reduction possibilities of nitrous oxide emissions. There is no linear relationship between the ammonium load and the measured nitrous oxide concentration.

After this chapter, **chapter three** will discuss how to determine the required nitrogen loads, based on which a reliable emission factor can be calculated. **Chapter four** focuses on the determination of nitrous oxide emissions, covering: the design of the measurement campaign, the purchase and installation of sensors, the management and maintenance of the sensors, how the data should be processed, and how the nitrous oxide emissions should ultimately be calculated. At the end of chapter four, the elements from chapters three and four come together, and it is explained how the emission factor calculation should be performed. The final and **fifth chapter** briefly discusses which additional measurements are necessary/very valuable to get the most out of a nitrous oxide study.

# 3

# DETERMINATION OF NITROGEN LOAD

## 3.1 FOCUS ON EMISSION FACTOR ONLY

The nitrogen load in the raw influent is determined through the regular sampling program. The required data is the concentration of $N_{Kj}$ in the influent, and the flow rate at sampling. The concentration of $N_{Kj}$ and the flow rate at sampling determine the incoming nitrogen load needed to calculate the emission factor. The concentration of $N_{Kj}$ gives insight into which part of $N_{tot}$ is in the influent as ammonium and organically bound nitrogen. The nitrogen load (kg N/d) in the raw influent is then calculated as follows:

$$(N_{Kj,\ raw\ influent}\ (mg/l)\ x\ Q_{at\ sampling}\ (m^3/d))/1000$$

For most WwTWs in the Netherlands, the incoming nitrogen load is only determined based on an $N_{Kj}$ measurement, because nitrate and nitrite concentrations are often negligible. However, at some WwTWs these concentrations may be higher, and an $N_{tot}$ of the influent is also available. For these WwTWs, the $N_{tot}$ load should be entered in the formula.

## 3.2 FOCUS ON EMISSION FACTOR AS WELL AS REDUCTION

For a nitrogen load on a quarter-hourly basis, a continuous measurement (or at least with a frequency of 3-4 times per hour) of the raw influent is needed. Combined with continuous flow measurement, this can determine the incoming ammonium load on a quarter-hourly basis. In the Netherlands, a distinction is made between WwTWs without and with primary sedimentation tanks. For WwTWs without a primary sedimentation tank, the ammonium measurement is placed in the raw influent. For WwTWs with a primary sedimentation tank, the ammonium measurement is placed in the overflow of the primary sedimentation tank. Any reject water flows from the dewatering installation are then also included in the nitrogen load going to the biological tanks. For the acceleration programme, the use of an ammonium analyser is strongly preferred, but a UV/Vis meter can also be used as an alternative.

With only a measurement of ammonium concentration, a conversion from ammonium to $N_{Kj}$ or N-tot is still needed. For this, a ratio between NKj and $NH_4$-N or between N-tot and $NH_4$-N needs to be determined. This can be done by using historical laboratory data of the raw influent. Data for both $NH_4$-N and NKj or N-tot should be available for this purpose. Based on historical data, an initial NKj/ $NH_4$-N or N-tot/ $NH_4$-N ratio can be determined. From the start of the measurement campaign, these ratios can be calculated as a moving average based on new data. With this moving average, the NKj or N-tot quarter-hour basis can then be calculated from the ammonium quarter-hour basis data.

### 3.2.1 AMMONIUM ANALYSER

The disadvantage of an ammonium analyser in the raw influent is its susceptibility to fouling and a higher degree of maintenance. It is therefore necessary to install a filtration (filtrax plates)/settling system in front of the analyser. To purchase an ammonium analyser, a tender was carried out by one of the participating water authorities. Here, the requirement was that a “Demonstrable positive experience for measurement in raw influent for at least one year” had to be submitted. Only Hach Lange was able to meet this requirement.

The measurement of ammonium in raw wastewater requires additional attention into the management and maintenance of the analyser. With cleaning once, but preferably twice a week of the analyser and filtrax plates, reliable measurement results are achieved. Maintenance and management of the filtrax analyser system is carried out on a weekly basis by the water utilities themselves.
Major maintenance by the supplier (Hach Lange) is performed on call. It is expected that calibration of the analyser will be more frequent when it measures in the influent, compared to a measurement in the activated sludge system. The use of an ammonium analyser typically provides a maximum of four measuring points per hour. The nitrogen load per quarter-hour (kg N-tot) in **the influent** should then be calculated as follows:

$C_{NH4\text{-}N}$ (mg/l$_{)}$x factor NKj (or N-tot)/$NH_4$-N (-) x$\Sigma$ Q (m$^3$/quarter)

### 3.2.2 UV- VIS MEASUREMENT N-TOT

An alternative to an ammonium analyser is to use a UV-VIS sensor. Such a sensor is supplied in the Netherlands by IMD. This sensor does allow direct measurement of N-total, in addition to other components such as TOC, with an interval of 1 to 2 minutes[8] . The disadvantage of this sensor is that a calibration is required for each site. Such a calibration (pilot) is needed per location to determine whether the sensor is applicable to the WwTW in question.

With a UV/Vis measurement, the N-tot concentration can be measured almost continuously. In this case, these measurements can be directly combined with the flow data of that time. By then averaging these results, the nitrogen load (kg) of that quarter of an hour is calculated as follows:

$$\Sigma\ (N_{tot}\ (\text{mg/l})\ \text{x}\ Q\ (\text{m}^3/\text{minute}))\ /\ n_{\text{monitoring point}}$$

---

[8] Information IMD (Unisense user day presentation 15 October 2024).

# 4

# DETERMINATION OF NITROUS OXIDE EMISSIONS

In the Dutch nitrous oxide acceleration programme, the decision was made to measure the nitrous oxide concentration in the liquid phase using sensors from Unisense. The considerations for this choice are:

- Measurements in the liquid phase are easier to implement and more accessible.
- The availability of the data is considered greater than with gas measurements, considering that measurements need to be taken at 50 to 60 WwTWs.
- A measurement in the liquid phase may be easier to implement in a process control system in the future.

To verify the sensors, the nitrous oxide concentration in both the water and gas phases will be measured at three fully covered WwTWs. Measurement in the gas phase is possible with a floating box that can be placed on the surface of part of the activated sludge system. Various suppliers are now available for this method of measurement, but in the acceleration programme, only the Unisense sensor is used. This means that in the remainder of this chapter, this will be the basis for the design and execution of a monitoring campaign.

## 4.1 SETUP OF THE MEASUREMENT CAMPAIGN

To obtain a reliable dataset, it is important to install the correct number of sensors at a WwTW and to place them in the right locations. Several studies have been conducted on the most common configurations in the Netherlands to determine the appropriate number of sensors and their optimal placement. This paragraph provides a summary of these findings. Appendix 1 describes the details for each configuration.

### 4.1.1 NUMBER AND LOCATION OF SENSORS

Nitrous oxide is formed during both nitrification and denitrification. Typically, these conversions take place in different zones of the tank and at different times in the WwTW. In the Netherlands, various treatment configurations are used for the treatment of municipal wastewater. This means that the placement of sensors can vary depending on the treatment configuration. The mixing pattern of the WwTW must also be considered whether it is plug flow or ideally mixed. Table 1 provides an overview of the number of sensors to be installed and the locations where they should be placed. For each configuration, it is indicated in which tank(s) at least one sensor should be present to meet the goals of the acceleration programme (see section 1.1.1).

**TABLE 1** **NUMBER OF SENSORS TO BE PLACED AND THE LOCATION(S) WHERE THEY SHOULD BE PLACED PER TREATMENT CONFIGURATION**

| Configuration | Number of sensors | Location(s) |
|---|---|---|
| A/B system | 2 | A-stage: at the end<br>B-stage: representative location |
| PhoSim | 1 | Simultaneous nitrification-denitrification tank |
| PhoRedox | 2 | End of pre-denitrification<br>Simultaneous nitrification-denitrification tank |
| (m)UCT | 2 | Beginning of facultative tank<br>Nitrification tank |
| Hoogvliet | 2 | Nitrification tank<br>Simultaneous nitrification-denitrification tank |

For (m)UCT and Hoogvliet systems, ideally three sensors are placed, one in each tank. However, a third sensor always requires a new controller, which increases installation costs. Therefore, the acceleration programme has chosen to use two sensors for (m)UCT and Hoogvliet systems. In an (m)UCT system, one sensor is placed at the beginning of the facultative zone (any nitrous oxide present from the pre-denitrification is stripped here or is taken as emission from the anoxic zone), the second sensor is placed in the nitrification tank. The nitrous oxide emission from the facultative zone can be calculated based on the methodology for aerated tanks (see more details in section 4.5.4). In a Hoogvliet system, the nitrification tank is often a plug flow reactor. In this case, the most representative location for the first sensor should be determined based on a location assessment. The second sensor can be placed in the simultaneous nitrification-denitrification tank. Two water utilities with a Hoogvliet system have placed three or more sensors, one of which is at the end of the pre-denitrification stage. The results of these measurement data will be verified in the programme to determine whether two sensors in a Hoogvliet or (m)UCT system can provide a reliable emission factor.

The determination of the most representative location for a sensor in ideally mixed aeration tanks were or are carried out at 24 WwTWs. More details about this are presented in Appendix 1. The local determinations that have been executed show that the concentration of nitrous oxide in ideally mixed tanks is almost homogenous[9]. For this reason, location determination is no longer required for these kinds of tanks. However, it is important not to place the sensor in the inner bend of a ring in an aeration tank. For tanks with a plug flow character, a location determination is always required. Based on this determination, the most representative location in the tank can be selected.

### 4.1.2 LOCATION WITH SURFACE AERATION

Measuring nitrous oxide concentrations and calculating nitrous oxide emissions in a WwTW with surface aerators is more challenging than in a WwTW with bubble aeration. When placing sensors in the aerated zone, it must be ensured that the nitrous oxide measurement is not damaged by the presence of the surface aerator. Additionally, the difference in how the air is dissolved in the water makes the determination of mass transfer ($k_LA_{N2O}$) more difficult than with bubble aeration. There are two scientific articles available that have examined the best location for measurements and the method for determining $k_LA_{N2O}$. The main findings are:

- The mass transfer coefficient $k_LA_{N2O}$ was determined based on the $k_LA_{O2}$ over the entire tank (Ye, et al., 2014) and by zone (immediately before surface aerator, one meter after surface aerator and 10 meters after surface aerator) by Domingo-Félez et al.

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[9] Due to a high recirculation factor (relative to influent) of 100 or higher, most tanks in the Netherlands are ideally mixed.

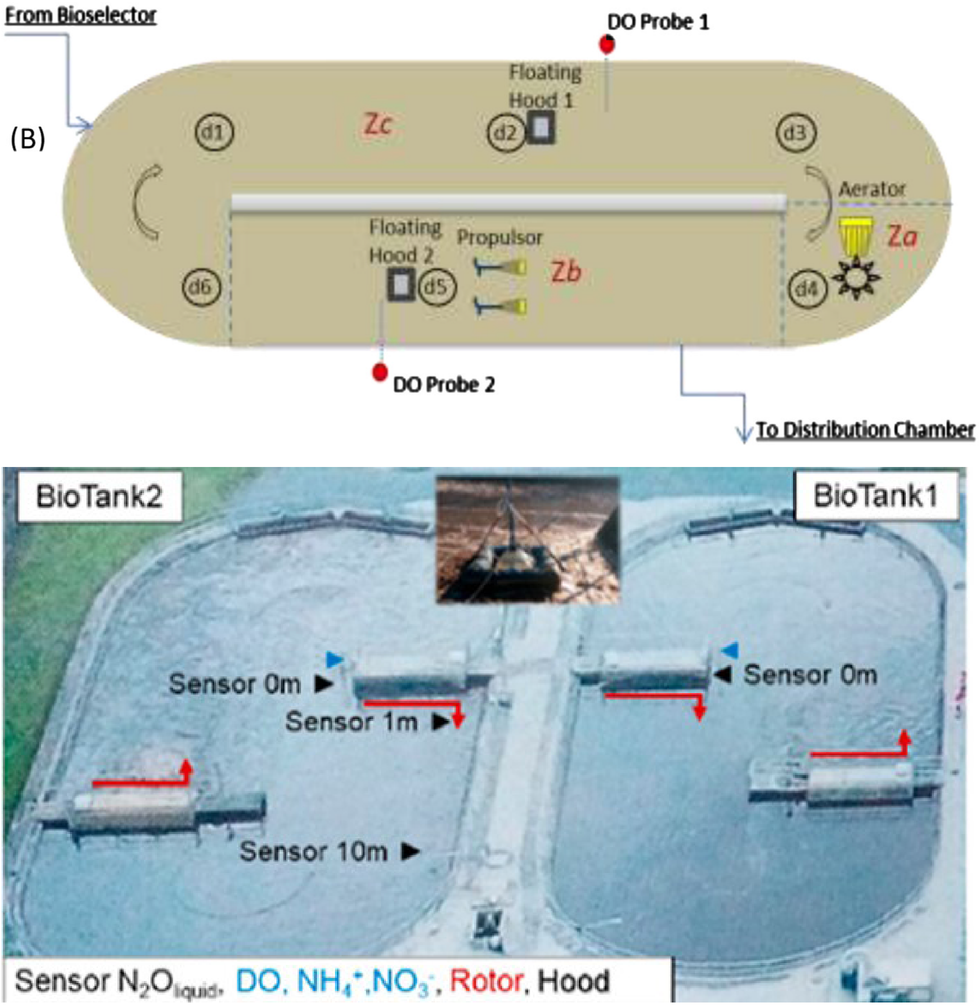
- The article by Ye, et al, 2014 shows on the basis of model-only calculations that 90% of nitrous oxide emission takes place within the aerated zone close to the surface aerator (Za), 8% of the emission takes place halfway down the leg where the surface aerator is installed (Zb), the remaining 2% takes place halfway down the bend (Zc) towards the surface aerator (for locations see Figure 2).
- The article by Domingo-Félez et al, 2024 shows, based on measurements, that just after the surface aerator (Sensor 1m) 94% of nitrous oxide emission takes place. Just before the surface aerator (Sensor 0m), the contribution to the total emission is 4% and 2% 10 meters after the surface aerator (Sensor 10m). Thus, these measurement-based findings agree well with the modelled data of Ye, et al., 2014).

The last two findings clearly show that most of the emission takes place in the vicinity of the surface aerator. To determine emissions in WwTWs with one or more surface aerator(s), one or more sensors should be placed at the following locations:

- The first sensor as close as possible **before** the surface aerator which is almost on (make sure this is easily and safely accessible for calibration and that there is sufficient distance so that no damage can occur). In the situation where there is no space directly in front of the surface aerator, because the supply from a selector enters directly at the surface aerator, the first sensor should be placed immediately after the surface aerator.
- For WwTWs with one surface aerator in the tank:
  - A second sensor at least 10 meters away from the surface aerator to determine the proportion from the anoxic zone.
- For WwTWs with two surface aerators in the tank:
  - Place the second sensor just in front of the second surface aerator so that it measures the contribution from the anoxic zone when this surface aerator is off or measures the emission when this aerator is on.

In a system with two or more surface aerators, ideally a sensor is placed just before the next surface aerator (third, fourth). Possibly, a location determination can first give insight into whether the placement of a third and/or fourth sensor is desirable. Such a determination can reveal whether emissions around a third and/or fourth surface aerator contribute significantly.

**FIGURE 2** **SITES STUDIED FOR NITROUS OXIDE EMISSIONS IN A BYPASS SYSTEM WITH SURFACE AERATION. ABOVE FROM ARTICLE YE, ET AL., 2014 AND BELOW FROM ARTICLE DOMINGO-FÉLEZ ET AL., 2024**



### 4.1.3 LOCATION DETERMINATION IN BUBBLE AERATION

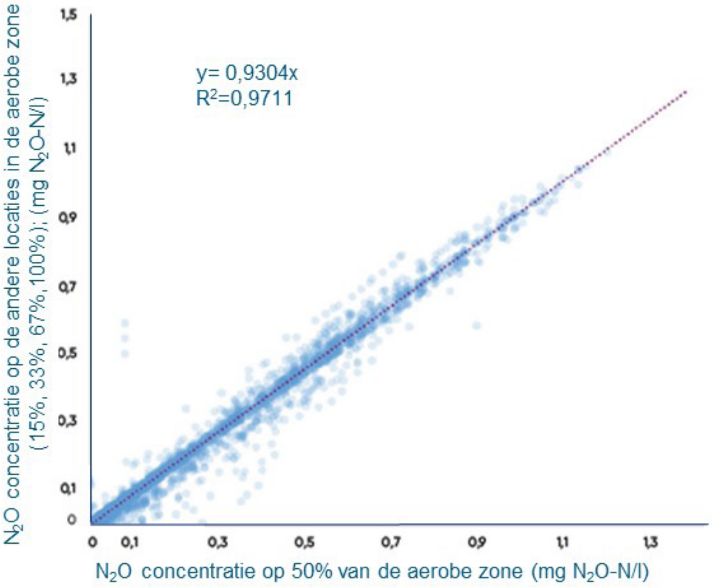
Two methods are possible for performing a location determination (for both mixed tanks and plug flow reactors):

1. Place multiple sensors in one tank, and measure during a period that includes DWF and RWF days adequately. This is to provide insight into whether the concentration distribution across the tank remains the same under different process conditions.
2. Placing one sensor at the beginning of the main aeration field and moving a second sensor along the length of the aeration field.

*Multiple sensors in one tank (method 1)*

When installing multiple sensors simultaneously, a mobile setup can be used that can be temporarily deployed for the sake of location determination. Another option is that when sensors are purchased for multiple WwTWs, the total sensors purchased are deployed at one WwTW for the duration of the location determination, after which they can then be distributed to the different WwTWs. Using this method, a graph can be produced for each of the locations in a tank, plotting the measured concentration at location X against the concentrations at the other locations. An example is shown in Figure 3.

**FIGURE 3** RESULT LOCATION DETERMINATION IN AEROBIC (FULLY MIXED) RING OF THE WWTW OF APELDOORN. [10]



The location determination in Apeldoorn took place in a mixed tank for a period of 111 days. The concentration at one site versus the concentration at the other sites shows a good relationship with high $R^2$ for Apeldoorn (see Figure 3).

*Moving one sensor in combination with one fixed reference sensor (method 2)*

When determining the most representative location, it is important to understand the concentration distribution under as many different process conditions as possible. The minimum measurement period therefore includes both DWF and RWF days. To understand the effect of changing process conditions, place one sensor at a fixed location (reference) at the beginning of the main aeration field (field that is always on) and move the second sensor. The number of locations that should be tested depends on the length of the aeration field. At minimum, the second sensor should also be placed in the middle and end of the aeration field.

In the following way, the most representative location is determined:

1. Calculate the average concentration within the period when the first location (e.g. centre of the tank) was monitored and calculate the average of the reference sensor for the same period.
2. Repeat step two for the second location tested (e.g. end of aeration field) and do the same for possibly more locations.
3. Then apply the same methodology as for method one (see Figure 3).

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[10] Unisense Tech Note, 2024, Positioning of N2O sensors in typical biological wastewater treatment processes

## 4.2 PURCHASE AND INSTALLATION

### 4.2.1 PURCHASE

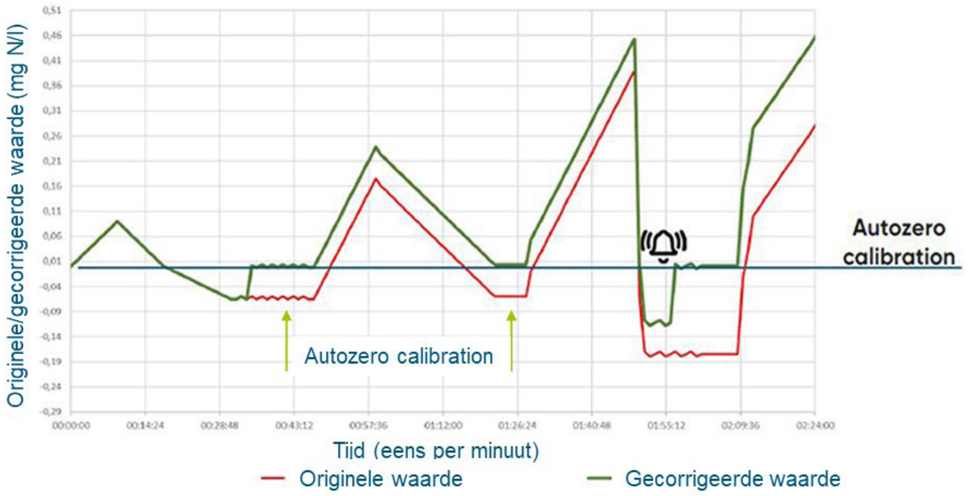
Several aspects should be considered when purchasing the nitrous oxide sensors:

- The total number of sensors required depends on the configuration of the WwTW (see section 4.1.1 ).
- Unisense supplies a Controller which can connect up to two sensors. The maximum recommended sensor cable length between a sensor and a controller is 100 meters. Take this into account when selecting locations of sensors on the WwTW.
- When buying the materials such as cable length, also consider:
  - The sensor remains easily accessible for calibration and maintenance, and that safety is always ensured.
- The sensor head has a limited lifetime of six months. For this reason, Unisense has as a possible service that the first sensor head can be delivered after the complete installation of the controller and sensor body.
- When starting measurements and replacing the sensor head, consider the delivery period of the sensor(s). The expected delivery time is around two weeks depending on the number of other orders at Unisense.
- From October 2023, all controllers will have Auto-Zero correction. If the controller was purchased before then**, the Auto-Zero correction should be added** to the controller's software. These new controllers also raise an **alarm** when the **temperature change** is **± 3°** C and when a new two-point calibration **is required.**

**OPERATION - AUTO-ZERO CORRECTION**

When the sensor shows values between 0.00 and -0.05 mg $N_2O$-N/l for 15 minutes, a "zero-point calibration" takes place automatically. From then on, the nitrous oxide concentration is again visible as 0.00 mg $N_2O$-N/l and the measurement points will start again from zero. On the controller screen, both values are visible, the value with auto zero correction and the value without auto zero correction (and can also be read out to, for example, SCADA). The moment the values are continuously lower than -0.05 mg $N_2O$-N/l, an alarm will be given and a new two-point calibration may have to be performed. The figure below illustrates this graphically.

**FIGUUR 4 DISPLAY OPERATION AUTO ZERO CORRECTION**



### 4.2.2 INSTALLATION

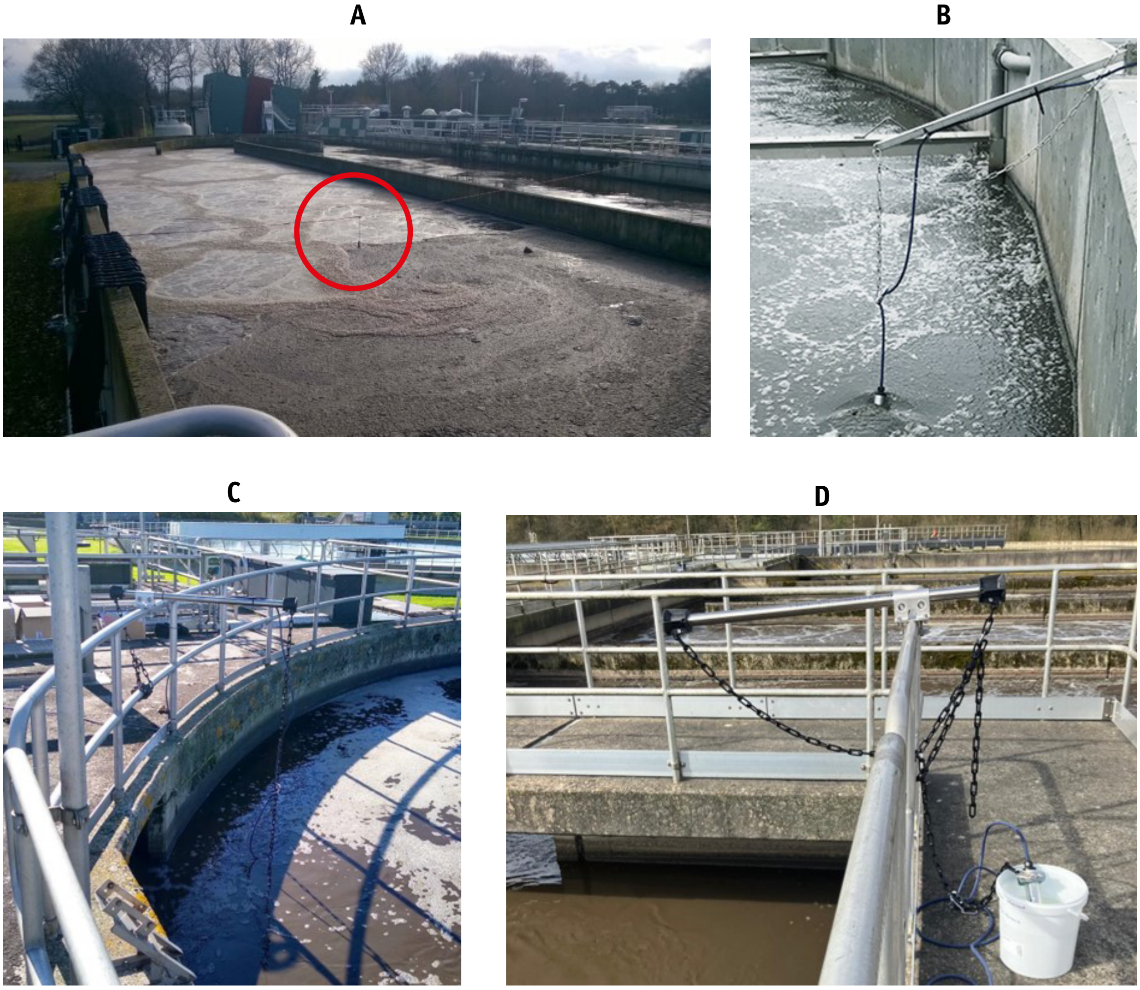
The following should be considered when placing and installing the sensors:

- A sufficient distance is maintained from the edge of a tank/basin.
- The entire sensor is submerged, so that the temperature measurement in the sensor body is also in the water phase.

The sensors must be mounted in such a way that damage to the sensor head is prevented, see examples in Figure 5. The sensors are mounted so that they remain in a fixed position due to the flow profile. This way, they cannot be damaged by, for example, drifting against the wall. It is recommended to mount the sensors with materials that are resistant to extreme weather and wear. Other points to consider during installation are

- Do not place the metal holder directly on the aluminium housing of the sensor this to prevent rust formation of the sensor.
- That the sensor cable (blue) does not rub along the edge of the tank.

**FIGURE 5** **EXAMPLES OF MOUNTING UNISENSE SENSORS: A SENSOR IN CENTRE OF THE LANE (SOERENDONK), B: SENSOR IN AERATED PART OF WWTW IN EINDHOVEN, C: SENSOR AT THE WWTW NIEUWE WATERWEG, AND D: SENSOR WITH POSSIBILITY OF PROPER CALIBRATION AT WWTW OLDENZAAL**

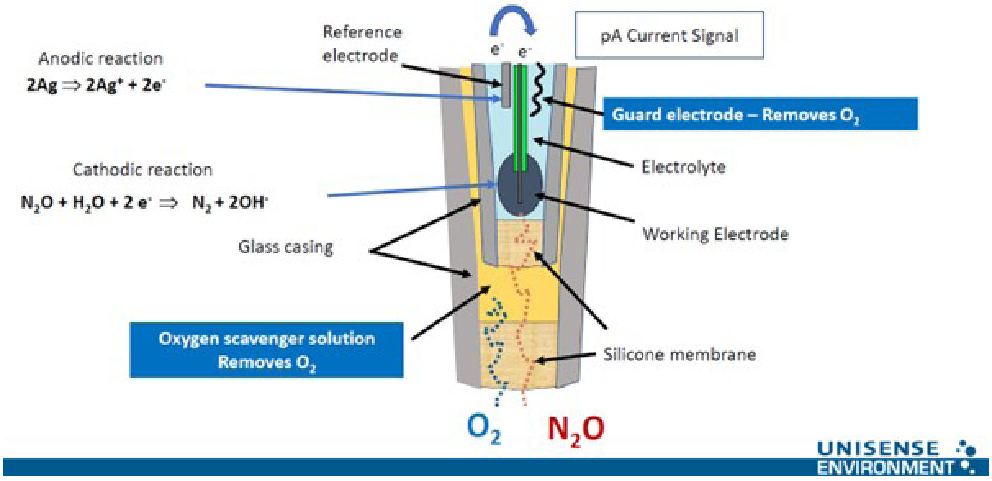


## 4.3 MANAGEMENT AND MAINTENANCE

### 4.3.1 WORKING PRINCIPLE UNISENSE SENSOR

Unisense's sensor measures the concentration of nitrous oxide in the aqueous phase based on an electrochemical reaction. A cross-section of the sensor with the main reaction mechanisms is shown in Figure 6 . For the proper functioning of the sensor, it is important to choose the right sensor at the time of purchase. This is because the sensor must be suitable for the conditions in the WwTW. For most WwTWs in the Netherlands, the "E-$N_2O$ Head SR" is the best suited sensor. This sensor has a detection limit of 0.002 to 0.005 mg N/l and a quantifiable lower limit between 0.008 and 0.016 mgN/l .[11]

FIGURE 6 WORKING PRINCIPLE OF UNISENSE'S SENSOR MEASURING NITROUS OXIDE CONCENTRATION IN THE AQUEOUS PHASE [12]



Due to the use of electrochemical reactions, the sensor head has a limited lifespan. This lifespan is six months. The lifespan can be negatively affected if the conditions in the treatment process deviate too much from the sensor's specifications. These conditions are[11]:

- Higher oxygen concentrations: service life is shortened because the "$O_2$ scavenger solution" is consumed faster.
- Higher nitrous oxide concentrations: the same applies to this as to oxygen, the chemicals needed for nitrous oxide measurement are consumed faster at higher nitrous oxide concentrations.
- Higher temperatures: This can shorten the sensor's lifetime.

### 4.3.2 CALIBRATION AND SENSOR HEAD REPLACEMENT

Proper use of the sensor is essential to measure reliable concentrations and achieve high data availability. Data analysis from the first group of WwTWs that have been measuring for a year or longer has shown that late or improper calibration, and late replacement of the sensor head are the main causes of (large) gaps in the datasets. Based on these lessons, the following calibration and replacement schedule is now prescribed in the acceleration programme:

- Calibration:
    - Calibrate after: 2, 4 and 5 months.
    - Or if a temperature difference of +/-3° C occurs.
- Replacement:
    - After six months, the sensor head should always be replaced (replace the sensor head on a dry day, not during rain, as the inside of the sensor body must not get wet).

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[11] Information Unisense based on implemented ISO certification (see presentation Bastian Pilz, SWIG event 26 February 2025, Coventry).

[12] art of Unisense presentation at SWIG event 26 February 2025, Coventry.

For reliable measurement data, it is important to carry out the calibration properly. The main points of interest are:

- For a new sensor head, or if the sensors have been disconnected (during relocation), calibration should only be performed after 24 hours to allow full polarization of the sensor. An alternative is to purchase an attachment from Unisense along with the sensor, which allows the sensor to polarize more quickly.
- Clean the sensor body thoroughly and, if necessary, carefully clean around the ‘glass’ tip to prevent contamination of the measurement fluid and thus disruption of the calibration. This means that any existing biofilm must be almost completely removed (see example in Figure 7) of extreme biofilm formation on a sensor.
- Wait patiently until the measured value in the nitrous oxide standard solution is stable and note the time it takes to get to a stable signal. This time is an indicator of the sensor head quality, in time this period will become longer as the sensor head is aging, and the quality becomes less. Make sure that the nitrous oxide standard solution is not older than 20 minutes. A new solution should always be made after this period if calibration is still required.
- Perform the calibration at the correct temperature (which is the temperature in the tank) and keep it constant. Additionally, consider an expected decrease (in autumn) or increase (in spring) in temperature during calibration. This can be prevented by calibrating at a temperature that is 1 degree lower or higher than the current temperature in the tank.
- **After** the calibration, enter (in the controller) the temperature of the standard solution.
- Preferably, have the sensor calibration performed by the same person, with a trained individual as a substitute if necessary.

**FIGURE 7** **EXAMPLE OF AN EXTREME BIOFILM ON A NITROUS OXIDE SENSOR (SOURCE RIJNLAND, WWTW VELSEN).**

After completion of the calibration, the following parameters should be recorded in the maintenance log:

- Time duration (response time) between 0-point and second point. This should not exceed 5 minutes. The response time indicates the age and quality of the sensor. As this time increases, it indicates that the sensor head needs to be replaced.
- The slope displayed at the end of the calibration should ideally have a value of 30% but should at least be between 15 and 75%.

- The zero-point should be between -0.050 and 0.000 mg N/l in most cases.
    - This value does not determine the success of the calibration, but it is a signal to look critically at the first two values.

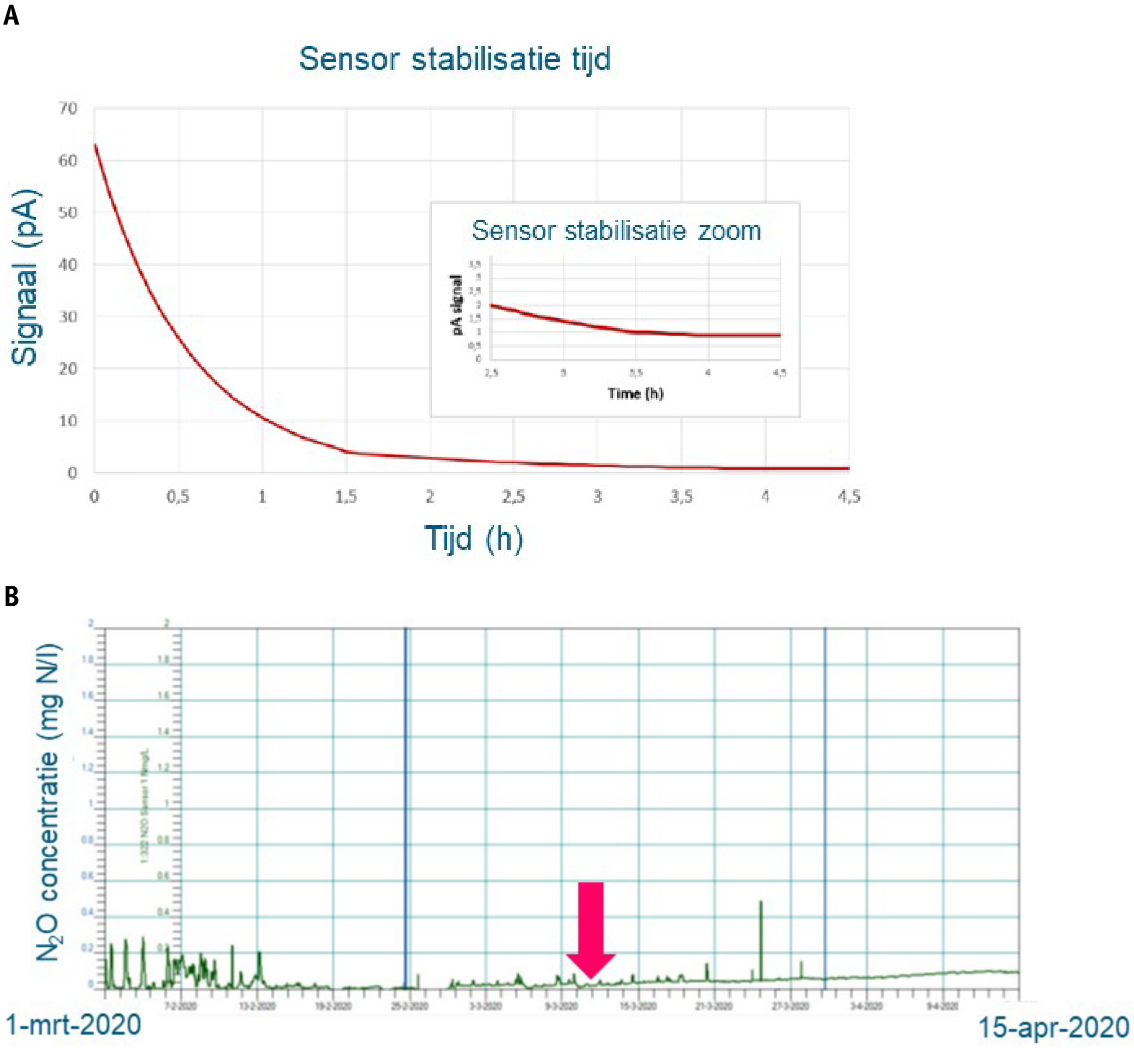
The results can also be read from the controller.

### 4.3.3 DETECT DEVIATIONS IN TIME

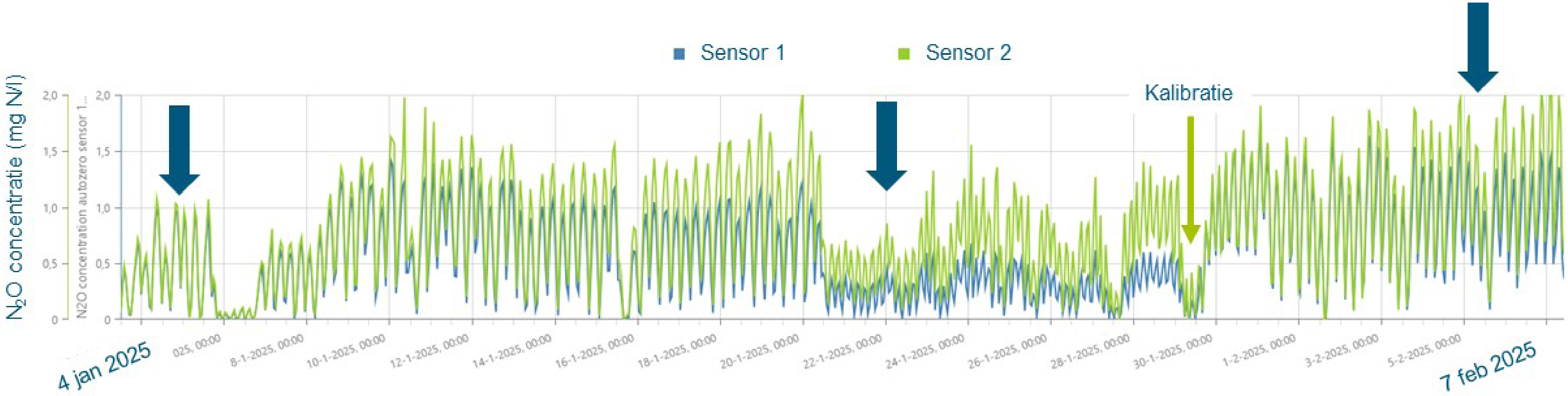
Timely detection of deviations in the measurement data is crucial to prevent large gaps of unusable data in a dataset. Therefore, preferably check daily, but at least weekly, whether logical values are visible. Deviations and alarm signals that require a quick response are:

- Controller boxes delivered from October 2023 onwards will give an alarm if:
    - The change in temperature is higher than +/- 3 °C;
    - When the measured values are continuously lower than -0.05 mg $N_2O$-N/l;
- A drift from the zero line downwards, where the distinction between drift and actual presence of nitrous oxide can only be observed if the concentration exceeds 0.05 mg N/l.
    - A drift downwards can be caused by a change in temperature or by having calibrated before the sensor is fully polarized (see Figure 8 A, source Unisense). With incomplete polarization, this continues after calibration leading to a negative signal.
- A drift from the zero-line upwards.
    - This applies to WwTWs where a clear baseline is visible, and the measurement values often return to zero after an increase (see Figure 8 B, Waterschap de Dommel), but do not do so in case of an upward drift.
    - For WwTWs where no clear zero line is visible, an upward drift can be observed if the measured values clearly deviate from previous comparable periods or a deviation is visible between two sensors that normally give equal values (see Figure 8C, Utrecht, two sensors in one mixed tank).
    - An upward drift mainly occurs with older sensor heads. In this situation, oxygen is captured less and is ‘seen’ as nitrous oxide.
- A straight line, for example, due to a disruption in data access (see Figure 8D, WwTW Nijmegen, Rivierenland).
- The measured value after calibration deviates too much from the value just before calibration.
- Measured value shows zero for unusually long time (several days), while measured values were still visible before.
- Deviating pattern of data at one sensor compared to short period (week) before with no plausible cause.

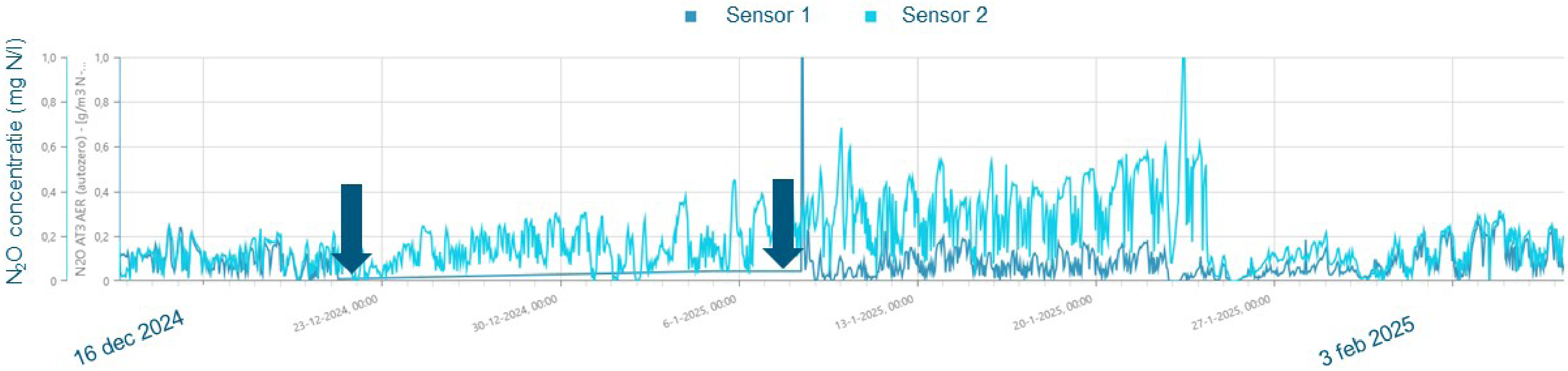
**FIGURE 8** EXAMPLES OF DEVIATIONS THAT CAN OCCUR IN MEASUREMENT SIGNAL OF THE NITROUS OXIDE SENSOR A: DRIFT DOWNWARDS DUE TO NO OR INCOMPLETE POLARIZATION OF THE NEW SENSOR BEFORE THE FIRST CALIBRATION (SOURCE UNISENSE), B: DRIFT UPWARDS, WHERE THE ZERO LINE VISIBLE FROM THE ARROW KEEPS INCREASING (SOURCE DE DOMMEL), C: DEVIATION BETWEEN TWO SENSORS PLACED IN THE SAME MIXED TANK (SOURCE IMD, HDSR), D: EXAMPLE OF NO DATA ACCESS, CREATING S STRAIGHT LINE BETWEEN THE TWO ARROWS (SOURCE IMD, WSRL)



**C**


Sensor 1
Sensor 2
Kalibratie
$N_2O$ concentratie (mg N/l)
N2O concentration autozero sensor 1...
2,0
1,5
1,0
0,5
0
4 jan 2025
025, 00:00
8-1-2025, 00:00
10-1-2025, 00:00
12-1-2025, 00:00
14-1-2025, 00:00
16-1-2025, 00:00
18-1-2025, 00:00
20-1-2025, 00:00
22-1-2025, 00:00
24-1-2025, 00:00
26-1-2025, 00:00
28-1-2025, 00:00
30-1-2025, 00:00
1-2-2025, 00:00
3-2-2025, 00:00
5-2-2025, 00:00
7 feb 2025

**D**


Sensor 1
Sensor 2
$N_2O$ concentratie (mg N/l)
N2O AT3 AER (autozero) - [g/m3 N-...
1,0
0,8
0,6
0,4
0,2
0
16 dec 2024
23-12-2024, 00:00
30-12-2024, 00:00
6-1-2025, 00:00
13-1-2025, 00:00
20-1-2025, 00:00
27-1-2025, 00:00
3 feb 2025

For some of the above-mentioned situations, it is not always clear whether there is a deviation, or if an increase or decrease in nitrous oxide is being measured. In general terms, a deviation is difficult to determine. This is highly dependent on the location(s) of the sensor(s) and the measured values in a WwTW. In a WwTW where lower average concentrations are measured (< 0.2 to 0.5 mg N/l), a deviation of 0.1 mg N/l has a higher impact on the emission factor than in a WwTW where the average concentration is around 1 mg N/l. Not every deviation will be equally visible, but with regular (weekly) checks of the data, one quickly gets a sense of when a nitrous oxide concentration is abnormal or not.

When **in doubt** as to whether an abnormality is visible, action should **ALWAYS** be taken **DIRECTLY**:

- Check if a deviation is not logically explainable (is somewhat arbitrary, but a person who knows the WwTW well can often determine this).
- Perform measurement in zero solution (tap water) and in nitrous oxide standard solution (both with wastewater temperature).
- Check if the approximate values indicate a correct value of ~0 or ~0.94 mg N/l.
- If values deviate too much from the above: re-run calibration and check data daily in subsequent days to see if signal returns to pattern before deviation.
- Replace the sensor head if upward drift becomes visible after recalibrating the sensor head.
- If the above actions do not resolve the deviation/problem, using tools from Unisense to check if the sensor body and/or controller are still functioning properly can be an option. Having these tools is highly recommended as it helps to solve the measurement problem more quickly, allowing to indicate to Unisense what the problem might be, or to state that the additional tests have not provided further insight. Available troubleshooting tables from Unisense can also be consulted to identify the cause of a problem.

Besides keeping track of the calibrations performed in a logbook, it is also highly recommended to keep a logbook for recording (major) malfunctions at the WwTWs, which have a clear impact on the process (load, oxygen concentrations, etc.). Consider (list is not exhaustive):

- Failure of blowers, impellers, recirculation-, and return sludge pumps, mixers and possible failure of chemical or Carbon-source dosing.
- Failure of analysers and sensors that may have resulted in switching to another process control system or even emergency control.
- Functioning of the aeration plates (do they still work; are they too dirty etc.); check this regularly.
- Waste regime for the discharge of excess secondary sludge to the thickening- or dewatering installation, i.e. proper tracking and recording of sludge concentration in the tanks.
- Any adjustments in process control to meet effluent requirements. In the reference year, such adjustments should not be made unless there is an urgent reason, such as meeting effluent requirements. This is to achieve the most representative emission factor possible for that WwTW, after which the impact of reduction measures can be assessed.
- Emergencies/events such as: extraordinary industrial discharge, events, and power outages, and the possible need to implement emergency ventilation.
- Major maintenance causing process components to possibly be temporarily out of operation.

## 4.4 DATA PROCESSING AND VALIDATION

By properly executing the actions from paragraph 4.3, a dataset can be created that contains sufficient data and sufficiently high-quality data. A dataset is never perfect; therefore, a validation step is always required before calculating the nitrous oxide emission to remove 'outliers' from the dataset. Currently, this is still done individually by each water utility, but there may be possibilities to use the available data platform 'Z-info' in the Netherlands for this purpose. The principle is that for a national emission factor, the validation of the data must be reproducible so that all data are comparable and lead to comparable emission factors. In addition to the raw measurement data of the nitrous oxide concentrations, other process parameters must also be stored in Historian/Z-info. These parameters are mentioned in the next paragraph.

## 4.5 NITROUS OXIDE EMISSION CALCULATION

For calculating nitrous oxide emissions (in kg $N_2O$-N per unit of time), it is essential that the air flow rate is available for WwtWs with bubble aeration. This is not the case for all WwTWs in the acceleration programme, hence a distinction is made between WwTWs with bubble aeration and air flow rate measurements (see paragraph 4.5.1) and WwTWs without air flow rate measurements (see paragraph 4.5.2). For WwtWs with surface aeration, it is assumed that the necessary data for that emission calculation are always available (see paragraph 4.5.3). Finally, there are WwTWs where intermittent aeration is applied with surface or bubble aeration. Paragraph 4.5.4 indicates how the emission calculation can be performed in this case.

### 4.5.1 WHEN AIRFLOW MEASUREMENTS ARE AVAILABLE - BUBBLE AERATION

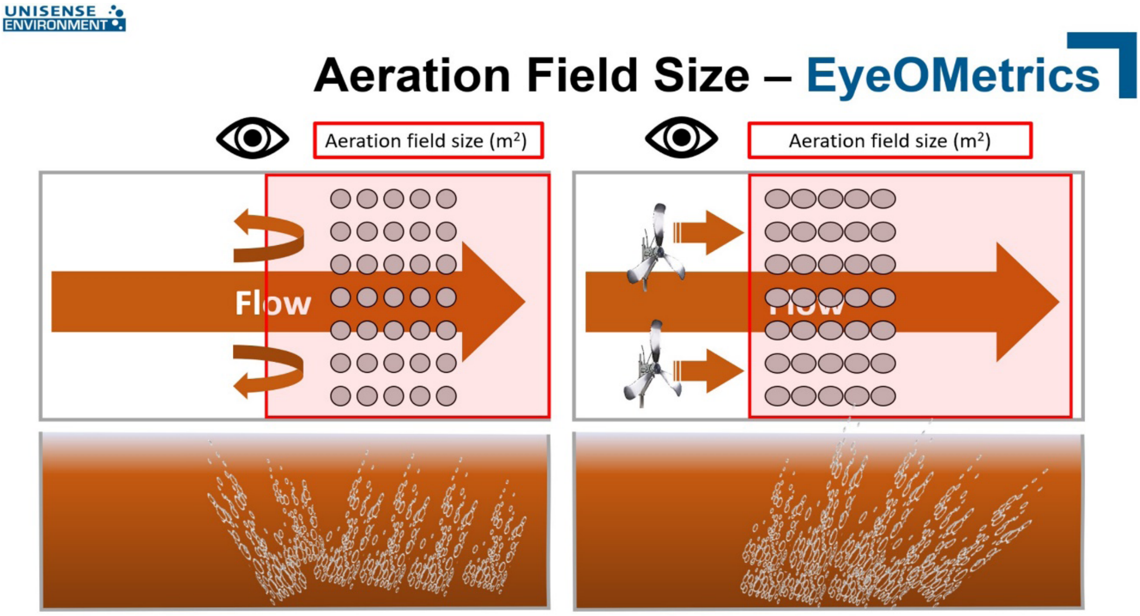
For WwTWs with bubble aeration, the data from Table 2 are required.

**TABLE 2** DATA REQUIRED TO CALCULATE NITROUS OXIDE EMISSIONS IN THE PRESENCE OF AIRFLOW MEASUREMENTS IN BUBBLE AERATION

| Parameter | Unit | To be delivered as |
|---|---|---|
| Process temperature | °C | Continuous data |
| Aerated zone | | |
| Nitrous oxide concentration ($S_{N2O}$) | mg $N_2O$-N/l | Continuous data |
| Air flow rate | in $m^3$/h (so NOT as $Nm^3$) | Continuous data |
| Aerated surface | $m^2$ | Fixed value |
| Depth from plate to water level | m | Fixed value |
| Aeration volume | $m^3$ | Fixed value |
| Non-aerated zone | | |
| Nitrous oxide concentration ($S_{N2O}$) | mg $N_2O$-N/l | Continuous data |
| Non-aerated surface | $m^2$ | Fixed value |
| Depth of non-aerated section | m | Fixed value |
| Volume of non-aerated section | $m^3$ | Fixed value |

For the aerated surface, do not consider the surface area of the aeration discs or plates, but rather consider the visible surface area with bubbles, as illustrated in Figure 9. In addition to the continuous measurement data from the WwTW and some fixed data, several constants are needed to calculate the nitrous oxide emission. Appendix 2 includes a 'screenshot' of the Unisense calculation sheet, which shows the calculation for one data point and the required data and constants.

**FIGURE 9** **THE AERATED SURFACE TO BE SPECIFIED SHOULD BE DETERMINED VISUALLY FROM ABOVE. THIS IS THE SURFACE WHERE BUBBLES ARE LOCATED, AND NITROUS OXIDE CAN BE STRIPPED (SOURCE UNISENSE)**



### 4.5.2 IN THE ABSENCE OF AIRFLOW MEASUREMENTS

The possibility of calculating nitrous oxide emissions in the absence of air flow rate measurements is still being investigated. A working group has been established within the acceleration programme to address this.

### 4.5.3 WITH SURFACE AERATION

For WwTW with surface aeration the data from Table 3 are required.

**TABLE 3** **DATA REQUIRED FOR NITROUS OXIDE EMISSION CALCULATION WITH SURFACE AERATION**

| Parameter | Unit | To be delivered as |
|---|---|---|
| Process temperature | °C | Continuous data |
| Power consumption | kWh | Continuous data |
| Input efficiency | kg $O_2$/kWh | Fixed value |
| Aerated volume | $m^3$ | Fixed value |
| Nitrous oxide concentration ($C_{N2O}$) aerated part | mg $N_2O$-N/l | Continuous data |
| Non-aerated zone | | |
| Nitrous oxide ($C_{N2O}$) concentration in unvented zone | mg $N_2O$-N/l | Continuous data |
| Non-aerated surface | $m^2$ | Fixed value |
| Depth of reactor non-aerated section | m | Fixed value |
| Volume of non-aerated part | $m^3$ | Fixed value |

Appendix 2 includes a screenshot of Unisense's calculation sheet, which shows the calculation for one data point and the data and constants required for it.

### 4.5.4 WITH INTERMITTENT AERATION

With intermittent aeration, the nitrous oxide concentration is alternately measured at the same location under anoxic conditions and then again under aerobic conditions. Ideally, the calculation of nitrous oxide emissions should be set up so that the calculation for anoxic conditions is applied alternately and then for aerobic conditions. Switching between one calculation or the other can be based on the measured air flow rate (for bubble aeration, if present) or the power consumption for surface aerators. It's easier to always use the calculation for aerobic conditions. In the situation where the aeration is turned off and is almost zero, this leads to a low value with the aerobic calculation. In practice, these two methodologies were tested side by side at one of the Dutch WwTWs, and no significant differences in emissions were found.

## 4.6 CALCULATION OF EMISSION FACTOR

For all the above calculations, the standard setting of Unisense is to record the nitrous oxide concentration per minute. During the installation of the sensors, this frequency can be adjusted. It should be at least once every 15 minutes, but shorter intervals are always allowed. Based on the established frequency for recording the nitrous oxide concentration, the nitrous oxide emission in kg $N_2O$-N per quarter of an hour (or shorter) is calculated. This is done for the emission from the anoxic zone and from the aerated zone.

For all the above calculations, Unisense's default setting is to record the nitrous oxide concentration per minute. When installing the sensors, you can choose to adjust this frequency. This should be at least once every 15 minutes, a shorter period is also allowed. From the set measurement frequency, the nitrous oxide concentration, the emission of nitrous oxide in kg $N_2O$-N per 15 minutes (or shorter) is calculated. This is done for emissions from the anoxic zone and from the aerated zone.

In the situation where the focus is on determining only an emission factor (see section 3.1), the calculated emission per quarter of an hour (or shorter) is averaged per day. With the nitrogen load per day then also available, an emission factor per day can be calculated:

$$\text{kg } N_2O\text{-N.d}^{-1} \text{ / kg NKj (or N-tot). d}^{-1}$$

In the situation where the focus is also on reducing nitrous oxide emissions (see section 3.2), the calculated emissions per quarter-hour are used directly, or if minute values are calculated they are averaged over a quarter-hour. The measured quarter-hourly value for incoming nitrogen load can then be used to calculate an emission factor per quarter-hour:

$$\text{kg } N_2O\text{-N/per quarer-hour / kg NKj (or N-tot)/per quarter-hour}$$

# 5

# ADDITIONAL MEASUREMENTS

## 5.1 FOCUS ON EMISSION FACTOR ONLY

The objective for the Dutch situation is to develop a decision tree based on which an emission factor for a WwTW can be derived. The research question is which parameters should be part of the decision tree. With the full knowledge of the parameters that have the most influence on nitrous oxide emissions, various parameters have been defined that are also representative for the Dutch situation:

- Treatment **capacity**: < 100,000 p.e. or > 100,000 p.e;
- The presence of a (central) **digester** yes or no;
- A low or high risk of nitrous oxide based on **nitrite**; At a nitrite concentration in the effluent (composite 24-hour sample) ≤ 0.25 mg $NO_2$-N/l, a WwTW has a low risk of nitrous oxide, at a concentration greater than 0.25 mg $NO_2$-N/l, a WwTW has a high risk of nitrous oxide.

Based on these three parameters, all Dutch WwTWs (313) were divided into eight groups:

- Group 1: < 100,000 p.e. - without digestion - low risk
- Group 2: < 100,000 p.e. - without digestion - high risk
- Group 3: < 100,000 p.e. - with digestion - low risk
- Group 4: < 100,000 p.e. - with digestion - high risk
- Group 5: > 100,000 p.e. - without digestion - low risk
- Group 6: > 100,000 p.e. - without digestion - high risk
- Group 7: > 100,000 p.e. - with digestion - low risk
- Group 8: > 100,000 p.e. - with digestion - high risk

For selecting enough representative WwTWs, the two design parameters that, besides temperature, are most decisive for the extent to which nitrogen can be removed were considered. These are the **nitrogen sludge load** expressed in kg N.kg $DS^{-1}.d^{-1}$, and the **BOD/N** ratio. High nitrogen removal is possible if the sludge load is very low (< 0.006 kg N.kg $DS^{-1}.d^{-1}$), or high (> 0.015 kg N.kg $DS^{-1}.d^{-1}$), but only when the BOD/N ratio is also greater than four. Based on this reasoning, nine categories were defined:

- Sludge load low: 0.006 kg N.kg $DS^{-1}.d^{-1}$ , with a BOD/N ratio of: <3, 3 to 4 or > 4
- Sludge load average: 0.006 - 0.015 kg N.kg $DS^{-1}.d^{-1}$ , with a BOD/N ratio of: <3, 3 to 4 or > 4
- Sludge load high: > 0.015 kg N.kg $DS^{-1}.d^{-}1$, with a BOD/N ratio of: <3, 3 to 4 or > 4

The **parameters in bold** are also the parameters included in the measurement programme for the purpose of being able to establish a decision tree.

The nitrite concentrations in the effluent based on 24-hour samples or semi-continuously with a nitrite analyser provide the opportunity to also look for a linear relationship between the nitrite concentration in the effluent and the emission factor.

## 5.2 FOCUS ON EMISSION FACTOR AS WELL AS REDUCTION

In addition to developing a decision tree with emission factors, the second goal of the programme is to determine a validated set of reduction measures that provide insight into the effect of the measure on nitrous oxide emissions and the effluent quality. Therefore, in addition to nitrous oxide emissions, the effluent quality is also monitored, consisting of the parameters: total nitrogen (**N-tot**), nitrate (**$NO_3$-N**), nitrite (**$NO_2$-N**), ammonium (**$NH_4$-N**), total phosphorus (**P-tot**), and phosphate (**$PO_4$-P**). Based on the existing kWh meters on the aeration tank and a possible dosing installation for phosphorus removal, electricity and chemical consumption are monitored.

Before developing and monitoring the impact of reduction measures, these measures must first be inventoried and selected. We do not start from scratch but start with what is already known. To further support this, the goal is to monitor as many process parameters as possible in the various biological tanks. These can include: **oxygen, temperature, sludge content, nitrate, nitrite, ammonium, redox potential, and phosphate.**

## APPENDIX 1

# TREATMENT CONFIGURATIONS AND LOCATION DETERMINATION

### WASTEWATER TREATMENT WORKS CONFIGURATIONS

This appendix lists the configurations most found in the Netherlands. For each configuration, it is specified in which tank(s) a minimum sensor must be present to meet the goals of the acceleration programme. In addition, for each configuration it is indicated on which WwTW it is already installed.

### A/B SYSTEM

**FIGURE 10** A/B SYSTEM

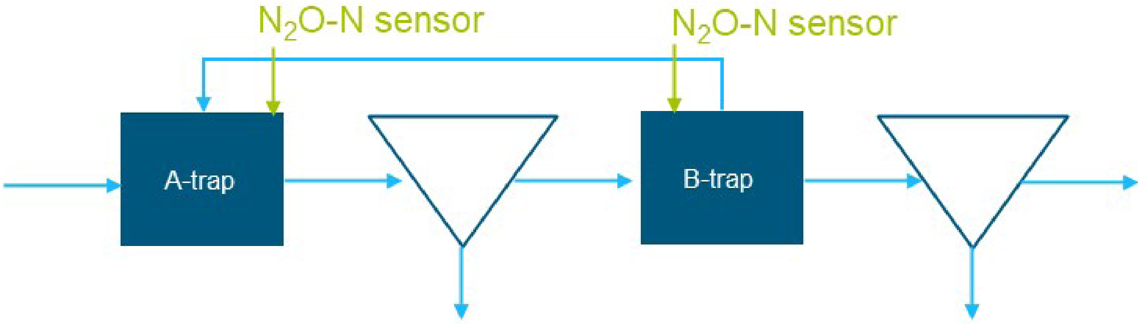


**TABLE 4** NUMBER OF SENSORS INSTALLED IN THE A/B SYSTEMS INCLUDED IN THE ACCELERATION PROGRAMME

| WwTW | Pre-denitrification | A-stage | B-stage | Total number of sensors | Location determination |
|---|---|---|---|---|---|
| Dokhaven | | 1 | 1 | 2 | Only in B-stage |
| Velsen | | 1 | 2 | 3 | Intention in A-stage |
| Garmerwolde | 1 | | 3 | 4 | |

- Velsen: A sensor was installed in the B-stage at ¼ and ¾ of the B-stage.
- Garmerwolde: In the B-stage at the start, and otherwise a proportional distribution across the B-stage.

## PHOSIM

**FIGURE 11** **PHOSIM CONFIGURATION**

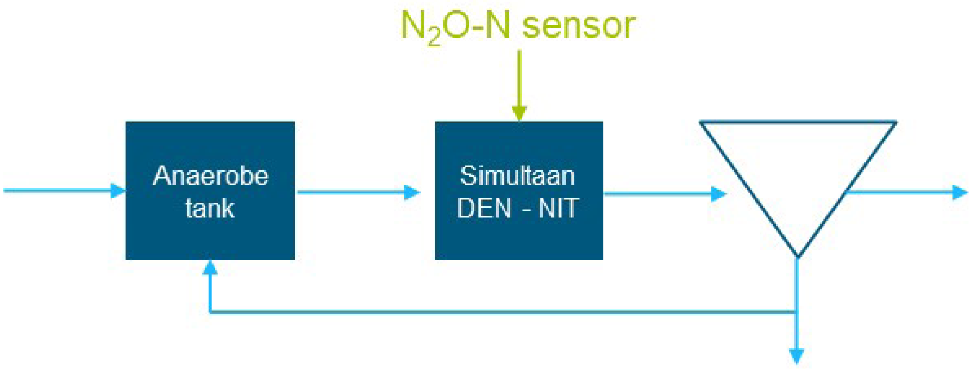


**TABLE 5** **NUMBER OF SENSORS INSTALLED IN THE PHOSIM SYSTEMS INCLUDED IN THE ACCELERATION PROGRAMME**

| WwTW | Simultaneous DEN-NIT | Total number of sensors |
|---|---|---|
| Zutphen | to be determined | to be determined |

## PHOREDOX

**FIGURE 12** **PHOREDOX CONFIGURATION**

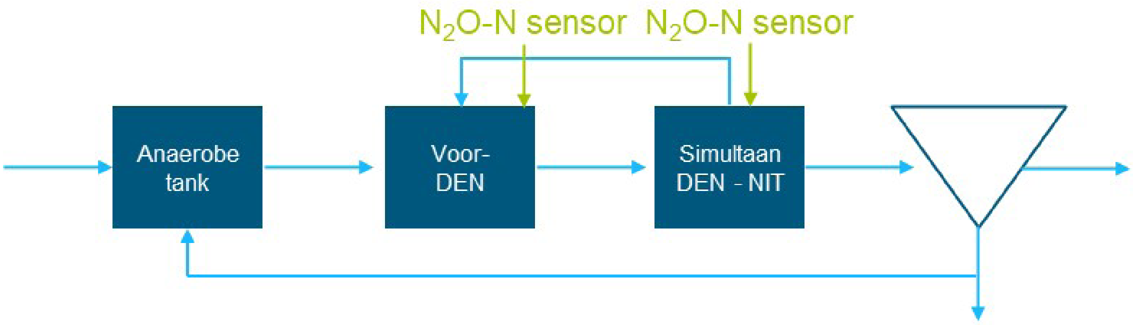


**TABLE 6** **NUMBER OF SENSORS INSTALLED IN THE PHOREDOX SYSTEMS INCLUDED IN THE ACCELERATION PROGRAMME**

| WwTW | Pre-denitrification | Simultaneous DEN-NIT | Total number of sensors | Location determination |
|---|---|---|---|---|
| Zwolle | 1 | 1 | 2 | Short in simultaneous tank |
| Uithuizermeeden | 1 | 2 | 4 | |

- Uithuizermeeden: 1 sensor just in front of surface aerator, 1 just behind, and 1 further away from the surface aerator.

## (M)UCT

FIGURE 13 (M) UCT CONFIGURATION

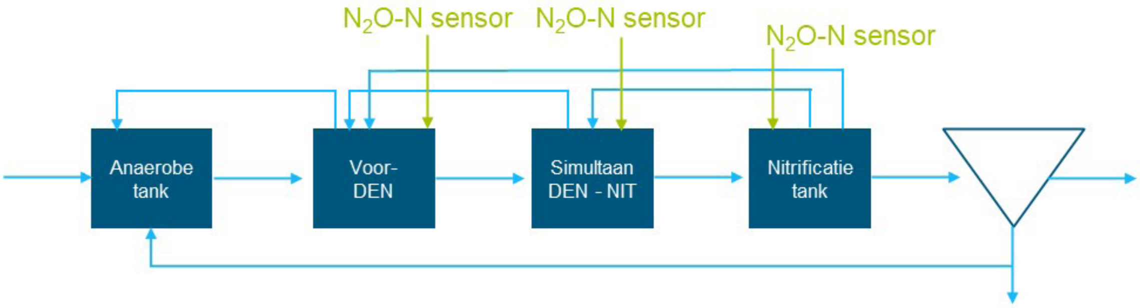


TABLE 7 NUMBER OF SENSORS INSTALLED IN THE (M)UCT SYSTEMS INCLUDED IN THE ACCELERATION PROGRAMME

| WwTW | Pre-denitrification | Optional | Nitrification | Total number of sensors | Location determination |
|---|---|---|---|---|---|
| Hessenpoort | 1 | | 1 | 2 | In nitrification tank |
| Apeldoorn | 1 | | 1 | 2 | In anoxic and aerobic ring |
| Amsterdam West | | 1 | 1 | 2 | |
| Aarle Rixtel | 1 | | 1 | 2 | In anoxic tank (plug flow)<br>In nitrification tank (mixed) |
| Land of Cuijk | 1 | 1 | 1 | 3 | In anoxic (plug flow), facultative (mixed) and nitrification (mixed) tank |
| Biest Houtakker | 1 | | 1 | 2 | |
| Eindhoven | 1 | | 1 | 2 | |

## HOOGVLIET

FIGURE 14 HOOGVLIET CONFIGURATION

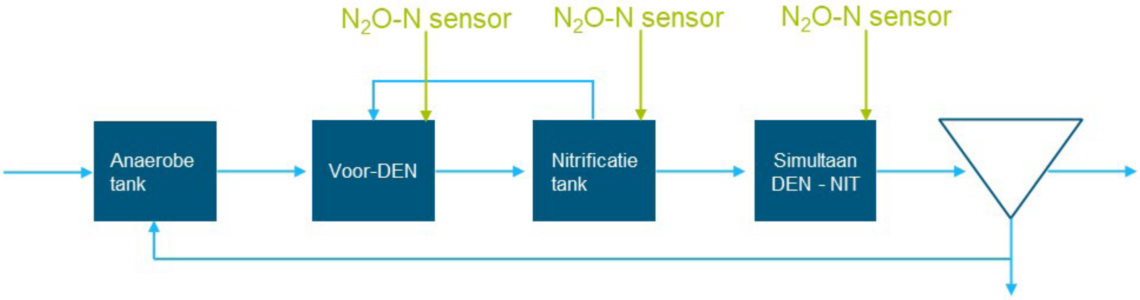


TABLE 8 NUMBER OF SENSORS INSTALLED IN HOOGVLIET SYSTEMS INCLUDED IN THE ACCELERATION PROGRAMME

| WwTW | Pre-denitrification | Facultative | Simultaneous | Total number of sensors | Location determination |
|---|---|---|---|---|---|
| Kralingseveer | 1 | 1 | 4 | 6 | In all tanks |
| Hoogvliet | 1 | 1 | 1 | 3 | In nitrification tank, and carousel |

- Kralingseveer: In simultaneous nitrification-denitrification tank: in each 2 sensors.

## APPENDIX 2

# NITROUS OXIDE EMISSION CALCULATIONS WITH BUBBLE AND SURFACE AERATION

### REQUIRED DATA AND CALCULATION OF NITROUS OXIDE EMISSIONS FOR WWTWS WITH BUBBLE AERATION ÁND AIR FLOW MEASUREMENTS

| | Constant name | Unit | Note | Value |
|---|---|---|---|---|
| witte cel is constante | **$K_H^{⍰}$** | mol/L.bar | | 0,0247 |
| groene cel is gemeten waarde | **-ΔsolNH/R** | K | | 2675 |
| **licht roze cel is berekende waarde** | **$C_{N2O,air}$** | $gN/m^3$ | | 0,0003 |
| | **R** | $m^3$·bar/mol·K | | 8,31E-05 |
| | **$k_La^{Non\text{-}aerated\ process}$** | $day^{-1}$ | 2-4 $day^{-1}$ | 3 |
| | **$T^{⍰}$** | °C | Standard temperature | 25 |
| | **Tprocess** | °C | Process temperature measured | 12,1 |
| | **Aerated zones** | **Unit** | **Note** | **Value** |
| | **$S_{N2O}$ concentration** | mg $N\text{-}N_2O/L$ | Nitrous Oxide measured Aerated | 0,02 |
| | **$Q_A$** | $m^3/h$ | Air flow measured | 136,80 |
| | **$Q_A$ per day** | $m^3/day$ | Use the actual air flow rate, not Nm3/day. | 3,28E+03 |
| | **$Q_A$ per second** | $m^3/s$ | Same as above. | 0,038 |
| | **Aerated field size** | $m^2$ | Air diffuser cylindrical total area | 1268,75 |
| | **$D_R$** | m | Depth reactor from diffuser to water level | 3,87 |
| | **$V_R$** | $m^3$ | Volume of aerated part of the reactor | 4910,1 |
| | **Non-aerated zones** | **Unit** | **Note** | **Value** |
| | **$S_{N2O}$ concentration** | mg $N\text{-}N_2O/L$ | Nitrous Oxide measured Non-Aerated | 0,10 |
| | **Non-aerated field size** | $m^2$ | Total area of non-aeration | 162 |
| | **$D_{R,Non\text{-}aerated}$** | m | Depth reactor | 5,5 |
| | **$V_{R,Non\text{-}aerated}$** | $m^3$ | Volume of non-aerated part of the reactor | 891,0 |

| Formula | Variables on T and air flow | Unit | Note | Value |
|---|---|---|---|---|
| 4.2 | **$K_H$** | mol/L.bar | Henrys constant at the std. Temp. | 0,0370 |
| 4.1 | **$H_{N2O}$,Tprocess** | dimensionless | Henrys constant | 1,14 |
| 1.1 | **$V_g$** | $m^3/m^2/s$ | Gas velocity | 0,00003 |
| 1.3 | $K_La_{N2O\ 20°C}$ | $day^{-1}$ | Mass transfer coefficient at std. Temp | 2,070 |
| 1.4 | $K_La_{N2O\ Tprocess}$ | $day^{-1}$ | Mass transfer coefficient at process Temp | 1,718 |

| Formula | Aerated zone | | | |
|---|---|---|---|---|
| 2 | **$r_{N2O,Tprocess}$** | $gN\text{-}N_2O/m^3/day$ | $N_2O$ emission rate | 0,014 |
| | **Emission** | $KgN\text{-}N_2O/day$ | $N_2O$ emission rate | 0,067 |

| Formula | Non-erated zone | | | |
|---|---|---|---|---|
| 3 | **$r_{N2O,Tprocess}$** | $gN\text{-}N_2O/m^3/day$ | $N_2O$ emission rate | 0,299 |
| | **Emission** | $kgN\text{-}N_2O/day$ | $N_2O$ emission rate | 0,267 |

| | | |
|---|---|---|
| **Total tank emission** | $kgN\text{-}N_2O/day$ | 0,334 |

## REQUIRED DATA AND CALCULATION OF NITROUS OXIDE EMISSIONS FOR SURFACE AERATION WWTWS

| Constant name | Unit | Note | Value |
|---|---|---|---|
| $T_{process}$ | °C | Process temperature measured | 22,0 |
| **P** | kWh | Power consumption (rotors) | 66 |
| **SAE** | $kgO_2/kWh$ | Standard aeration efficiency | 1,8 |
| $V_{aerated}$ | $m^3$ | Volume of process tank | 4000 |
| $C_{N2O}^{Process}$ | $mgN\text{-}N_2O/L = gN\text{-}N2O/m^3$ | Nitrouc oxide liquid phase concentration | 0,1 |
| **Non-aerated zones** | **Unit** | **Note** | **Value** |
| $C_{N2O,non\text{-}aerated}^{Process}$ | $mgN\text{-}N_2O/L = gN\text{-}N2O/m^3$ | Nitrouc oxide liquid phase concentration | 0,01 |
| $k_La^{Non\text{-}aerated\ process}$ | $day^{-1}$ | 2-4 $day^{-1}$ | 3 |
| **Non-aerated field size** | $m^2$ | Total area of non-aeration | 162 |
| $D_{R,Non\text{-}aerated}$ | m | Depth reactor | 5,5 |
| $V_{R,Non\text{-}aerated}$ | $m^3$ | Volume of non-aerated part of the reactor | 891,0 |
| **Constant name** | **Unit** | **Note** | **Value** |
| $T^{⍰}$ | °C | Standard temperature | 20 |
| **α** | (-) | Correction from clean water to process conditions | 1 |
| **β** | (-) | Change in saturation concentration from clean water to process conditions | 0,95 |
| **F** | (-) | Fouling factor, usually 1 for surface aerator rotors | 1 |
| $D_{N2O}$ | $m^2/s$ | Diffusion coefficient | 1,77E-09 |
| $D_{O2}$ | $m^2/s$ | Diffusion coefficient | 2,12E-09 |
| $C_{O2}^{Process}$ | mg/L | Oxygen Process Concentration | 0 |
| $C_{O2}^{Sat}(20°C)$ | $kg/m^3$ | Oxygen Saturation Concentration | 0,0090324 |
| $C_{O2}^{Sat\_Tprocess}$ | $kgO_2/m^3$ | Oxygen Saturation Concentration | 0,008830014 |

| Formula | Aerated zone | | | |
|---|---|---|---|---|
| 1.4 | **SOTR** | $kgO_2/h$ | Standard oxygen transfer rate | 118,80 |
| 1.5 | **AOTR** | $kgO_2/h$ | Actual Oxygen Transfer Rate | 115,69 |
| 1.6 | $K_La_{O2\ Tprocess}$ | $h^{-1}$ | Mass transfer coefficient | 3,28 |
| 0.2 | $K_La_{N2O\ Tprocess}$ | $h^{-1}$ | Mass transfer coefficient | 2,99 |
| 0.4 | $NTR_{Aerated}$ | $gN\text{-}N_2O/h$ | $N_2O$ Emission rate | 1197,17 |
| | **Emission** | $kgN\text{-}N_2O/day$ | $N_2O$ Emission rate | 28,73 |

| Formula | Non-erated zone | | | |
|---|---|---|---|---|
| 0.5 | **Emission** | $kgN\text{-}N_2O/day$ | $N_2O$ Emission rate | 0,027 |
| | | | | |
| | **Total tank emission** | $kgN\text{-}N_2O/day$ | $N_2O$ Emission rate | 28,759 |