

OFF-GAS EMISSION TESTS

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4.1 INTRODUCTION

Wastewater treatment technology and biological nutrient removal (BNR) processes are used mainly to achieve improved water quality. However, BNR processes are a potential contributor to nitrous oxide (N₂O) and methane (CH₄) emissions to the atmosphere, depending on the plant configuration and operating conditions (Kampschreur, 2009). For measuring the carbon footprint of wastewater treatment and BNR processes, this flux of greenhouse gases (GHGs) to the atmosphere should be measured. GHG emissions can be further enhanced by increasing attention on energy neutral treatment plants based on methane generation by anaerobic processes. The release of methane, and especially of nitrous oxides, is of concern because the greenhouse impact of N₂O on a mass equivalent basis is about 300 times that of carbon dioxide (CO₂) and 34 times of CH₄ (IPCC, 2013).

During the past few decades, there have been ever increasing attempts to characterize off-gas (and GHGs) emissions from full-scale wastewater treatment plants

(WWTPs), and to develop a methodology to collect full-scale plant data in many parts of the world. In this chapter, the approaches applied in several such studies are described. One of the original protocols developed by researchers in the US, which was reviewed and endorsed by the United States Environmental Protection Agency (USEPA), is presented in detail, as well as methods from other studies elsewhere. It is expected and approaches presented in this chapter will enable off-gas and greenhouse gas emissions from WWTPs to be monitored and quantified using standardized experimental approaches. Because plant operation has a key role in off-gas and greenhouse gas emissions, the results of such monitoring and quantifying efforts could ultimately lead to WWTPs not just improving their aqueous discharges, but at the same time minimizing their gaseous emission. This chapter focuses on the emissions from wastewater treatment by activated sludge and similar processes. Methane gas measurements are well-established as a standard method, whereas an overview of all nitrous oxide measurement methods is given by Rapson *et al.* (2014).

Off-gas measurements of carbon dioxide and oxygen (O_2) are a good tool for evaluating plant performance. The CO_2 and O_2 content in off-gas can be measured with similar strategies described here for GHGs. A combination of off-gas measurements and titration measurements forms an excellent way to monitor biological processes (Pratt *et al.*, 2003; Gapes *et al.*, 2003). Oxygen depletion in the off-gas is a measure of the respiration rates and can be seen as a (full-plant) respirometric approach, similar to those described in Chapter 3. Carbon dioxide production is also related to the aerobic and anoxic respiration processes. However it is more difficult to interpret since the change (usually a net decrease) in alkalinity also significantly influences the carbon dioxide content in the off-gas (Hellings *et al.*, 1996). Measuring the oxygen and carbon dioxide conversion could be of great value for better process monitoring and data handling (see Chapter 5), since they allow a better evaluation of mass balances over the wastewater treatment process (Takacs *et al.*, 2007; Puig *et al.*, 2008).

4.2 SELECTING THE SAMPLING STRATEGY

A major consideration for off-gas measurements from WWTPS is a representative sampling procedure. Given the biological nature of N_2O production and link to processes such as nitrification and denitrification, spatial and temporal variability in the measured emission fluxes of these gases is expected. A correlation with wastewater constituents such as ammonia, nitrite and nitrate could also be expected and has been observed in nearly all the measurement campaigns conducted to date. Since emissions from full-scale WWTPs of especially N_2O have proven to be highly dynamic, a measurement program has to be decided upon in a case-by-case evaluation (Daelman *et al.*, 2013). The sampling strategies employed during sampling campaigns must adequately capture such variability. Some factors that influence the sampling strategies are described below.

4.2.1 Plant performance

One of the most significant results of past studies has been the implication that N_2O emissions from WWTPs are linked to overall or local accumulation of nitrogen species such as ammonium (NH_4^+) or nitrite (NO_2^-). There is especially a need for characterization of emissions from plants that do not show a stable nitrification or denitrification performance. Such characterization is important given that many plants are

not designed or operated in a BNR mode. Under certain conditions (such as high temperatures during the summer when these highly-loaded plants exhibit incomplete nitrification), these plants can emit more N_2O in comparison to well-designed and operated BNR plants. In contrast to N_2O , CH_4 emissions are likely to occur due to lack of control in an activated sludge process. For instance, poor aeration or dissolved oxygen (DO) control in the activated sludge process may lead to anaerobic zones and associated CH_4 production. Besides, CH_4 that was formed in the sewer system and enters the plant with the influent is likely to be stripped in the activated sludge tank, even though it could also be aerobically oxidized. CH_4 stripping in the activated sludge tank could be minimized while its biological conversion could be promoted through adequate process design and control (Daelman *et al.*, 2014)

4.2.2 Seasonal variations in emissions

The link between temperature and emissions of N_2O or CH_4 is not straightforward and needs to be considered in combination with the plant design. For plants operating at a high sludge retention time (SRT) and sustaining complete NH_3 removal all year round, higher emissions can be expected during the summer period, owing to overall higher microbial activity at higher temperatures. Especially for such plants, the off-gas emission may shift more downstream in plug-flow installations at lower temperatures. The slower nitrification occurs more downstream at these lower temperatures. For plants that cannot fully nitrify at low temperatures and foster non-limiting NH_3 concentrations at lower temperatures, off-gas emission can actually be higher at lower temperatures. In contrast, as these plants can achieve full nitrification during the higher temperature, their emissions could be lower. Seasonally nitrifying treatment plants could have higher emission as well. Such plants can 'wash-out' nitrifying bacteria at low temperatures and consequently have extremely low off-gas emission. As nitrification is supported during higher temperatures but often not sufficiently to achieve the required effluent NH_3 concentration, off-gas emission could be higher during the summer. For planning gas measurement locations the measurement of nitrite might be helpful since there is a general, but not unique, correlation between the presence of nitrite in the liquid phase and N_2O formation. CH_4 emissions from aeration tanks result largely from processes in sewer and sludge processing facilities, and therefore the link between temperature and measured emissions is much less obvious than for N_2O emissions.

4.2.3 Sampling objective

A range of different sampling strategies for the quantification of N₂O emissions has been reported in literature, such as 24 h online sampling, 1-week online sampling, long-term weekly grab sampling and taking a single grab sample. The difference in the sampling methods may partly explain the large variability in N₂O emissions reported, aside from the differences in the real emission, which is related to the plant performance and shows both diurnal and seasonal variations.

The optimal sampling strategy depends on the objective of the sampling campaign. Daelman *et al.* (2013) applied several N₂O sampling strategies applied in literature to the extensive dataset of a long-term online monitoring campaign. They showed that a reliable determination of the actual average N₂O emission requires long-term sampling, be it online or grab sampling, covering the entire temperature range that can possibly be encountered. Short-term sampling unavoidably ignores the long-term variation that is present. For long-term grab sampling, nighttime and weekend samples contribute significantly to a more accurate estimate. High-frequency (online) sampling is indispensable to identify correlations between the emission and the process variables that induce the emissions and in this way gain insight into the underlying N₂O formation mechanisms. A method to obtain the number of grab samples or online sampling periods required to obtain a sufficiently precise estimation of the emission was presented by Daelman *et al.*, (2013), serving as a guideline for sampling campaigns, to balance cost and precision.

4.3 PLANT ASSESSMENT AND DATA COLLECTION

4.3.1. Preparation of a sampling campaign

A sampling program (or campaign) is primarily carried out to (i) collect routine operating data concerning the overall WWTP performance, (ii) acquire information that can be used to document the performance of a given treatment operation or process, (iii) collect data that can be used to implement proposed new programs for sewerage and WWTP, and (iv) obtain records needed for reporting regulatory compliance. In general this information is:

- a. Influent characterization measurements.
- b. Mass balance measurements.
- c. Activated sludge characterization measurements.
- d. Effluent characterization.
- e. All other necessary information.

A well-prepared sampling plan should not only give the type (e.g. chemical oxygen demand: COD, total Kjeldahl nitrogen: TKN, total phosphorus: TP) and location (e.g. influent, effluent or aeration tank) of the sampling point, but it should also indicate what the sampling frequency is and how the sample should be taken, handled, stored, and processed in the laboratory for analytical measurements. The goal of the campaign planning is to communicate all this information to the staff responsible for acquiring the samples (operators or plant technical personnel) and the laboratory personnel analysing the samples. Tables should be developed indicating all of this information, preferably in a single table overview. Also, a dedicated process flow diagram should be developed indicating precisely all the measurement points related to the planning.

While designing the sampling campaign one must address at least the following practical questions:

1. WHY: What is the purpose of taking the samples?
2. WHAT: Which parameters are to be sampled?
3. WHERE: Where are the sampling locations?
4. WHEN: When are the samples taken?
5. HOW OFTEN: What is the frequency for each sampled parameter?
6. HOW: How will the sampling be executed?
7. BY WHOM: Who will take the samples and who will analyse them?
8. EQUIPMENT: What will be used for collecting, storing and analysing the samples?

The six criteria for quality data are:

1. Collecting representative samples.
2. Formulating the objectives of the sampling program.
3. Proper handling and preservation of the samples.
4. Proper chain-of-custody and sample identification procedures.
5. Field quality assurance.
6. Proper analysis.

The sample, in order to serve its purpose, has to be representative, reproducible, defensible and useful. It is also important to realize that proper understanding of the sampling procedures is crucial for the design and success of the sampling program. This should not only be realized

by the designer but also by all the others involved in the project. Therefore, it is advised to organize a preoperational meeting to communicate the measurement planning to all the personnel involved. During this meeting, it should be clearly stated what the goal of the project is, what will be done with the specific measurements and also the importance of acquiring accurate information. It is possible that it will be necessary to give (short practical) training in (grab) sampling techniques.

To ensure that the measurement planning is properly understood and executed, the measurement plan should relate as much as possible to the practical routines of the plant and laboratory personnel. Where possible, references should be made to standard (practical) routines. For example, measurement locations on the process flow diagram should be indicated in the same way as used by the operators. Often the designer has his own preferred way of indicating the flows (e.g. in a flow diagram using the logical numbering Q_1 to Q_n to indicate flows in the mass balance), to communicate this information effectively, and the practical names of the process units and flows should also be indicated in all the diagrams and tables.

Also, for analytical measurements the designer can have different names that do not always correspond with the names and practical methods applied in the laboratory. Therefore the measurement plan should also be checked with the laboratory personnel and the applied measurement routines (analytical methods and equipment).

For the purpose of a campaign, samples should preferably be taken in dry weather conditions unless otherwise specified. In practice it is not always clear if and when these conditions are met. Typically it is advised to plan a day of sampling after three days without (major) rain. This means that the measurement planning can never be planned on an exact date. However, it should incorporate a period of several days in which the planning can be executed, depending on the weather conditions.

Some of the samples can be done automatically with 24-h continuous (or quasi-continuous) flow proportional composite measurement devices. These automatic samplers collect samples over a 24-h period and have to be started 24 h ahead of time to provide a collected sample on the desired sampling day. It should be born in mind that operators have to be notified a day in advance

to be able to collect the samples on time. All the other samples taken on the day of sampling will mostly be spot samples (also called grab, random, catch, individual, instantaneous, and snap samples). Because the sampling program contains multiple measurement points and for each measurement point, multiple parameters have to be measured, the amount of containers required to store the samples will rapidly increase; e.g. the amount of samples needed for a relatively small campaign can easily exceed 100. Also, it should be realized that for each sampling point the sampled volume should allow analytical measurements, washing of filters and vessels, possible spills and possibly duplicate or triple measurements in the laboratory. Also, the laboratory should be prepared to handle this large amount of samples in one (or more) days. Some of the samples can easily be stored to be measured at a different time. However, for other measurements it is critical that the samples are pre-treated (e.g. filtered) before they can be stored. Again, other samples cannot be stored at all (e.g. as the result of biological conversions which occur in the sample vessel). Also, this should be planned in cooperation with the laboratory personnel to avoid a possible work overload and possible inaccurate measurement results.

4.3.2 Sample identification and data sheet

As was pointed out previously, in the sample measurement plan many samples may need to be analysed for one sampling day. Clearly this requires a good administration and sample identification (sample ID). A list of the samples collected should be kept. The samples should be listed in one overview and include the information below. In addition, the individual sample containers should be labelled accordingly.

The container label requirements are:

- a. Sample site location.
- b. Container number if more than one container/sample.
- c. Name of sample collector.
- d. Facility name/location.
- e. Date and time of collection.
- f. Identified as a grab or composite.
- g. Test parameters - list analysis to be done.
- h. Preservative used.

Proper administration of the sampling program is necessary for quality assurance. The following checklist can be used for constructing custody forms supporting the measurement campaign. Often, forms of this kind will already be available and used for the regular sampling

program. It can be helpful to find out if these forms and also the forms in the measurement campaign are available instead of constructing new ones.

- a. Project number: assign a number to the sampling episode that can be used on the bottles to track the samples.
- b. Sampler: the sampler should print and/or sign their name.
- c. Project name: the project name, and if necessary, the project address.
- d. Project contact name: the name of the person who is in charge of the project.
- e. Project telephone number: the phone number where the project contact person can be contacted.
- f. Sample date: list the dates for grab and composite samples.
- g. Sample time: list the sample time for each sample.
- h. Sample type: composite (collected over a 24-h period) or grab (taken as grab samples).
- i. Station location: the site where the sample was taken.
- j. Number of containers: list the number and type of containers for each sampling event.
- k. Analysis requested: list the analysis needed that is compatible with reference to official methods.
- l. Remarks: note any special requirements for the samples for the laboratory.
- m. Split samples: when a sample is split into different proportions for analysis, the receiving party can accept or reject the samples and they must sign this box on the custody form.

4.3.3 Factors that can limit the validity of the results

When evaluating the results of the sampling program, there are several factors that can limit the validity of the results, such as:

- a. Missing values.
- b. Sampling frequencies that change over the recorded period of time.
- c. Multiple observations within the sampling period.
- d. Uncertainty in the sample preservation and measurement procedures.
- e. Censoring the measurement signals.
- f. Small sample size.
- g. Improper data handling.
- h. Equipment inaccuracies.

It is always useful to check the sampling procedure and the measurement results against the above criteria.

4.3.4 Practical advice for analytical measurements

Some typical re-occurring errors in the case studies in the sample procedure or analytical measurements have been documented and are listed below:

- The method used for analytical measurements of suspended solids is different for concentrated and diluted activated sludge samples; if the concentration is above a certain range, then filtration, drying and weighing the solids will no longer be possible. In this case the dry mass method is often used (evaporation of the sample). This includes the soluble salts, which especially for lower concentrated sludge samples, will not give representative results for total suspended solids. This should especially be taken into account when measuring activated sludge, thickened sludge and dirty water flows. For the more concentrated sludge flows (> 20%), dry mass analysis can be used.
- When measuring the filtrate of the sample containing suspended solids, the filter paper should not be washed other than with the sample itself and not with demineralized water, which will cause dilution of the measured filtrate.
- When handling samples containing suspended solids, it is important to take well stirred homogeneous samples when taking the samples or pouring a sample into another vessel. It should be noted that TSS measurements are essential for the model design study and at the same time are very difficult to sample accurately. It is advised to instruct all personnel on how to take reliable TSS samples.
- When carrying out the activated sludge characterization, all the samples should be taken from the same vessel as it is important to know the relative concentration of TSS (total suspended solids), VSS (volatile suspended solids), COD, TKN and TP in the sample. This is not usually a standard procedure and therefore all the personnel, especially those working in a laboratory responsible for analysing, should be well instructed in this matter.
- A common known problem is the destruction of suspended solids, which is necessary to analytically measure TP (and also COD and TKN). When the destruction procedure is not long enough, phosphorus measurements will be underestimated. Especially when there are chemical precipitates (e.g. as a result of dosing of iron-salts) including phosphorus in the sample, destruction can be difficult.

- Measurements of nitrate in samples containing activated sludge (denitrifying heterotrophic bacteria) should be done quickly before denitrification occurs.
- Measurement of volatile fatty acids (VFAs) in samples containing activated sludge (denitrifying heterotrophic bacteria) is practically impossible for the same reason; VFAs are almost immediately oxidized by living organisms. These types of samples are highly unreliable and should not be used. Measurement of volatile fatty acids in the influent is possible; however, it should be immediately filtrated after sampling and stored under prepared conditions.

4.3.5 General methodology for sampling

In general, there is a standard approach developed regarding the design of a water quality monitoring system; the approach for a sampling program at a WWTP can be derived from this that consists of six distinctive steps:

Step 1: Evaluation of the existing information

- Wastewater collection and treatment.
 - Domestic wastewater.
 - Industrial effluents.
 - Combined sewer overflows and pumping stations.
 - Wastewater treatment plants.
- Lab-scale and pilot plant investigations.
 - Wastewater treatment plants.
 - Wastewater collection networks.

Step 2: Evaluation of the information expectations

- Water quality goals and objectives.
- Water quality problems and issues.
- Management goals and strategy.
- Monitoring role in management.
- Monitoring goals (as statistical hypotheses).

Step 3: Establishment of statistical design criteria

- Statistically characterise the population to be sampled.
 - Variation in quality.
 - Seasonal impacts.
 - Correlation (independence).
 - Applicable probability distributions.
 - Out of the many statistical tests select the most appropriate.

Step 4: Design the monitoring network

- Where to sample (from the monitoring role in management).
- What to measure (from the water quality goals and problems).
- When to sample (from specific circumstances).

- How frequently to sample (from the needs of the statistical tests).

Step 5: Develop the operating plans and procedures

- Sampling routes and points.
- Field sampling and analysis procedure.
- Sample preservation and transportation.
- Laboratory analysis procedures.
- Quality control procedures.
- Data management and retrieval hardware and database management systems.
- Data analysis software.

Step 6: Develop reporting procedures

- Type of format of the reports.
- Frequency of report publication.
- Distribution of reports (information).
- Evaluation of the report's ability to meet the initial information expectations.

Based on the above, a general wastewater and sludge sampling program can be carried out following the steps listed below:

- Definition of the purpose of the sampling.
- Determination of the type, scope and required accuracy of the analyses to be carried out.
- Definition of the character of the samples to be collected.
- Selection of the localities and sources to be sampled, and of the sampling points at these localities.
- Determination of the hydraulic and other parameters relating to the subject of the sampling program.
- Consideration of the occupational safety and hygiene of those collecting the samples.
- Preparation of an optimal sampling programme.
- Selection of the sampling and measuring equipment suited to the sources to be sampled, and determination of its state.
- Selection of the most suitable sampling technique in line with a fixed programme and selected equipment for the given source/site, including preparations, subsidiary measurements and observations. When implementing a sampling programme the techniques used should comply with a number of general requirements such as reliability, economy, repeatability and conservation.
- Selection of appropriate procedures, sample handling equipment and tools, transportation from site to laboratory, storage after delivery.
- Consideration of the most suitable methods of analysis on site and in the laboratory, the quickest possible interpretation of the analyses including reliability checks, and possible repetition of the

sampling, and other factors likely to influence the accuracy or representativeness of the analyses.

- Use of feedback whenever possible to modify a programme to an optimal sampling programme.
- Establishment of the conditions necessary for the immediate use of the results and for their storage as primary sources of information in the future, whether for short- or long-term use.
- Selection of an appropriate system for data management (i.e. handling, processing, transfer and manipulation).
- Selection of the method of documentation to be used throughout the programme.

Logistically, performing the measurement campaign in the design study is a complicated task and at the same time it is the most important and critical step. Therefore it is advised to carefully prepare the measurement campaign in all possible aspects. It is also advised to accompany the first rounds of the measurements together with all the personnel involved to make sure that all the instructions in the measurement plan are correct and as intended, and properly understood by all the personnel. The analytical results of a sample are only as accurate as the quality of the sample taken. If the technique for collecting samples is poor, then no matter how accurate your lab procedures are, the results will be poor. By sampling according to set procedures, one reduces the chance of error and increases the accuracy of the sample results. It should be born in mind that for a lot of samples the measurement campaign is a one-off opportunity; redoing samples at a different stage will often not lead to satisfactory results because the activated sludge plant is a dynamic system that is continuously changing over time. With this in mind, for the study the samples should be collected simultaneously in such a way that their relative information can be used for the plant assessment. Therefore, individual grab samples will often not be representative, meaning that (missing or incorrect) measurements often cannot be redone. In conclusion, data collection through sampling at WWTPs is a critical activity that needs a systematic and professional approach and the design of a sampling program is often a task for an experienced specialist.

4.3.6 Sampling in the framework of the off-gas measurements

The strong relation between N₂O emissions and operational conditions makes the development of a preliminary reconnaissance analysis crucial. The field

teams need to gather process-operating data during meetings with plant operators (and process engineers) prior to the sampling campaign. The following background information is typically collected from the evaluation site:

- An overall plant description which includes general information related to the plant configuration, liquid and solids process flow diagrams, design criteria, major technological process equipment from the plant's design documentation and/or operation and maintenance manuals.
- Process units and layouts which entail information on anaerobic/aerobic/anoxic zone configuration, zone volumes, operating set points, basins in service, aeration flow and distribution, recycle streams and flow rates (if applicable), and
- Plant operating data, ideally providing a summary of a minimum of 3 months' of plant data on relevant treatment process(es) to allow for characterization of the influent and effluent, and target and actual operating set points for key operational parameters (e.g. DO, SRT). The operating data is needed to check that the plant was not in an upset condition before and during the period of investigation (sampling).

The collected data and information can be used to make analyses by conventional techniques such as the development of solids and nitrogen mass balances as well as through the use of process modeling. Details of model-based evaluation are not presented in this chapter and can be found elsewhere (Melcer, 1999; Puig *et al.*, 2008; Rieger *et al.*, 2012).

In order to collect the necessary data for the assessment it is necessary to determine the influent flow, and organic matter and nitrogen content in the influent, in preparation for the detailed liquid and air measurement campaign at the WWTP. For the initial sampling the following parameters need to be monitored regarding the activated sludge process:

- Influent flow rates (minimum of once per hour).
- Influent and effluent ammonia (up to eight times per day or continuously).
- Influent and effluent nitrite and nitrate (up to eight times per day or continuously).
- Influent and effluent COD (start with once per hour, can be reduced depending on observed variability).

Additionally, diurnal performance and in-tank profiles should be gathered at the time of the N₂O gas phase sampling. As far as feasible, all the liquid phase

The collection of conventional wastewater samples for analysis of parameters in Table 4.2 should preferably be conducted by facility personnel who usually collect operational and compliance samples. In advance of each sampling event, the team conducting the monitoring campaigns should consult with the laboratory personnel to ensure that the samples for the conventional parameters are collected during the GHG monitoring event to meet the requirements of both the research design and the WWTP's laboratory operating procedures.

The plant's sample handling and custody requirements can be utilized as far as possible for each field sampling campaign. To confirm the adequacy of the procedures, the plant's procedures for field sample handling and chain of custody should be reviewed with the project team approximately two weeks prior to the full-scale testing. At that time, if modifications are

deemed necessary by the project team, they can be defined and documented in the site-specific sampling protocol.

4.3.7. Testing and measurements protocol

Table 4.3 provides examples for the sample location, the chemical parameter, sample container, preservative and holding time for wastewater samples to be collected during the measurements. This example is a starting point and can be customized and expanded as required for the specific plant where the sampling is conducted. For the full-scale field testing, the plant laboratory will follow their specific laboratory standard operating procedures for each parameter. Standard operating procedures from participating laboratories must be reviewed for adequacy and consistency prior to the measurement campaigns.

Table 4.3 Examples of sampling specifications to accompany off-gas monitoring.

Parameter	Measurement classification			Sample location	Sample volume ¹ (mL)	Sample preservation	Max. holding time
	Type	Frequency	Sample equipment				
pH	C	NA	NA, <i>in situ</i>	Reactor	NA	NA	None, online
COD: Colorimetric	I, C	2/7 d	35 mL glass vial	Reactor, effluent	8	4 °C	1 d
NH ₃ -N: Potentiometric (ISE)	I, C	2/7 d	200 mL glass bottle	Effluent	80	4 °C ²	1 d
NO ₂ ⁻ -N: Spectrophotometric	I, C	2/7 d	200 mL glass bottle	Effluent	40	4 °C ²	2 d
NO ₃ ⁻ -N: Potentiometric (ISE)	I, C	2/7 d	200 mL glass bottle	Effluent	40	H ₂ SO ₄ , pH < 2	28 d
N ₂ O	C	1/7 d	Gas sampling assembly	Reactor headspace	NA	NA	NA
NO _x	C	1/7 d	Gas sampling assembly	Reactor headspace	NA	NA	NA
DO	C	NA	NA, <i>in situ</i>	Reactor	NA	NA	None, online

¹The tabulated sample volume is twice that required for routine duplicate analysis and is apportioned into two sample containers. The additional volume is collected to determine quality control measures such as accuracy (analysis of spiked samples), precision (duplicate analysis) and to account for potential sample loss while handling or analysing.

C: continuous measurement; I: intermittent measurement; Frequency of measurement applies only to continuous measurements

²Storage at 4 °C. Note: the biomass is removed from the sample via centrifugation at 3,500 g for 10 min. Biomass removal arrests further biochemical oxidation of NH₄⁺-N and NO₂⁻-N.

4.4 EMISSION MEASUREMENTS

The various methods for off-gas measurements used in the research and practice are summarized in Table 4.4. When a treatment plant is covered, the concentrations can be easily measured in the ventilation air. Combining the concentration measurements with airflow measurements by e.g. use of a pitot tube (Klopfenstein, 1998) gives a direct estimation of the emitted fluxes (Daelman *et al.*, 2015). Most treatment plants are however directly open to the air and the collection of off-gas is a problem that needs special attention for representative sampling. This can be solved by either using gas hoods for gas collection or measuring in the gas plume downwind of the treatment

plant. The former is the most common approach and is therefore presented in detail in this chapter.

When off-gas measurements are difficult (e.g. in open tanks or when surface aerators prevent the placement of flux chambers), emissions can be calculated from the measurement of dissolved CH₄ and N₂O concentrations. These can be integrated with mass transfer coefficient measurements in mass balance calculations to estimate the emission fluxes (Foley *et al.*, 2010). For dissolved N₂O, microelectrodes can be used to measure the concentration in the water phase on line (Foley *et al.*, 2010, Section 4.7.1), but sampling and gas chromatographic analysis is also possible. For this purpose, sampling the liquid phase and salting out the

soluble gasses to analyse them as a gas has been shown to be an accurate and reliable method (Daelman *et al.*, 2012; Section 4.7.3).

Concentrations of dissolved gases such as N₂O can be continuously measured based on gas phase measurements, according to a gas-stripping method proposed by Mampaey *et al.* (2015) (Section 4.7.4)

Table 4.4 Comparison of different off-gas measurement techniques and approaches.

Method	Liquid phase	Gas phase	Advantages	Disadvantages
Direct measurements from off-gas in covered tanks	Sampling depending on accessibility to treatment tanks	Continuous	Well-developed and easy to apply method. Gives integral emission loads of a treatment plant, with temporal variations.	Needs covered tanks. Difficult to use for spatial variations inside the plant.
Flux chamber for open-surface process tanks	Grab sample, N ₂ O sensor, or using a stripping device with gas measurement	Continuous monitoring	Well-developed and widely applied protocols. Mechanisms and processes contributing to emissions can be inferred based on spatially and temporally based measurements (also zone-specific measurements).	Multiple measurements needed to address spatial and temporal variability and to obtain full emission loads of a plant.
Measuring the emission plume downwind of the treatment plant	Not sampled	Continuous	Straightforward data analysis and calculation when gases are fully mixed. Downwind plume changes can be instantaneously detected and the measurements adjusted accordingly. Flexibility to carry the equipment around either by car or small trolley. Capability to point out emissions from hotspots. Whole plant emission quantification.	A skilled operator is required. Dependence on favourable wind conditions combined with road access. Monitoring only possible with favourable wind. Very limited spatial resolution.

A third alternative for measuring the emission of a total wastewater treatment plant is the detection of the CH₄ and N₂O concentrations in the downwind plume of the plant. This needs very specialized equipment such as photoacoustic or cavity down-ring spectroscopy (Yoshida *et al.*, 2014, Rapson *et al.*, 2014) and is therefore only usable by specialists. The advantage is that monitoring can be done outside plant boundaries, and the full plant with all its process units is monitored. Hotspots at the plant can be identified (e.g. influent works for methane emission or ventilation air stack); however, accurate spatial resolution for e.g. the aeration tanks is not possible. Given the costs of the equipment, long-term monitoring is economically often not possible. The method is established for landfill monitoring, where emissions are estimated by sampling a few days per year with mobile equipment.

4.5 N₂O MEASUREMENT IN OPEN TANKS

The overall procedure for measuring off-gas fluxes from the headspace of open surface activated sludge tanks can involve a flux-chamber approach, which has been used by most published work to date. This works for most

installations, except for surface-aerated systems. When the surface-aerated space is covered, the gas composition in the ventilation air (and its flow rate) can be measured. When the aerators are open in the air, one has to rely on the use of liquid phase balances for N₂O or CH₄ (Foley *et al.*, 2010; Section 4.7). The principal advantage of the flux chamber approach is that it can yield some understanding of the spatial variability in emissions across different zones or the reactor of an activated sludge process. On the other hand, it is operationally intensive to conduct due to the need for multiple sampling locations to get representative measurements. In the US, the off-gas measurement method is a variant of the EPA/600/8-86/008 and the South Coast Air Quality Management District (SCAQMD) tracer methods. This variant was developed to measure sources that have a relatively high surface flux rate when compared to diffusion (for instance, spilled oil containment).

Commercially available replicas of the US EPA surface emission isolation flux chamber (SEIFC, figures 4.1-4.3) are used to measure gaseous nitrogen fluxes from activated sludge reactors. The SEIFC consists of a floating enclosed space from which exhaust gas can be

collected as a continuous or grab sample. Because the surface area under the SEIFC can be measured, the specific flux of the gaseous compound of interest can be indirectly determined. The SEIFC ‘floats’ on the activated sludge tank surface, and several replicate measurements can be taken at different locations in a single tank as well as from different tanks (nitrification, denitrification) along a treatment train.

The SEIFC is equipped with mixing (a physical mixer or via sweep gas circulation) to ensure adequate gas mixing and, ideally, an online temperature probe. The SEIFC is currently one of the few devices accepted by the US EPA for measuring gaseous fluxes (Tata *et al.*, 2003). Continuous gas-phase analyses are conducted via infrared ($\text{N}_2\text{O}/\text{CH}_4$). Although not discussed in this chapter, the gas could also be measured for oxygen and carbon dioxide for measuring bio-conversions in the wastewater treatment process.

In general, sampling in open surface tanks needs to be conducted at multiple locations of the activated sludge train in each wastewater treatment facility. These locations include aerobic, anoxic, and anaerobic zones, depending upon the configuration of the given facility. In non-aerated zones a sweep gas is used to produce an effective gas flow through the flux chamber. During the course of the gas phase sampling, liquid phase samples for dissolved compounds such as ammonium, nitrate and nitrite also need to be collected adjacent to the hood location. The samples should be filtered immediately upon collection in the field and can be analysed utilizing readily available field methods (i.e. Hach kits) and standard laboratory analytical methods (APHA *et al.*, 2012). This allows the measured gas data to be linked with the actual concentrations of relevant compounds at the point of measurement. Comparing the data with influent/effluent measurements or measurements at other spots in the tank might give biased correlation between the off-gas and liquid phase samples.

In open surface tanks, the specific locations selected are typically close to the influent or effluent end of each demarcated anoxic or aerobic zone in the WWTP. Continuous measurement at each of these specific locations is typically conducted over a minimum 24-h period or longer.

The treatment trains of selected wastewater treatment plants that accomplish nitrification and denitrification are characterized based on their liquid-phase and gas-phase nitrogen concentrations and speciation. Testing is

conducted at each location during a sampling campaign during which gas-phase monitoring is conducted in real-time continuous mode and liquid-phase sampling is conducted via discrete grab sampling. Trends and variations in gaseous emissions and speciation are also ascertained. This sampling effort is intended to assist in the development of process-operating criteria that minimize both gaseous and liquid-phase nitrogen emissions from wastewater treatment facilities. The analysis of nitrogen GHG compounds and precursors in both the air and liquid phases is complemented by analysis of conventional wastewater parameters.

Monitoring of the liquid phase and the gas phase can be conducted in seasonally distinct regimes, for instance, once in warm temperature conditions (i.e. summer, early autumn), and cold temperature conditions (winter/early spring) to account for annual variability.

The overall procedure for measuring N_2O and CH_4 fluxes from the headspace of activated sludge tanks involves a variant of the EPA/600/8-86/008 and the SCAQMD tracer methods. Gas-phase analyses can be conducted via infrared ($\text{N}_2\text{O}/\text{CH}_4$) analysers.

In the absence of an approved method for N_2O in air or water, method modification can be necessary to measure N_2O emissions. In a recent study (Ahn *et al.*, 2010a), in order to evaluate the performance of the measurement of N_2O fluxes using the procedure developed by the researchers, three side-by-side monitoring events were conducted along with the research procedure during the first sampling event at a step feed BNR facility. In addition to the standard research protocol, two additional side-by-side monitoring events were conducted as follows (Table 4.5).

Plant wastewater research engineers measured fluxes using the EPA isolation flux chamber and SCAQMD tracer method and with a photo acoustic analyser to directly determine N_2O . Plant consultants used the textbook EPA isolation flux chamber and SCAQMD tracer dilution method to measure the flux and the following analytical methods to measure ozone precursors and GHGs. These side-by-side tests were not designed to validate the modified analytical approach to establish an approved methodology. However, they provided an independent verification that the approach accurately measured nitrogen GHG emissions to meet the objectives of that study, for zones where concurrent side-by-side measurement was conducted. This study was part of the original Water Environment Research Foundation

(WERF) project, during which this protocol was developed.

Table 4.5 Additional comparative analytical methodologies for measuring off-gas emissions from wastewater treatment plants.

Method/Species	Technique	Application
ASTM method 1946- permanent gas analysis	GC/TCD	Relevant fixed gases: CH ₄ , CO, CO ₂ , and helium (He) as a separate analysis.
NIOSH 6600	FTIR	N ₂ O

Based on this side-by-side comparison, it was further recommended that subsequent studies should consider the helium (He) tracer method (based on ASTM D1946) to measure the gas flow rate from the flux chamber, the results of which are reported in (Ahn *et al.*, 2010b).

4.5.1 Protocol for measuring the surface flux of N₂O

The following protocol is intended to provide researchers and field sampling teams with a detailed description of the data collection methodology and analysis requirements to enable the calculation of gaseous nitrogen fluxes from different zones of activated sludge trains in a WWTP.

4.5.1.1 Equipment, materials and supplies

The following equipment is needed to perform the protocol; suppliers and manufacturers may vary:

1. A surface emission isolation flux chamber (commercially available from vendors or custom-built based on specifications from the US EPA (Kienbusch, 1986)).
2. Teledyne API N₂O Monitor Model 320E (Teledyne API, San Diego, CA).
3. Zero gas (containing zero ppm N₂O and CH₄), and N₂O and CH₄ gas standards (Tech Air, White Plains, NY).
4. Dwyer series 475 Mark III digital manometers to measure the flux chamber pressure from 0 to 1" (2.54 cm water column) (high sensitivity) and 0 to 100" (low sensitivity) of a water column (Dwyer Instruments Inc., Michigan City, IN).
5. A rotameter to measure the influent sweep gas flow rate, 0-30 L min⁻¹ (Fisher Scientific, Fairlawn, NJ).
6. An adjustable air pump, 0-10 L min⁻¹ (Fisher Scientific, Fairlawn, NJ) to provide sweep gas flow into the flux chamber.
7. A vacuum pump, 0-30 L min⁻¹ (Fisher Scientific, Fairlawn, NJ) for active pumping of gas from the flux chamber, if needed.
8. 0.2 μm cartridge filters, set of 10 (Millipore, Ann Arbor, MI) to prevent fine particulates from entering the gas analysers.
9. A silica gel column for capturing moisture (Fisher Scientific, Fairlawn, NJ).
10. A glass water trap consisting of a 100 mL glass bottle placed in ice within a Styrofoam[®] box.
11. Teflon[®] tubing (approximately 0.5") and fittings.
12. A 100-300' extension cord and power strip.
13. A laptop personal computer (with at least 512 MB RAM) with data acquisition programs for N₂O and CH₄ analysers pre-installed.
14. A set of miscellaneous hand tools including adjustable wrenches, different size screwdrivers and adjustable pliers.

4.5.1.2 Experimental procedure

The overall procedure for measuring N₂O and CH₄ fluxes from the head-space of activated sludge tanks involves a variant of the EPA/600/8-86/008 and the South Coast Air Quality Management District (SCAQMD) tracer methods, which allow sampling of gaseous emissions from high surface flux rate operations.

This variant has been developed to measure those sources that have a relatively high surface flux rate when compared to diffusion; this facilitates increased sampling at composting and wastewater treatment plants.

Commercially available replicas of the US EPA surface emission isolation flux chamber (SEIFC) are used to measure gaseous N fluxes from activated sludge reactors. The US EPA SEIFC essentially consists of a floating enclosed space through which carrier gas (typically nitrogen or argon) is fed at a fixed flow rate and exhaust gas is collected in a real-time or discrete fashion. Since the surface area under the SEIFC can be calculated or measured, the specific flux of the gaseous compound of interest can thus be determined. Since the SEIFC 'floats' on the activated sludge tank surface, several replicate measurements can be taken at different locations in a single tank as well as from different tanks (nitrification, denitrification) along a treatment train. The SEIFC is also equipped for mixing (with a physical mixer or via sweep gas circulation) to ensure adequate gas and

in some cases, an online temperature probe. The SEIFC is currently one of the few devices accepted by the US EPA for measuring gaseous fluxes (Tata *et al.*, 2003). Gas-phase analyses are conducted via infrared (N_2O , CH_4) methods.

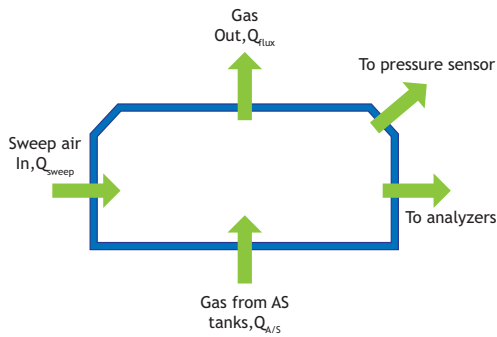


Figure 4.1 Schematic of the US EPA surface emission isolation flux chamber (modified from Tata *et al.*, 2003).

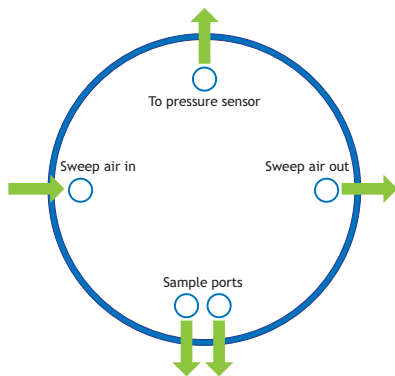


Figure 4.2 Modified schematic of the flux chamber.

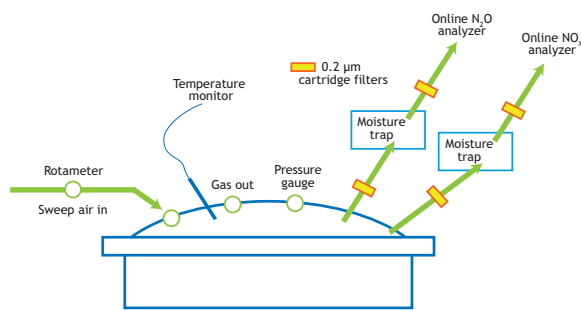


Figure 4.3 Schematic of flux-chamber set-up for gas flux measurements.

In general, sampling is conducted at multiple locations of the activated sludge train in each wastewater treatment facility. These locations are the aerobic, anoxic and anaerobic zones, depending upon the configuration of the given facility. Additionally, within each zone, multiple points (approximately three, but not less than two) must be sampled to address any variability in gas fluxes that may result from variations in mixing or flow patterns therein.

Pressure build-up can be minimized by equipping the flux chamber with multiple vents or a variable size vent and continuously monitoring the pressure drop across the hood using a sensitive pressure gauge. In all the field locations, the gas flow rate should be measured using the tracer gas technique and pressure across the flux chamber should be passively monitored if necessary. Alternatively, the aeration rate from plant records (available as an order of magnitude verification) can be used. The modified setup of the flux chamber used in this study is depicted in figures 4.1–4.3.

During the course of the gas phase sampling, liquid phase samples are collected adjacent to the hood location. The samples should be filtered immediately upon collection in the field and analysed by the host plant personnel for ammonia, nitrite and nitrate concentration, utilizing readily available field methods (i.e. a Hach Kit). As the primary purpose of these measurements is to ensure the presence of the targeted nitrogen species, without consideration for the accuracy in the concentration measurements, the simplest available field method will be used for these preliminary measurements.

4.5.1.3 Sampling methods for nitrogen GHG emissions

The gas-phase sampling method in aerobic zones

1. Seal all but one vent in the flux chamber and connect a high-sensitivity pressure gauge to the one open vent.
2. Lower the flux chamber into the aerobic zone (the bottom of the rim should be below the surface of the water by 2.5–5.0 cm minimum).
3. Wait for the N_2O analyser to equilibrate, based on the stability indicator (<0.03).
4. Pull the flux chamber up. Open two vents and connect the gas analyser. The other vents should be left open to the atmosphere.

- Record the temperature of the gas in the flux chamber using a digital temperature gauge (Fisher Scientific number 15-077-8 or a suitable alternative).
- Care must be taken that the flow going to the two analysers does not exceed the gas flow rate from the flux chamber. Otherwise, atmospheric air will be drawn in through the vents in the flux chamber.

Determination of the gas flow rate from the flux chamber in aerobic zones

- Disconnect the gas analysers and connect one outlet vent to the inlet line of a field gas chromatograph equipped with a thermal conductivity detector. Close the other vent.
- Introduce tracer gas (10 % helium, 90 % zero air) through an inlet vent into the flux chamber at a known flow rate (for instance 1 L min⁻¹).
- Measure the concentration of helium gas exiting the flux chamber (see the protocol in Section 4.6).
- Based on the measured helium concentrations, calculate the flow rate of the aeration tank headspace gas entering the flux chamber (Eq. 4.1, Section 4.6).

The gas-phase sampling method in anoxic zones

- Seal all but one vent in the flux chamber and connect a high-sensitivity pressure gauge to the one open vent.
- Lower the flux chamber into the anoxic zone with a 1-2 inch minimum submergence, into the liquid surface.
- Wait for the N₂O analyser to equilibrate, based on the stability indicator (< 0.03)
- Pull the flux chamber up. Open two vents and connect the gas analyser and the sweep gas pump (Note: sweep gas is only used during anoxic zone sampling). The other vents should be left open to the atmosphere.
- Record the temperature of the gas in the flux chamber using a digital temperature gauge (Fisher Scientific number 15-077-8 or a suitable alternative).
- Care must be taken never to allow the flow going to the two analysers to exceed the sweep gas rate, or dilution air will be drawn in through an opening in the chamber.

Determination of the gas flow rate from the flux chamber in the anoxic zone

- Disconnect the gas analysers and connect one outlet vent to the inlet line of a field gas chromatograph equipped with a thermal conductivity detector. Close the other vent.

- Introduce sweep gas to the chamber at a flow rate of 4 L min⁻¹ and wait 6 min for a steady state.
- Introduce tracer gas (10% He, 90% zero air) through an inlet vent into the flux chamber at a known flow rate (for instance 1 L min⁻¹).
- Measure the concentration of He gas exiting the flux chamber.
- Based on the measured He concentrations, calculate the flow rate of aeration tank headspace gas entering the flux chamber (Eq. 4.1, Section 4.6).

Table 4.6 summarizes the data recording requirement checklist that needs to be followed for the flux-chamber setup and operation. Additional parameters can be added by sampling teams based on a case-specific basis.

Table 4.6 Checklist for flux chamber set-up and operation in field.

Measurement	Sampling location 1	Sampling location 2	Sampling location 3
Pressure in flux chamber			
Gas flow rate from flux chamber			
Gas temperature in flux chamber			
Wastewater temperature			
Air-pump flow rates			

Continuous and real-time gas measurement

- Turn on the power by pressing the on/off switch on the front panel. The display should turn on and the green (sample) status LED should blink, indicating the instrument has entered the HOLD-OFF mode. Sample mode can be entered immediately by pressing the EXIT button on the front panel. The red 'fault' light will also be on until the flows, temperatures and voltages are within operating limits. Clear the fault messages. After the warming up, review the TEST function values in the front panel display by pushing the button TEST on the left of the display.
- Activate the DAS data acquisition software and set the sampling frequency for 1 sample per minute.
- Start the data acquisition.
- Connect the inlet tubing of the analyser to the outlet tubing from the SEIFC securely using a standard 1/4" compression fitting connector.
- Acquire data for about 20 min in anoxic zones and about 10 min in aerobic zones after stable readings

- are obtained, as indicated by the stability indicator on the N₂O analyser.
6. Stop the DAS software and immediately save the acquired data.
 7. Repeat steps 2-5 for each sampling point and sampling locations (individual tanks).
 8. Note that the measurement range is 0-1,000 ppm.
 9. Before each sampling event, calibrate the instrument by using 'zero gas' and N₂O standard gas as per the manufacturer's instructions.

Principles of real-time N₂O and CH₄ measurements

Continuous N₂O and CH₄ measurements are performed via infrared (IR) gas-filter correlation, which is based on the absorption of IR radiation by N₂O and CH₄ molecules at appropriate wavelengths. As part of the measurement process, a broad wavelength IR beam is generated inside the instrument and passed through a rotating gas filter wheel, which causes the beam to alternatively pass through a gas cell filled with nitrogen (a measure cell), and a cell filled with N₂O/N₂ mixture (a reference cell) at a frequency of 30 cycles per second. N₂O concentrations are inferred based on the amount of IR absorption. Ultimately, the 'stripped' beam strikes the detector, which is a thermo-electrically cooled solid-state photo-conductor. This detector, along with its pre-amplifier converts the light signal into a modulated voltage signal.

4.5.1.4 Direct measurement of the liquid-phase N₂O content

In addition to measuring gaseous phase N₂O concentrations in the headspace of aerobic and anoxic zones, liquid phase N₂O concentrations could also be measured to discriminate between N₂O generation in the liquid phase and N₂O emission in the gas phase. Liquid-phase N₂O concentrations can be measured using a polarographic Clark-type electrode (Unisense, Aarhus, Denmark). For additional details of the liquid phase measurements summarized in this section, please refer to the protocols in Section 4.7.

1. Withdraw a sample of about 20 mL from the test reactors in 50 mL conical centrifuge tubes or alternatively similar containers (plastic or glass beakers are acceptable).
2. Take out the microsensor from the calibration chamber (containing deionized water), rinse out with deionized water, and mop dry with a tissue.
3. Immerse the microsensor into the samples. Proceed as rapidly as possible after obtaining the sample.

4. Record the numbers from the display on the picoammeter. The measurement numbers should become stable within one minute.
5. Pull out the microsensor, rinse out and place it back into the calibration chamber.
6. Repeat steps 1 to 5 for each sampling point and location.

The overall sampling effort is rather involved and thus needs to be closely coordinated. The real-time data from the analysers or probes should be automatically downloaded onto a field computer or recorded in laboratory notebooks. All the electronic data should be backed up frequently and where feasible electronic data should be stored on a temporary disk drive (in addition to the PC hard drive) during the field testing events.

4.6 MEASUREMENT OF OFF-GAS FLOW IN OPEN TANKS

This section describes a protocol for the measurement of off-gas flow rates using a helium tracer gas method (after ASTM method D1946). While measuring and reporting gaseous emission fluxes or while performing mass balances, the measurement of both headspace gas concentrations and the overall off-gas flow rates is needed. While gaseous N₂O and CH₄ concentrations from the activated sludge surface can be measured online, it is often not practical to conduct online or even discrete round-the-clock advective gas flow measurements. While blower operational data can be used as an approximation for determining advective flow, however usually only run time or electricity use are measured and conversion to actual air flow has uncertainties. Moreover, this approach suffers some serious uncertainties in the link between overall bulk blower air flow and actual distribution among different aerated zones. Direct measurement of the gas flow in aeration air pipes is an option, or for closed tanks often the off-gas flow rate can be measured. For open tanks a helium tracer method can be used, but not in a continuous mode owing to cost and plant access issues. At this point, the only way to overcome this limitation for open tank systems and reduce the inherent variability from extrapolating flow data from a few discrete measurements is to measure the advective flow rate using the He tracer method more frequently and employ a correlation analysis to translate the discrete flow

measurements through the flux chamber to continuous tank-scale measurements.

4.6.1 Protocol for aerated or aerobic zone

Advective flow of gas through the flux-chamber (Q_{emission}) in aerated zones is measured using a modification of the ASTM method D1946. Briefly, a tracer gas consisting of 100,000 ppmv ($C_{\text{helium-tracer}}$) helium is introduced into the flux-chamber at a known flow rate, Q_{tracer} (Eq. 4.3). Helium concentrations in the off-gas from the flux chamber ($C_{\text{helium-FC}}$) can be measured using a field gas chromatograph equipped with a thermal conductivity detector (GC-TCD). Q_{emission} can then be computed using Eq. 4.1.

Protocol steps

1. Activate the field gas chromatograph approximately prior to the actual helium measurements to allow for the thermal conductivity detector (TCD) and GC column to attain the desired temperatures.
2. After measuring the gas-phase concentrations, disconnect the gas analysers and connect one outlet vent to the inlet line of the field GC. Close the other vent.
3. Introduce tracer gas (10 % helium, 90 % zero air) through an inlet vent into the flux chamber at a known flow rate (for instance 1 L min⁻¹).
4. Measure the concentration of helium gas exiting the flux chamber (as per the ASTM method D1946).
5. Based on the measured helium concentrations, calculate via linear algebra the flow rate of the aeration tank headspace gas entering the flux chamber (Eq. 4.1).

$$Q_{\text{tracer}} \cdot C_{\text{helium-tracer}} = (Q_{\text{tracer}} + Q_{\text{emission}}) \cdot C_{\text{helium-GC}}$$

$$Q_{\text{emission}} = \frac{Q_{\text{tracer}} \cdot (C_{\text{helium-tracer}} - C_{\text{helium-GC}})}{C_{\text{helium-GC}}} \quad \text{Eq. 4.1}$$

6. For each sampling location, repeat steps 2-5 at least three times.

4.6.2 Protocol for non-aerated zones

The only modification to the protocol to measure the emission flow rate from non-aerated zones is the introduction of sweep gas (air) or carrier gas through the flux chamber at a known flow rate (Q_{sweep}), in addition to the helium tracer gas. The corresponding Q_{emission} is computed using Eq. 4.2. The addition of sweep gas is needed to promote mixing of the SEIFC contents, owing

to the low advective gas flow from the anoxic-zone headspace. Sweep-air N₂O and CH₄ concentrations always need to be measured and checked to ensure that they remain below the detection limits of the N₂O or CH₄ analysers.

Protocol steps

1. The only modification to the protocol for adaptation to measuring the emission flow rate from the anoxic zone is the introduction of sweep gas.
2. Introduce sweep gas to the chamber at a flow rate of 4 L min⁻¹ and wait 6 min for a steady state.
3. Follow steps 2-6 as described above for determination of the emission flow rate from aerobic zones.
4. Calculate the emission flow rate from the anoxic zone using Eq. 4.2.

$$Q_{\text{tracer}} \cdot C_{\text{helium-tracer}} = (Q_{\text{tracer}} + Q_{\text{sweep}} + Q_{\text{emission}}) \cdot C_{\text{helium-GC}}$$

$$Q_{\text{emission}} = \frac{Q_{\text{tracer}} \cdot (C_{\text{helium-tracer}} - C_{\text{helium-GC}})}{C_{\text{helium-GC}}} - Q_{\text{sweep}} \quad \text{Eq. 4.2}$$

Each sampling campaign consists of discrete and continuous N₂O measurements. During the discrete N₂O measurements, Q_{emission} should be determined at each location in the treatment plant where N₂O is measured. During continuous N₂O measurements, Q_{emission} should be determined several times a day in correspondence with liquid-phase measurements.

In the case of surface-aerated tanks measuring actual gas flow rates, the actual fluxes of greenhouse gasses is usually an even more difficult task. In these cases emissions can be best estimated from liquid-phase measurements and balances over the liquid phase.

4.7 AQUEOUS N₂O and CH₄ CONCENTRATION DETERMINATION

The aqueous concentrations of nitrous oxide can be directly measured by oxygen electrodes that are polarized differently than for oxygen measurement. For strict anaerobic or anoxic conditions (i.e. no oxygen present) these adapted electrodes can be directly used. For measuring N₂O concentrations in an aerated aqueous phase, a miniaturized Clark-type sensor with an internal reference and a guard cathode is available, and can be successfully applied (Foley *et al.*, 2010). The sensor is equipped with an oxygen front guard to prevent oxygen from interfering with the N₂O measurements. This

method is described in Section 4.7.1. For methane no dissolved gas-phase measurement is available.

The concentrations of N_2O and CH_4 in a liquid sample can be determined by driving the dissolved gas into the gas phase. In a grab sample this can be done by salting out the gasses into the headspace of the sample tube, and analysing the gas phase on a GC (Section 4.7.3). With a gas-stripping device it is possible to continuously monitor the dissolved gas concentrations (Section 4.7.4).

4.7.1 Measurement protocol for dissolved N_2O measurement using polarographic electrodes

4.7.1.1 Equipment

1. A nitrous oxide microsensor N2O25 (Unisense, Aarhus, Denmark).
2. A two-channel picoammeter PA2000 (Unisense, Aarhus, Denmark).
3. A calibration chamber CAL300 (Unisense, Aarhus, Denmark).
4. Zero air and N_2O gas standard (Tech Air, White Plains, NY).
5. Teflon[®] tubing, silicone tubing and fittings.
6. A squeezer with deionized water.
7. Kimwipes.
8. BD Falcon 50 mL conical tubes.

4.7.1.2 Experimental procedure

The Unisense nitrous oxide microsensor is a miniaturized Clark-type sensor with an internal reference and a guard cathode. In addition, the sensor is equipped with an oxygen front guard, which prevents oxygen from interfering with the nitrous oxide measurements. The sensor is connected to a high-sensitivity picoammeter and the cathode is polarized against the internal reference. Driven by the external partial pressure, nitrous oxide from the environment will penetrate through the sensor tip membranes and be reduced at the metal cathode surface. The picoammeter converts the resulting reduction current into a signal. The internal guard cathode is also polarized and scavenges oxygen in the electrolyte, thus minimizing zero-current and pre-polarization time.

The measurement steps are as follows:

- a. Turn on the power switch located on the front panel of the picoammeter.
- b. Check that the 'Gain' screw for Channel 1 is turned fully counter-clockwise.
- c. Turn the display switch, located on the centre of the panel, to 'Signal 1' and check that the display reads zero. If not, adjust the offset, as per the manufacturer's instructions.
- d. Turn the display switch to 'Pol. 1'. Check if the polarization voltage shows -0.8 V. If not, adjust the volt and polarity switch.
- e. Connect the leads of the 'pre-polarized' microsensor to the meter in the following order: (1) Signal wire (black) to 'Input' of Channel 1 on the front panel. (2) Guard wire (yellow) to 'Guard' of Channel 1.
- f. Rinse out the sensor with deionized water and absorb the moisture with tissue paper.
- g. Place the sensor into the calibration chamber, which contains deionized water.
- h. Select the 'Normal' setting for the 'Mode' switch on the front panel, unless you need the extremely fast response.
- i. Select the appropriate measuring range using the 'Range' switch on the panel. Usually 200 pA is selected, but if not suitable, select an alternative available range.
- j. Withdraw about 20 mL sample from test reactors in 50 mL conical centrifuge tubes or alternatively similar containers (plastic or glass beakers are acceptable).
- k. Take out the microsensor from the calibration chamber (containing deionized water), rinse out with deionized water, and mop dry with a tissue.
- l. Immerse the microsensor into the samples. For (j) and (k), proceed as rapidly as possible after acquiring the sample.
- m. Record the numbers from the display on the picoammeter. The measurement numbers should be stable within one minute.
- n. Pull out the microsensor, rinse out and place it back in the calibration chamber.
- o. Repeat steps (j) to (n) for each sampling point and location.
- p. When the measurements are complete, disconnect the sensor leads in the reverse order to which they were connected.

The measurement range is adjustable, 0-0.616 ppmv- N_2O (with 500 ppm N_2O gas standard).

If the sensor is new or has not been operated for several days, then it must be polarized for at least 2 h and up to 12 h before it can be calibrated and/or used, as follows:

- a. Secure the nitrous oxide sensor with its tip, immersed in nitrous oxide-free water.
- b. Turn the display switch to 'Pol. 1' and adjust the polarization to -1.30 V.
- c. Turn the display switch to 'Signal 1' and adjust the 'Gain' screw completely counter-clockwise. Adjust the display to zero on the 'Offset' dial, if needed.
- d. Connect the signal wire (black) of the microsensor to the 'Input' terminal.
- e. After 5 min, adjust the polarization to -0.8 V and then connect the guard wire (yellow) to the 'Guard' terminal.
- f. Pre-polarize for up to 12 h if possible to get the maximum stability.

After the sensor has been polarized, it must be calibrated with zero air and N₂O gas standards. Typically, we have used 500 ppm N₂O gas standards for calibration. Note that N₂O gas standards are specialised items and can be purchased from vendors such as TechAir.

To be consistent in terms of units for liquid and gas phase N₂O, the results of this study are expressed in terms of N₂O. Alternatively, liquid and gas phase N₂O concentrations can also be expressed as 'N' to estimate the fraction of influent nitrogen discharged as N₂O.

4.7.2 Measurement protocol for dissolved gasses using gas chromatography

Both nitrous oxide and methane can be readily analysed by standard gas chromatographic analysis (Weiss, 1981). For liquid samples this can be performed by taking a sample and transferring it directly to a closed bottle or tube with a calibrated volume. In the bottle an equilibrium will establish for the volatile compounds between gas and liquid phase. After equilibration the gas phase concentration can be measured. With the Henry coefficient (corrected for temperature and ionic strength) the liquid concentration for methane or nitrous oxide can be calculated. Using these concentrations and the known gas and liquid volumes in the sample bottle then gives the total mass of compound in the bottle and the original concentration in the sample. This method is prone to many measurements and uncertainties for e.g. the true Henry coefficient for the actual fluid composition.

It is therefore more reliable to drive all the soluble gasses into the gas phase by e.g. a high salt concentration (the salting-out method). This has been described in detail by Daelman et al. (2012) based on the salting-out method described by Gal'chenko *et al.*, (2004). The measurement protocol is described below.

4.7.3 Measurement protocol for dissolved gas measurement by the salting-out method

Before the start of each sampling round, serum bottles of 120 mL are filled with 20 g NaCl. At the different sampling locations at the WWTP, samples are collected with a sampling beaker. From this beaker, 50 mL of the sample is added carefully to a serum bottle filled with salt, using a syringe with a catheter tip and a 10 cm silicone tube. While emptying the syringe into the bottle, the silicon tube is held under the rising liquid surface in order to keep the liquid-gas interface as small as possible to avoid stripping. Immediately after adding the syringe content to the bottle, the bottle is sealed with a rubber stopper and an aluminium cap. The sealed bottle is shaken vigorously in order to speed up the dissolving of the salt. At 20 °C the solubility of NaCl in water is about 360 g L⁻¹, so these samples, containing 400 g NaCl L⁻¹, are oversaturated. As a consequence of the high salt concentration, the microbial activity in the sludge samples is halted, and the dissolved gases are salted out. Dissolved methane, but also the other dissolved gases such as carbon dioxide escape from the liquid phase to the headspace of the serum bottles. This results in a pressure build-up in the headspace. Before sampling the headspace of the samples for analysis with GCFID, the pressure in the headspace needs to be equilibrated with the atmosphere by allowing the gas in the headspace to expand in a submerged graduated syringe. The increase in gas volume is used to calculate the pressure build-up in the headspace. After the gas pressure in the headspace is brought to atmospheric pressure, the headspace is sampled with a gas syringe and analysed in the conventional procedure by gas chromatography. The amount of methane in the headspace before expansion is calculated from the concentration, the measured volume of the headspace of the sealed bottle and the headspace pressure after the pressure build-up that is calculated from the volume expansion of the headspace. Before the sample was saturated with salt, this amount of methane in the gas phase must have been completely dissolved in the liquid sample. By dividing this amount by the sample

volume (50 mL), the original methane concentration in the liquid can be established.

4.7.3.1 Equipment

The equipment needed in this protocol is as follows:

- A sampling beaker.
- A graduated syringe with a catheter tip and tube of ca. 15 cm.
- A serum bottle of ca. 120 mL.
- A rubber stopper.
- An aluminum seal.
- A crimper for aluminium seals.
- 20 g NaCl.
- A beaker.
- A graduated syringe (or burette) with a catheter tip and without a plunger.
- A tube of ca. 30 cm.
- A hypodermic needle.

4.7.3.2 Sampling procedure

- Before sampling starts, add 20 g NaCl to the serum bottle.
- Take a sample from the liquid surface of the reactor or from the valve of a pipe using a sampling beaker.
- Suck 50 mL (V_{sample}) of the sample from the sampling beaker into the syringe with the catheter tip and tube.
- Release the content of the syringe into the serum bottle, while keeping the end of the tube under the liquid surface.
- Seal the serum bottle with the rubber stopper and the aluminium seal.
- Shake the bottle vigorously.

4.7.3.3 Measurement procedure

Measurement of the volume expansion due to pressure build-up in the bottle

- Place the graduated syringe (or burette) in a beaker with water.
- Connect the graduated syringe (or burette) with the catheter tip to the needle with a tube.
- Make sure that the open end of the syringe is submerged in the water in the beaker.
- Register the headspace volume in the syringe V_0 .
- Pierce the rubber stopper of the serum bottle with the needle connected to the syringe (Figure 4.4).
- The headspace volume of the syringe will expand.
- Bring the water level in the syringe to the water level in the beaker to cancel out the pressure of the water column.

- Register the new headspace volume in the syringe V_1 .
- $V_1 - V_0 = V_s$ with V_s the volume expansion due to the pressure build-up in the serum bottle.



Figure 4.4 Measurement of the volume expansion due to the pressure build-up that is caused by the salting-out of the dissolved gases (photo: van Dongen, 2015).

Measurement of the methane or the nitrous oxide concentration in the headspace

Draw a sample from the headspace of the serum bottle with a gas syringe and measure it with a gas chromatograph equipped with a flame ionization detector, according to the appropriate method for measuring methane.

Measurement of the headspace of the serum bottle

- Mark the level of the NaCl saturated sample in the serum bottle.
- Mark the lower side of the rubber stopper.
- Empty and rinse the bottle.
- Fill the bottle with clean water up until the mark of the liquid level.
- Register the weight of the bottle W_0 .
- Add clean water to the bottle up until the mark of the stopper.

- g. Register the weight of the bottle W_1 .
- h. $(W_1 - W_0) \times \rho = V_{HS}$ with ρ the density of the water and V_{HS} the volume of the headspace of the serum bottle.

4.7.3.4 Calculations

Volume

$$V = V_s + V_{HS} \quad \text{Eq. 4.4}$$

Where, V is the expanded volume of the headspace (m^3), V_s is the volume expansion due to the pressure build-up (m^3), and V_{HS} is the headspace of the serum bottle before expansion (m^3).

Amount of methane

$$n = \frac{P \cdot V}{R \cdot T} \quad \text{Eq. 4.5}$$

Where, n is the amount of methane in the expanded headspace of the serum bottle (mol), P is the atmospheric pressure (Pa), V is the expanded volume of the headspace (m^3), R is the ideal gas constant: $8.314 \text{ m}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$, and T is the temperature (K).

Concentration

$$C = \frac{n}{V_{\text{sample}}} \quad \text{Eq. 4.6}$$

Where, C is the concentration (M), n is the amount of methane in the expanded headspace of the serum bottle (mol), and V_{sample} is the volume of the sample (L).

4.7.4 Measurement protocol for dissolved gas measurement by the stripping method

4.7.4.1 Operational principle

This method was first published in Mampaey *et al.* (2015). By using a gas-stripping device, it is possible to monitor dissolved gases, e.g. N_2O , on a continuous basis. The unknown liquid concentration can be calculated from the measured gas-phase concentration in the off-gas of a stripping device. The proposed method relies on a gas-stripping device, consisting of a stripping flask and a scum trap flask, as displayed in Figure 4.5.

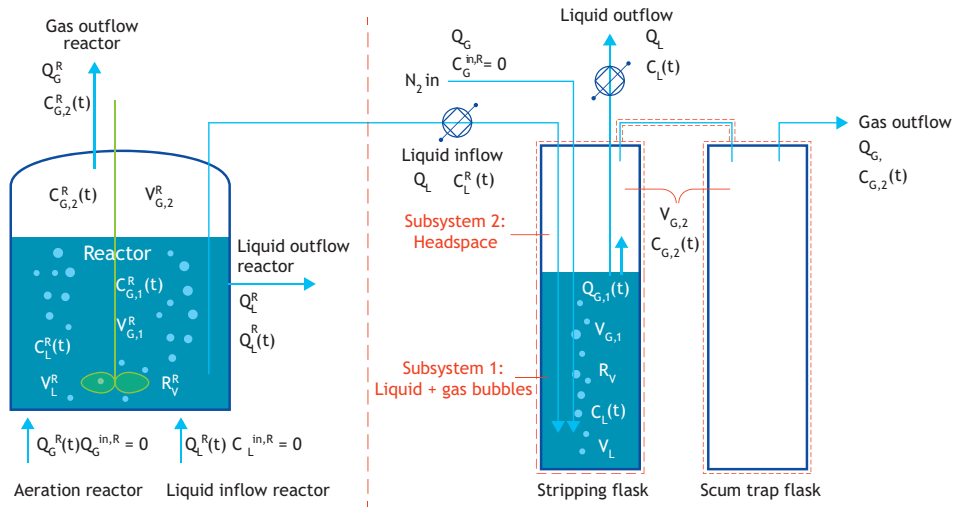


Figure 4.5 Lay-out of the reactor (left) and the gas stripping device (right) for monitoring dissolved gases (Mampaey *et al.*, 2015).

A liquid sample stream from the reactor is continuously supplied to the stripping flask at a constant flow rate Q_L , while maintaining a constant liquid volume V_L in the stripping flask. The scum trap flask is an empty bottle to collect entrained scum from the stripping flask.

Nitrogen is used as the stripping gas in the stripping flask through fine bubble aeration at a constant flow rate Q_G^{in} . The gas outflow of the gas-stripping device is analysed by an online gas-phase analyser. The dissolved

concentration in the reactor, $C_L^R(t)$, is calculated from the measured gas concentration $C_{G,2}(t)$ according to Eq. 4.7.

$$C_L^R(t) = \frac{Q_G}{Q_L} \cdot \left(1 + \frac{Q_L}{a_3 \cdot V_L} \right) \cdot C_{G,2}(t) - \frac{Q_G}{Q_L} \cdot a_1 \quad \text{Eq. 4.7}$$

The parameters a_1 and a_3 are determined from a batch-stripping test. During this test, the stripping flask is filled in batches with a liquid sample from the reactor under study from which the dissolved N_2O is subsequently stripped with N_2 . The monitored gas phase profile $C_{G,2}(t)$ from the stripping device is then described by Eq. 4.8.

$$C_{G,2}(t) = a_1 + a_2 \cdot \exp(-a_3 \cdot t) - a_4 \cdot \exp(-a_5 \cdot t) \quad \text{Eq. 4.8}$$

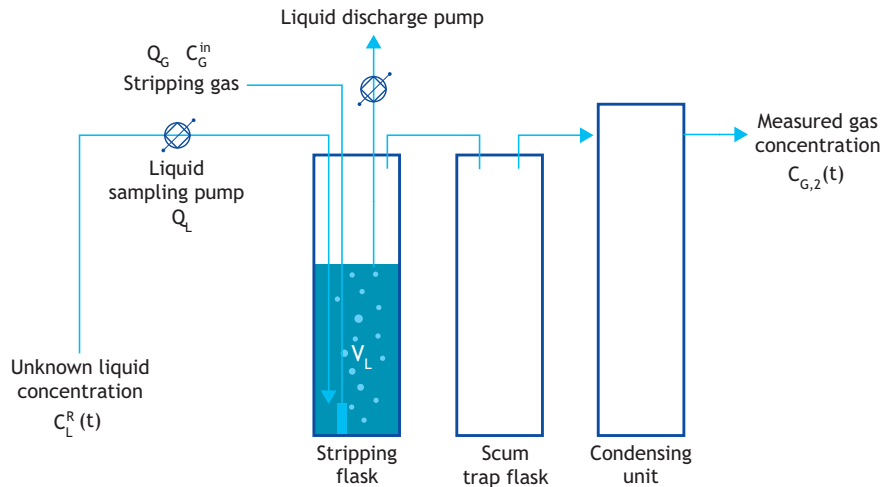


Figure 4.6 Layout of the gas-stripping device.

4.7.4.2 Equipment

The detailed layout of the gas-stripping device is shown in Figure 4.6, and consists of:

- A stripping flask: a graded plastic cylinder of 250 mL with an (aquarium) aeration stone for the stripping gas and a rubber stopper with four connections (stripping gas in, stripping gas out, sampled liquid in and liquid out) to seal the stripping flask. The liquid is introduced at the bottom of the stripping flask, next to the aeration stone for intense mixing. The liquid is extracted 10 cm below the rubber stopper, which results in a constant liquid volume V_L of 100 mL. A larger liquid volume increases the sensitivity of the device (K) but decreases the frequency of measurements (or decreases the observability of rapid changes in concentrations).
- A scum trap flask: a 2 L bottle to collect any entrained scum was used.
- A liquid sampling pump: a peristaltic pump with a tube with an inside diameter of 3.1 mm (Masterflex tubing size L/S = 16), which yields a liquid flow rate of 85 mL min^{-1} . It is advised to keep the length of the liquid feed tube as short as possible. A larger liquid flow rate (Q_L) increases the sensitivity of the device.

The gas-stripping device provides an adequate method to indirectly measure dissolved gases (N_2O or other gases) in the liquid phase, for aerated as well as non-aerated conditions/reactors, following variations both in time and in space. Its application to an intermittently aerated (on/off) partial nitrification (SHARON) reactor was demonstrated by Mampaey *et al.* (2015). Castro-Barros *et al.* (2015) applied the method to a one-stage partial nitrification-anammox reactor, subject to alternating high and low aeration. In both cases, the mass balance approach on which the liquid N_2O concentration measurement method is based also allowed the determination of the N_2O formation rate.

- d. A liquid discharge pump: a peristaltic pump with a tube with an inside diameter of 6.4 mm (Masterflex tubing size L/S = 17), which yields a liquid flow rate of 245 mL min⁻¹.
- e. Stripping gas: a stripping gas flow rate (Q_G) of 1.2 NL min⁻¹ is required for the analyser. The following two possibilities of stripping gas can be utilized: (i) gas cylinder N₂ is utilized, a mass flow controller can be used to control the stripping gas flow rate (at 1.2 NL min⁻¹), and (ii) ambient air can also be utilized as stripping gas. A diaphragm pump in combination with a mass flow controller can be used to provide the required gas flow rate (1.2 NL min⁻¹).
- f. A condensing column / gas drying unit for the removal of air moisture.
- g. Tubing: it is advised to use neoprene tubing to prevent diffusion of O₂.
- h. A weatherproof box to protect the electronic part of the setup.

The gas phase is measured by a gas-phase measurement device as described in Section 4.5.

4.7.4.3 Calibration batch test

The parameters a_1 and a_3 are characteristics of the gas-stripping device and are determined from a batch-stripping test. During this test, the stripping flask is filled in batches with a liquid sample (containing dissolved N₂O) from the reactor under study and flushed with the stripping gas (typically N₂). The monitored gas-phase profile $C_{G,2}(t)$ from the stripping device is then described by a double exponential profile (Eq. 4.9):

$$C_{G,2}(t) = a_1 + a_2 \cdot \exp(-a_3 \cdot t) - a_4 \cdot \exp(-a_5 \cdot t) \quad \text{Eq. 4.9}$$

Eq. 4.9 is fitted to the batch test measurement to obtain the values for the coefficients. A calibration example is shown in Figure 4.7.

Parameter a_1 is related to the (N₂O) conversion rate in the stripping flask and its concentration in the stripping gas, a_3 is related to the interphase transfer rate in the stripping flask, and a_5 is related to the gas delay by the scum trap flask. The exact meanings of these parameters can be found in Mampaey *et al.* (2015).

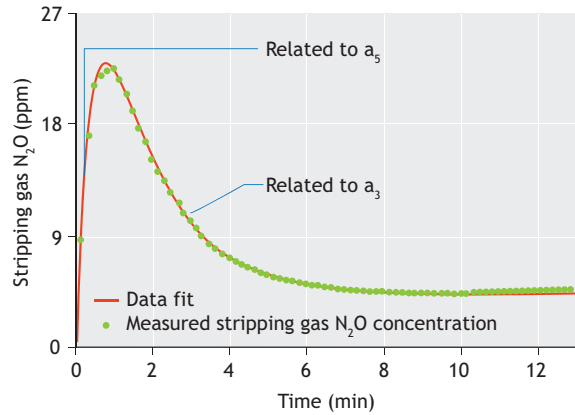


Figure 4.7 Example of a calibration batch test with data fit.

4.7.4.4 Measurement accuracy

The sensitivity of the setup can be calculated from Eq. 4.6. In the current setup, an accuracy for $C_L^R(t)$ of 0.03 g N m⁻³ is achieved. The fastest measurable changes in $(C_L^R(t))$ is estimated from Eq. 4.11, given as a frequency of sampling (f_{sample}).

$$K = \frac{a_3}{a_3 + D_L} \cdot \frac{Q_L}{Q_G} \quad \text{Eq. 4.10}$$

$$f_{\text{sample}} < a_3 + D_L \quad \text{Eq. 4.11}$$

The parameter a_3 is the decreasing exponential term in the calibration batch test (Eq. 4.8), $D_L = Q_L/V_L$ is the liquid dilution rate, Q_G is the stripping gas flow rate (1.2 NL min⁻¹), Q_L is the liquid sampling flow rate (84 mL min⁻¹), and V_L is the liquid volume in the stripping flask (100 mL).

4.7.4.5 Calculation of the N₂O formation rate in the stripping device

N₂O formation can occur in the stripping flask and is reflected in parameter a_1 . The N₂O formation rate in the gas-stripping device is calculated from Eq. 4.12. C_G^{in} is the N₂O concentration in the fresh stripping gas; if no N₂O is present, $C_G^{\text{in}} = 0$.

$$R_V = (a_1 - C_G^{\text{in}}) \cdot \frac{Q_G}{V_L} \quad \text{Eq. 4.12}$$

The formation rate in the sampled water body is calculated as the sum of the gas emission and change in dissolved N₂O through a mass balance, Eq. 4.13.

$$R_V(t) = \frac{\Delta C_L^R(t)}{\Delta t} + \text{Emission} \quad \text{Eq. 4.13}$$

4.8 DATA ANALYSIS AND PROCESSING

4.8.1 Determination of fluxes

The net flux of gaseous N₂O or CH₄ (kg m⁻² d⁻¹) can be calculated based on the gas flow rate out of the flux chamber (Q_{emission}, m³ d⁻¹), the gas concentration (C, kg m⁻³), and the cross-sectional area of the SEIFC (A, m²) (Eq. 4.14).

$$\text{Flux} = \frac{Q_{\text{emission}} \cdot C}{A} \quad \text{Eq. 4.14}$$

The calculated flux should be corrected to reflect standard temperature (20 °C) and pressure (1 atm).

4.8.2 Determination of aggregated emission fractions

As previously described, the specific locations selected for measuring gaseous and aqueous concentrations of N₂O and CH₄ can be close to the influent or effluent end of each demarcated anoxic or aerobic zone in the WWTP, or, alternatively, at locations where the production of these two gases could be inferred based on initial screening of the process variable concentrations. Using these point measurements and assuming that these measured concentrations were uniform over a particular zone, the emissions from any given zone can be computed according to the following equation:

Emissions from *i*th zone in a WWTP = Emissions from SEIFC × (Area of *i*th zone/Area of SEIFC).

Emission measurements must be repeated at multiple zones for any given plant. The overall emissions of the plant are then calculated by summing the emissions from each zone measured over a 24-h period (at the very minimum). The surface flux calculated from Eq. 4.14 is translated into the flux of a given zone by multiplying with the specific zone area. The N₂O emission fractions (mass/mass) for each WWTP at any given time point can be computed by normalizing the measured flux from each

zone in the facility to the daily influent total Kjeldahl nitrogen (TKN) loading according to Eq. 4.15. Correspondingly, for methane, the measured flux could be normalized to the influent COD loading. Emission fractions are typically averaged over the course of the diurnal sampling period and reported as the average (avg) ± standard deviation (sd) for each individual process sampled.

During each campaign, wastewater nitrogen species and COD concentrations including influent, bioreactor, and effluent concentrations are measured simultaneously about six times per day according to APHA *et al.* (2012) to supplement the gas-phase measurements. The discrete measurements are to be averaged to generate the emission fractions described in Eq. 4.15.

$$\text{Emission fraction} = \frac{\sum_{i=1}^n \text{Flux}_i \times \text{Area}_i \text{ (kg N}_2\text{O-N)}}{\text{Daily influent TKN load (kg-N)}} \quad \text{Eq. 4.15}$$

Where, Flux_{*i*} is the N₂O emission flux calculated from the *i*th zone (kg N₂O-N m⁻² d⁻¹), Area_{*i*} is the surface area of the *i*th zone (m²), *n* is the number of zones in a given facility from which the N₂O fluxes are captured, and the Daily influent TKN load is the average influent load (influent flow rate × influent TKN concentrations) over the course of 24 h. It should be noted that the above calculations reflect the emission factor calculated from discrete N₂O measurements. In plants where significant diurnal variability exists, such variability will be accounted for by a combination of explicit measurements in select zones and mathematical modeling output of N₂O fluxes from the remaining zones.

Virtually identical equations can be used for methane, with the only distinction of normalizing to total COD mass loads in the influent or, as applicable, the COD mass removal rate.

On average, wastewater characterization about six times per day is recommended at each gas sampling location as well as in the tank influent and effluent. At facilities where analysis is not as frequent (for instance in the influent and effluent samples), daily composite measurements can be used. Alternatively, in some facilities, online devices (for measuring pH, DO, oxidation-reduction potential (ORP), and select N-species, including NH₄⁺-N and NO₃⁻-N) can also be used at different locations of the activated sludge tank to facilitate the characterization of the wastewater.

4.8.3 Calculation of the emission factors

To directly compare results from off-gas monitoring campaigns with the approaches suggested by the EPA and IPCC, it becomes necessary to summarize the monitoring campaign results in terms of emission factors. Such emission factors can be computed by normalizing the total reactor N₂O or CH₄ mass flux to the unit population equivalent flow rate (100 gal PE⁻¹ d⁻¹, or

equivalently, 378.5 L PE⁻¹ d⁻¹ in the US, US EPA, 2012). The resulting emissions fluxes are expressed in units consistent with the US EPA inventory report (g N₂O or CH₄ PE⁻¹ d⁻¹) (US EPA, 2012). Although the dynamic variability in WWTP off-gas emissions renders the use of point emission factors (such as the ones presented by the EPA and IPCC) somewhat limited, the added step of computing emission factors could be useful for a side-by-side comparison of estimated emissions and those that are actually measured.

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