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Chapter 5

Full-scale quantification of N₂O and CH₄ emissions from urban water systems

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SUMMARY

The quantification of direct greenhouse gas (GHG) emissions from sewers and wastewater treatment plants is of great importance for urban sustainable development. In fact, the identification and assessment of anthropogenic sources of GHG emissions (mainly nitrous oxide and methane) in these engineered systems represent the first step in establishing effective mitigation strategies. This chapter provides an overview of the currently available nitrous oxide and methane quantification methods applied at full-scale in sewers and wastewater treatment plants. Since the first measurement campaigns in the early 90 s were based on spare grab sampling, quantification methodologies and sampling strategies have evolved significantly, in order to describe the spatio-temporal dynamics of the emissions. The selection of a suitable quantification method is mainly dictated by the objective of the measurement survey and by specific local requirements. Plant-wide quantification methods provide information on the overall emissions of wastewater treatment plants, including unknown sources, which can be used for GHG inventory purposes. To develop on-site mitigation strategies, in-depth analysis of GHG generation pathways and emission patterns is required. In this case, process-unit quantifications can be employed to provide data for developing mechanistic models or to statistically link GHG emissions to operational conditions. With regard to sewers, current available methods are not yet capable of capturing the complexity of these systems due to their geographical extension and variability of conditions and only allow the monitoring of specific locations where hotspots for GHG formation and emission have been identified.

Keywords: Greenhouse gas; quantification method; sewers; wastewater treatment

TERMINOLOGY

Term	Definition
Carbon footprint	A carbon footprint is the total greenhouse gas emissions caused by an individual, event, organization, service, or product, expressed as carbon dioxide equivalent.
Greenhouse gas (GHG)	Gas that absorbs and emits radiant energy within the thermal infrared range.
Hydraulic retention time (HRT)	HRT is a measure of the average length of time that a volume of wastewater remains in a given sewer section or a process unit.
$K_L a$	$K_L a$ describes the rate of mass transfer process. " K_L " is the mass transfer coefficient while "a" refers to the liquid-gas interface area per volume (A/V). Due to the difficulties in separating the two parameters experimentally, the two are combined in a term $K_L a$, and measured as an overall parameter.
Mass transfer	In this chapter, mass transfer refers to the liquid-to-gas or gas-to-liquid transport process of a gaseous species such as nitrous oxide. The rate of mass transfer is proportional to the difference between the equilibrium concentration and the concentration of concern. The rate of transfer reduces to zero, when the equilibrium is reached.
Negative pressure	In this chapter, negative pressure refers to a pressure under the hood that is lower than the atmospheric pressure.
Off-gas	Refers to any gas that is emitted from a given unit-process.
Sewer	A network of artificial underground conduits that convey and transport wastewater and/or stormwater from its origin to its treatment point.
Sewer rising main pipes	A rising main is a type of drain or sewer through which sewage and/or surface water runoff is pumped from a pumping station to an elevated point. Rising main pipes are fully pressurized and anaerobic conditions prevail in these sections of sewers.
Sewer gravity pipes	Opposite to rising main pipes, gravity sewer pipes are conduits that use a difference in elevation points, from high to low, and gravity to transport wastewater. Gravity pipes have a liquid and a gas phase which implies a certain reaeration of wastewater.

5.1 INTRODUCTION

A key to formulating strategies to control and reduce greenhouse gas (GHG) emissions to the atmosphere is the identification and quantification of all sources. This chapter describes the current existing quantification methodologies that are capable of quantifying fugitive GHG emissions from engineered urban water systems. Special focus is given to full-scale quantification in sewer systems and wastewater treatment plants (WWTPs), which have been revealed so far to be anthropogenic sources of direct N_2O and CH_4 emissions. The impact of these engineered systems is lower than some other natural and anthropogenic sources on a global scale. According to the estimations of the United Nation Framework Convention on Climate Change (UNFCCC), in 2018 N_2O and CH_4 emissions from wastewater treatment and discharge in industrialized (Annex I) countries contributed 2.6% and 3.6% to the total CO_2e emissions, respectively (UNFCCC, 2018). However, mitigation strategies aiming to achieve a sustainable development of urban areas must address these emission pathways. In response to this, measurement methods for source identification and quantification of overall N_2O and CH_4 emissions in these systems have been developed. In addition, tailored methodological approaches that provide a deeper insight in the GHG production and emission mechanisms in sewers and WWTPs can be applied when the focus is on the implementation of mitigation measures at process-unit scale. In this way the operation of single process-units can be optimized to reduce the overall carbon footprint.

To the authors' knowledge, GHG emission measurements at WWTPs were firstly performed by Czepiel P.M., Crill P.M., and Harries R.C. at Durham, New Hampshire (US) and date back to 1993. The measurement campaign aimed to quantify CH_4 emissions from the primary and secondary wastewater

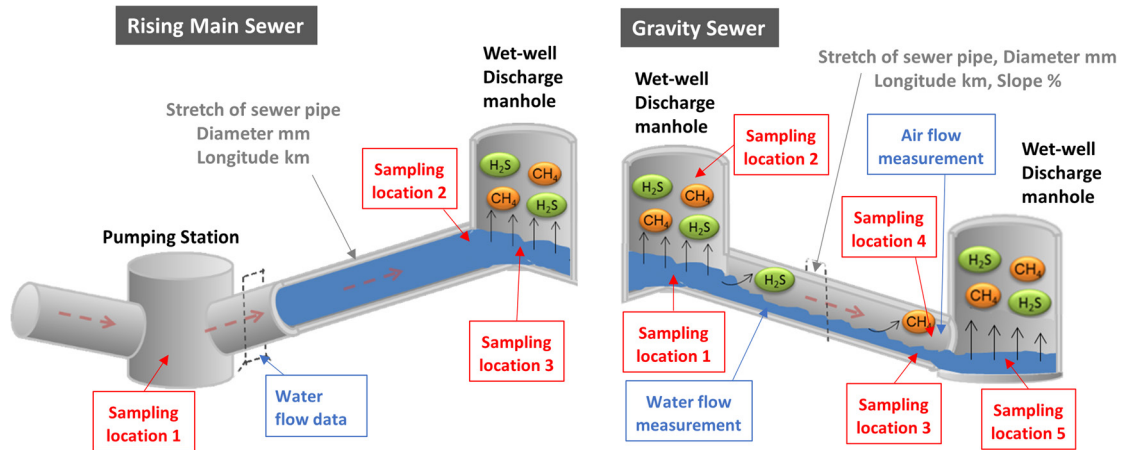


Figure 5.1 Sampling points and data required to quantify CH₄ emissions depending on the typology of sewer (adapted from Liu *et al.*, 2015a).

treatment processes and correlated these emissions with fluctuations in wastewater temperature (Czepiel *et al.*, 1993). The results of a second measurement campaign which targeted N₂O emissions were published two years later (Czepiel *et al.*, 1995). These pioneering works represented, till 2019, the scientific basis supporting the default emission factors suggested by the IPCC guidelines for national GHG Inventories (IPCC, 1996, 2006). Since then, the number of GHG emission measurements conducted at full-scale has increased steadily and hence the applied quantification methodology has been significantly improved. As a matter of fact, first measurement campaigns were performed using a grab sampling approach and therefore did not capture the temporal and seasonal variability of emissions, as clearly indicated by later full-scale surveys and experimental research works. The development of more rigorous quantification protocols was multilateral proceeding from grab sampling to online monitoring, from short-term to long-term measurement campaigns, and from process-unit to plant-wide quantification methodologies. With the “2019 Refinement” of the IPCC Guidelines (IPCC, 2019), default emission factors were revised using state-of-the-art knowledge and also CH₄ emissions from the sewers were considered. Nevertheless, the provided estimation of GHG emissions for inventory protocols still remains questionable, as it relies on fixed and generic emission factors that do not depict the wide variability of emission pattern against time, local process specification and operating conditions. Consequently, in most cases, the quantification and monitoring of GHG emissions at full-scale remains the only possibility to accurately describe emission loads and patterns.

This chapter is intended to give a general overview on the most widely applied methods to quantify GHG emissions from full-scale sewers and WWTPs. Sections 5.2 and 5.3 are dedicated to the quantification of GHG emissions in sewers and in WWTPs, respectively. Most of the methods applied to these engineered systems can quantify both N₂O and CH₄ emissions.

5.2 QUANTIFICATION OF GHG EMISSIONS IN SEWERS

Even though GHG emissions from sewers have been long realised, current quantification methods do not account for the complexity of the sewer systems due to their geographical extension and the high variability of conditions that exist within these systems (changing flows, temperatures, turbulence, loads, etc.). Ideally, longitudinal GHG concentrations in sewer networks (both dissolved and in the headspace) should be assessed to capture the spatio-temporal variability of GHG production under

different conditions. However, available methods are not sufficiently advanced and are only applied to monitor specific locations that have been identified as hotspots for GHG formation and emission.

GHG emissions from sewers depend highly on the configuration of the sewer sections. Operationally, sewer systems can be divided into two categories: (i) fully filled pressure sewers (rising main sewers), which are predominantly anaerobic, and (ii) partially filled gravity sewers, where re-aeration processes can take place (Figure 5.1). In sewers, microbial processes that lead to GHG production mainly take place in wetted biofilms and sediments, with little contribution from the suspended biomass in the water phase or in the gas phase (see Chapter 3). Thus, quantification should typically include measurements of both liquid and gas phases, combined with water and air flow measurements to close the balance between GHG produced and emitted.

CH₄ is the main GHG produced in sewer systems. For instance, in rising main pipes, CH₄ can be produced and accumulated even beyond saturation concentrations in the transported sewage and then released to the atmosphere at ventilated locations such as pumping stations, manholes or influent headworks of WWTPs. CH₄ produced in gravity sewers is usually released into the gas phase along the sewer pipe, with more intensive emissions at locations with higher sewage turbulence (Liu *et al.*, 2015a, 2016). These aspects need to be considered when identifying sampling points for a measuring campaign.

N₂O has also been detected in a few field-scale sewer sampling campaigns, which could contribute to the overall GHG inventory (Short *et al.*, 2014). The methods used for N₂O quantification are similar to those traditionally used for CH₄ detection. To date, little information exists regarding the role that sewers play in the production and emission of N₂O due to the low number of studies and limited monitoring of this compound in wastewater collection networks.

To date, the primary method for GHG measurement in sewers is by manual sampling at regular intervals over several hours followed by offline gas chromatography (GC) analysis (Foley *et al.*, 2011a; Guisasola *et al.*, 2008; Short *et al.*, 2014). This approach has several limitations as production and emission of CH₄ in sewers displays a significant temporal and spatial variation which is difficult to capture with this approach. Thus, continuous and extended online monitoring of CH₄ is recommended although the number of options is still limited, especially with regard to the measurements of dissolved CH₄ and N₂O. Although there is no fixed duration for sampling campaigns, their length should be sufficient to include variations in sewer conditions, which typically occur over several days to weeks. In sewers, there is a diurnal flow pattern with mostly quiescent conditions overnight due to lower flows followed by higher turbulence during the daytime due to higher flows. Ideally, samples should be taken across several time points of the day to include daily variations. In addition, it is also recommended to perform measurement campaigns in warm and cold seasons of the year as sewage temperature, among other parameters, can play a significant role in CH₄ production (Liu *et al.*, 2015b).

5.2.1 Quantification methods of CH₄ emissions in sewers

Due to the operational complexity of sewer systems and dynamic nature of CH₄ emissions it is impractical to estimate overall CH₄ emissions from large networks through either online or offline measurements. The large number of GHG forming and emission points makes full large network monitoring practically impossible. The most common monitoring approach consists of first identifying the main GHG hotspots in sewers and then carrying out individual measurements on those points. This approach assumes that the measurements will include the majority of emissions and will reduce the error of overall estimated emissions.

As stated above, the majority of the CH₄ is formed in rising mains and then completely stripped to the atmosphere via ventilation in manholes, gravity sewers or at WWTPs. This is also supported by the fact that biological CH₄ oxidation in gravity sewer conditions is expected to be a slow process (Valentine and Reeburgh, 2000). CH₄ estimations from rising main sewers are simpler and more accurate because CH₄ generated along the pipe will be released only in the upstream discharge point. Therefore, rising main data can be used to calculate the maximal potential overall CH₄ emission rates of a particular rising main section of a sewer. The CH₄ load in a rising main pipe can be calculated from the following equation:

$$M_{\text{CH}_4} = C_{l, \text{CH}_4} \cdot Q_d \quad (5.1)$$

where M_{CH_4} is the mass of CH₄ potentially emitted to the atmosphere per time unit (g/d), C_{l, CH_4} is the dissolved CH₄ contained in the bulk liquid in mass/volume (g/m³) and Q_d is the flowrate of wastewater in the rising main pipe (m³/d).

Flow measurements are usually carried out by means of flowmeters or can also be estimated from the functioning regime of the pump stations upstream of rising mains. Dissolved CH₄ is calculated by applying the headspace method because of the lack of practical methods to directly measure the dissolved concentration in wastewater. A sewage sample is placed in a vacuumed partially-filled container where dissolved CH₄ is stripped from the liquid to the gas phase. Once under equilibrium, CH₄ gas can be measured and converted back to the liquid phase concentration using Henry's Law gas-liquid equilibrium and mass balance as described in the following equations:

$$C_{l, \text{CH}_4} = \frac{(V_c - V_s) \cdot C_{g, eq} + V_s \cdot C_{l, eq}}{V_s} \quad (5.2)$$

$$C_{l, eq} = H \cdot R \cdot T \cdot C_{g, eq} \quad (5.3)$$

where C_{l, CH_4} is the dissolved methane concentration in the sewage sample (mol/L), V_s is the volume of the liquid sample (L), V_c is the volume of the sample container (L), $C_{g, eq}$ is the methane concentration in gas under equilibrium (mol/L), $C_{l, eq}$ is the methane concentration in water under equilibrium (mol/L), H is the Henry's Law constant (mol/L·atm), R is the ideal gas constant (0.0821 L atm/mol·K) and T is the temperature (K).

On the other hand, quantification in gravity sewers is complex and still highly impractical. Gravity sewers combine a liquid and a gas phase, which are highly dynamic since CH₄ can be formed and stripped heterogeneously over an extensive distance. A comprehensive analysis would require simultaneous long-term measurements in the gas and liquid phase combined with reliable data of wastewater and airflow in multiple locations of a network (Figure 5.1). Due to this constraint, studies to date have focused on the quantification of CH₄ emissions by direct measurement of CH₄ gas flux from single discharge manholes (Willis *et al.*, 2011). However, this methodology is expected to underestimate emissions as CH₄ could also be emitted at several other locations in the network.

5.2.2 Measurement of CH₄ in the liquid phase

Dissolved CH₄ sampling in fully-filled rising main sewers is mainly carried out through tapings connecting a sampling tap at ground level to the tapping arrangement of the underground pipe. Wastewater samples are collected from the pipe using a hypodermic needle and plastic syringe to prevent exposure of sampled wastewater to the atmosphere and oxygen, as shown in Figure 5.2 below (Foley *et al.*, 2009). Dissolved CH₄ is then measured and calculated by applying the headspace method for GC using Henry's Law and mass balance as described in Section 5.2.1.

For sampling dissolved CH₄ in gravity sewers, manholes, wet wells and pumping stations, wastewater samples are usually collected with a sampling device consisting of an open-head cylindrical container which is lowered and filled below the water level, and then gently retrieved. Within the container, sample aliquots are extracted with a plastic syringe from ca. 5 cm below the water surface to avoid contact with air (Foley *et al.*, 2011b). Alternatively, a submersible pump can be used to collect a sample from below-ground at low speed in order to avoid turbulence. Sub-samples are subsequently extracted into evacuated Exetainer® tubes (Labco, Wycombe, UK) or a pre-treated serum bottle (Daelman *et al.*, 2012). The contents of the tube or bottle are mixed overnight to reach gas-liquid equilibrium. CH₄ concentration in the headspace is again measured by GC, and the dissolved CH₄ concentration of the sample is then calculated using Henry's Law and mass balance. A more accurate method using evacuated Exetainer® tubes for both gas and liquid phase CH₄ sampling and measurement was proposed



Figure 5.2 Collection of dissolved CH_4 sample directly from the rising main into an airtight syringe, adapted from [Foley *et al.* \(2009\)](#). Reprinted from *Water Science & Technology*, volume 60, issue number 11, pages 2963–2971, with permission from the copyright holders, IWA Publishing.

by [Sturm *et al.* \(2014\)](#) which uses nitrogen gas to thoroughly flush the tubes before evacuating and sampling, to minimize the residual CH_4 present in the Exetainer[®] tubes.

A limited number of commercial sensors are available for online, dissolved CH_4 measurement ([Boulart *et al.*, 2010](#); [Camilli and Hemond, 2004](#)). However, these are mainly designed for measuring CH_4 in clean water, using gas-permeable membranes to extract CH_4 gas from water, and cannot be used in sewage containing a large amount of impurities as well as high sulfide concentrations ([Boulart *et al.*, 2010](#)). Liu and co-authors (2015b) developed an online, dissolved CH_4 sensor that uses an online gas phase CH_4 sensor to measure CH_4 under equilibrium conditions after stripping from the sewage. The data is then converted to liquid phase, dissolved CH_4 concentrations according to Henry's Law. The detection limit (ca. 0.24 mg/L) and range (ca. 0–24.2 mg/L) are both suitable for sewer application, and can be adjusted by varying the ratio of liquid-to-gas phase volume settings according to specific applications, i.e., at a ratio of 4, a resolution of 0.09 mg/L can be achieved at the expense of a reduced measurement range of 0 to 9.3 mg/L. The sensor demonstrated good performance over a six-week period when positioned at the end of a rising main sewer network ([Figure 5.3](#)).

5.2.3 Measurement of CH_4 in the gas phase

Several online sensors for gas phase CH_4 monitoring are available but most are not applicable in sewer conditions due to interference from hydrogen sulfide which is simultaneously produced and emitted from sewers ([Deng *et al.*, 1993](#); [Schierbaum *et al.*, 1992](#)). Infrared (IR) spectroscopy is the most promising method for online CH_4 measurement in sewer conditions ([Foley *et al.*, 2011b](#)). Particular sampling arrangements are required for measuring gas phase CH_4 concentrations. Gas may be sampled from a ventilation point ([Shah *et al.*, 2011](#)) or from a purpose-built sampling chamber connected to the sewer headspace ([Liu *et al.*, 2015b](#)). For grab sampling, gas bags or evacuated Exetainer[®] tubes can be used. The gas samples can be then analysed using GC equipped with a flame ionization detector (FID).

A key feature of sewer air is the high humidity, typically in the range 80–100% RH (relative humidity) ([Joseph *et al.*, 2012](#)), which could potentially interfere with IR CH_4 measurement ([You-Wen *et al.*, 2011](#)). [Liu *et al.* \(2015b\)](#) evaluated the suitability of IR spectroscopy-based online sensors

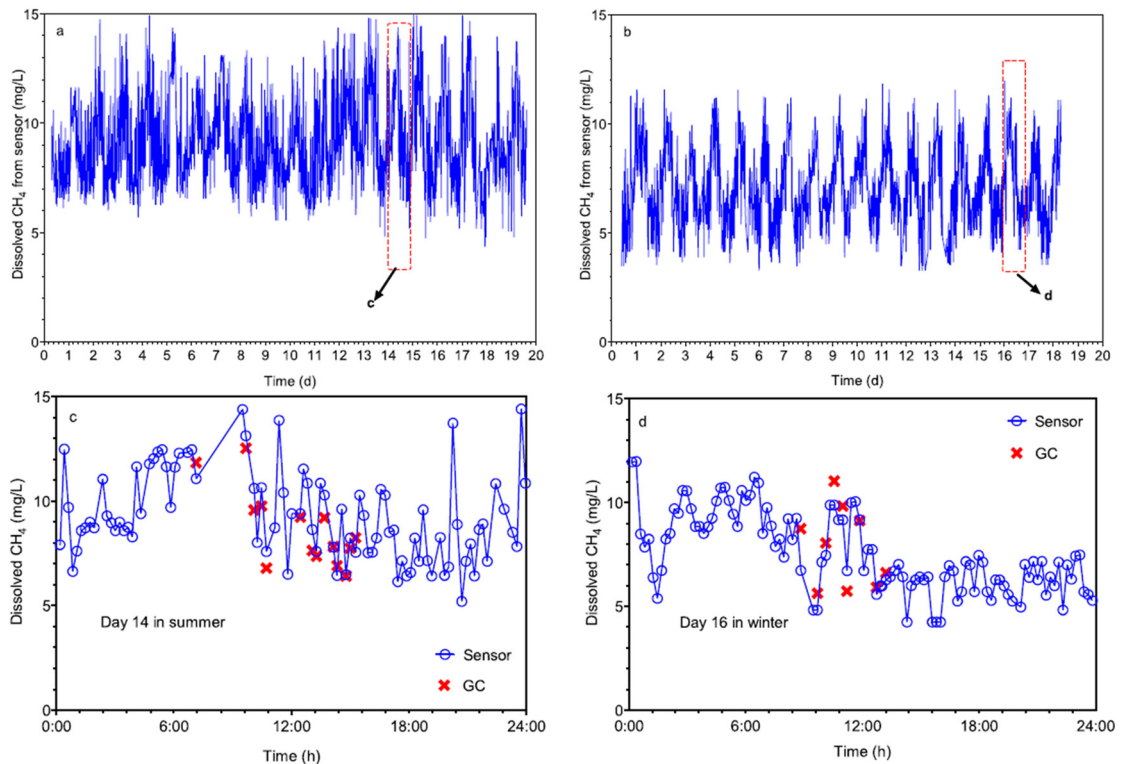


Figure 5.3 Three-week field CH₄ measurement with the online CH₄ sensor at the end of a rising main sewer network at Gold Coast: (a) summer; (b) winter. The agreement between the sensor measured results and those obtained through manual sampling and offline GC measured results is shown in (c) and (d). This figure was published in *Water Research*, Vol number 68, Y. Liu, Keshab R. Sharma, M. Fluggen, K. O'Halloran, S. Murthy, Z. Yuan, Online dissolved methane and total dissolved sulfide measurement in sewers, Page Nos 109–118, Copyright Elsevier (2015).

for measuring CH₄ gas in humid and condensing sewer air. An IR sensor with external power supply was extremely robust in variable and high humidity. A battery-operated IR sensor was sensitive to changes in humidity, but the problem was resolved by maintaining the humidity on the sensor probe surface at 50–70% RH through increasing surface temperature or refrigeration (Figure 5.4). Both sensors exhibited excellent linearity and can be applied with factory calibration. The detection limit of sensors i.e., ca. 0.023–0.110% vol, corresponds to a dissolved CH₄ range of 0.005 to 0.026 mg/L under equilibrium conditions at 20°C and 1 atm, which was suitable for measuring CH₄ gas in sewers. In-sewer application (with external power supply) for nearly one month confirmed accuracy and longevity of the sensor. In the future, infrared spectroscopy will be a powerful tool for accurate quantification of CH₄ emission from sewers.

Another system proposed by Kim *et al.* (2009) consists of an innovative and fully automated sewer gas monitoring device based on a floating and drifting embedded sensor platform (Sewer Snort). This sensor float can be introduced upstream and drift to the end of the network, collecting location-tagged gas measurements, thus providing a gas concentration profile along the sewer line. However, to date, the experiments have been based on a dry land emulator, and verification in actual sewers is needed before field application.

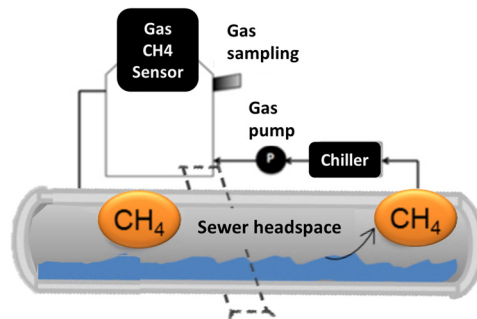


Figure 5.4 A purpose-built device for gas sampling or infrared (IR) gas sensor application in sewer headspace: a gas pump continuously recycles the gas from the sewer headspace to the chamber and then back to the sewer. A chiller is used in the gas line feeding the chamber to maintain the desired level of 50–70% relative humidity (RH) for the IR sensor (adapted from Liu *et al.*, 2015a).

5.2.4 Recommended measurement practice

Direct measurements of GHG in sewers can only be carried out in specific location-sections (such as rising main pipes, gravity pipes, manholes or pumping stations) due to the limited tools available to date. Those individual sections of sewers make up only a small part of a much larger network and hence more GHG production is expected when the wastewater is transported through the remaining parts of the network before reaching the WWTP (Pikaar *et al.*, 2014). Due to the operational complexity of sewer systems and dynamic nature of CH₄ emissions, it is not recommended to estimate overall CH₄ emissions from large networks with online or offline measurements. However, the combination of measurements in selected hotspots (rising mains, for instance) with mathematical modelling of GHG production is a viable solution to obtain estimations of full-network emissions (Willis *et al.*, 2019). See Chapter 8 for further information.

Sampling campaigns in those selected spots should encapsulate diurnal flow variations (Figure 5.3) with samples taken from the whole range of HRTs and also, should be carried out in different seasons of the year to include differences due to temperature.

Also, there is a need to develop GHG monitoring equipment able to work in harsh sewer conditions. These conditions limit the capacity to carry out more comprehensive sampling campaigns, having to rely on assumptions that need to be always carefully taken.

5.3 QUANTIFICATION OF GHG EMISSIONS IN WASTEWATER TREATMENT PLANTS

Over the past two decades there have been intensive efforts to quantify and investigate GHG emissions from WWTPs. The majority of the measurement campaigns were research related and their objectives varied from quantifying and understanding potential emissions under different WWTP conditions (e.g., Ahn *et al.*, 2010; Daelman *et al.*, 2013; Foley *et al.*, 2010) to mechanistic modelling of GHG production and emission from full-scale WWTPs (e.g., for N₂O emissions, Guo and Vanrolleghem, 2014; Ni *et al.*, 2013).

Although, the floating hood method is the most frequently applied measurement method to date, specific local requirements and measurement objectives have led to the development and application of alternative measurement approaches for full-scale GHG quantification. In general, quantifying methods can be classified into plant-wide and process-unit measurement approaches. Plant-wide quantification enables the determination of the overall GHG emissions of the plant including sources that might be difficult to investigate (accessibility) or might be missed by process-unit methods (unknown sources such as e.g., biogas leakages). However, the contribution from each single emission

source to the overall emission cannot be differentiated. In contrast, the process-unit approach identifies and quantifies single GHG emission sources, allowing a deeper understanding of the mechanisms of GHG production and emission patterns at the plant. This information is essential not only for research and modelling purposes, but also required for the development of mitigation measures for GHG emissions at WWTPs.

The aim of the chapter is to provide researchers and practitioners a general overview on the methodologies currently available for the quantification of N₂O and CH₄ emissions at full-scale WWTPs, highlighting the field of applicability, instrumental requirements, and strengths and limitations of those methods that have been already successfully applied. Methods in the development stage are not presented. Due to the focus of the chapter being on quantification methodology, analytical methods for the detection of the GHGs N₂O and CH₄ will only be briefly described. References to analytical methods will be provided for more information.

5.3.1 Plant-wide quantification of N₂O and CH₄ emissions

N₂O and CH₄ can be emitted from almost all stages of the wastewater and sewage sludge treatment (please refer to Chapters 2 and 3). GHG emissions occur from several small sources located in a large area, have different shapes (e.g., small leaks from biogas holding units and large liquid surfaces from biological reactors), and take place at different heights. These emission features result in a complex diffusive and fugitive emission pattern (Delre *et al.*, 2017). The emission pattern is diffusive because emissions are scattered throughout the WWTP, and it is fugitive, because gases escape unintentionally from process units (Delre, 2018). The complexity of the GHG emission pattern from WWTPs is increased by operational conditions that produce different emissions over time (Delre *et al.*, 2017; Yoshida *et al.*, 2014).

The literature offers several methods that allow the quantification of emission rates from area sources: mobile tracer gas dispersion method (MTDM), inverse dispersion modelling method (IDMM), solar occultation flux (SOF), differential absorption light detecting and ranging (DIAL), and radial plume mapping (RPM) (Mikel and Merrill, 2011). All these methods calculate the emission rate of the target gas through two main steps: (1) describing the plume generated by the target area, and (2) defining the atmospheric dispersion that the target gas undergoes travelling downwind from the target area. The plume is described by measuring downwind atmospheric gas concentrations from the ground. For this reason, these methods are called ground-based remote sensing methods. In the majority of the cases, the atmospheric dispersion of the target gas is defined by using local atmospheric models (e.g., backward Lagrangian stochastic model used in the IDMM). Only in the case of the MTDM, is the atmospheric dispersion of the target gas obtained by releasing a tracer gas from the target area, without deploying any atmospheric model.

Among the ground-based remote sensing methods, only the MTDM was implemented for quantifying N₂O and CH₄ emissions from WWTPs. The MTDM was applied at eight WWTPs with different plant layouts, using different process units and technologies. Investigated WWTPs were located in Denmark, Sweden and France (Delre *et al.*, 2017; Samuelsson *et al.*, 2018; Yoshida *et al.*, 2014; Yver Kvok *et al.*, 2015). Although the use of the other ground-based remote sensing methods is potentially possible, the literature still lacks in applications of these methods at WWTPs. The IDMM was used for quantification of CH₄ emissions from biogas plants, while SOF, DIAL and RPM were applied for CH₄ emission quantifications from industrial sites and landfills (Mikel and Merrill, 2011).

All ground-based remote sensing methods are highly dependent on the analytical technology used, because it affects the measurable type of target gas and the quality of the atmospheric plume description at a proper distance from the emitting area. Any ground-based remote sensing method can only be successfully deployed if the analytical technology is capable of distinguishing properly, at a suitable distance from the emitting area, the atmospheric plume concentrations from the background values.

In the following section, the application of the MTDM at WWTPs is described. Detailed information about other ground-based remote sensing methods can be found in Mikel and Merrill (2011).

5.3.1.1 Mobile tracer gas dispersion method (MTDM)

The MTDM uses a controlled release of a tracer gas with measurements of atmospheric gas concentrations taken downwind of the target area. Additionally, the MTDM benefits from the features of gases with long atmospheric lifetimes to keep a constant concentration ratio during transportation and mixing in the atmosphere (Lamb *et al.*, 1995; Stiversten, 1983). Thus, when the tracer gas is released at a constant rate from the emitting area, the target gas emission rate can be calculated in real-time by relating the measured plume traverse concentrations of the target and tracer gases, as shown in Equation (5.4).

$$M_{tg} = Q_{tr} \cdot \frac{\int_{\text{plume start}}^{\text{plume end}} (C_{tg} - C_{tg \text{ baseline}}) dx}{\int_{\text{plume start}}^{\text{plume end}} (C_{tr} - C_{tr \text{ baseline}}) dx} \cdot \frac{MW_{tg}}{MW_{tr}} \quad (5.4)$$

where M_{tg} is the target gas emission in mass per time, Q_{tr} is the known tracer release in mass per time, C_{tg} and C_{tr} are the detected plume concentrations within the plume traverse in parts per billion (ppb), $C_{tg \text{ baseline}}$ and $C_{tr \text{ baseline}}$ are baseline concentrations of the target and the tracer gas (ppb), and MW_{tg} and MW_{tr} are the molecular weights of the target gas and tracer gas, respectively (Scheutz *et al.*, 2011). Acetylene (C_2H_2) is usually used as a tracer gas, due to there being very few possible interfering sources and its long atmospheric lifetime (Delre *et al.*, 2017).

The mobile measurement platform used in most of the studies was a vehicle equipped with two gas analysers for measurements of atmospheric gas concentrations and a global navigation satellite system for recording measurement locations. Each of the gas analysers detected target and tracer gases simultaneously. Atmospheric gas was sampled from the roof of the vehicle and analysed, while screens displayed detected concentrations in real time. The tracer gas was constantly released using gas cylinders with calibrated flowmeters.

Figure 5.5 shows the key phases of a measurement campaign, which consists of a screening phase, carried out off-site and on-site, and a quantification phase. The screening phase starts outside the facility, to guarantee the absence of off-site sources that could interfere with the target and the tracer gas. Later, screening inside the facility allows identification of on-site emitting sources. The on-site screening (Figure 5.5 A) allows the right placement of the tracer gas cylinders (Figure 5.5 B1), so that the target gas emission pattern is properly simulated by the tracer release. During the quantification phase, tracer gas is constantly released (Figure 5.5 B2) while the plume is crossed multiple times at a suitable distance away from the emitting source (Figure 5.5 C). The measuring distance should guarantee enough mixing between target and tracer gas and produce a proper signal-to-noise ratio in the concentration of gases recorded along the plume traverses. Proper simulation of the target gas emission is continuously checked through a good correlation between target and tracer gases within a plume traverse.

The success of the MTDM relies on mutual dependence among the following factors: (1) features of the analytical instrument, (2) size of the emitting source, (3) emission rate of the target gas, (4) atmospheric stability and target gas dispersion, (5) measurement distance from the emitting source, and (6) simulation of the target gas emission pattern.

A suitable analytical instrument should have good precision and high detection frequency when measuring concentrations of target and tracer gases. Such features allow a better plume definition and a faster measurement execution, resulting in smaller measurement uncertainties and lower method application costs (Delre *et al.*, 2018). An analytical instrument with a good precision is especially relevant when emissions are to be quantified from large area sources. In this situation, measurements must be carried out at a long distance from the emitting area to obtain proper mixing between target and tracer gases at the measuring location. At long distances, atmospheric gas dispersion produces,

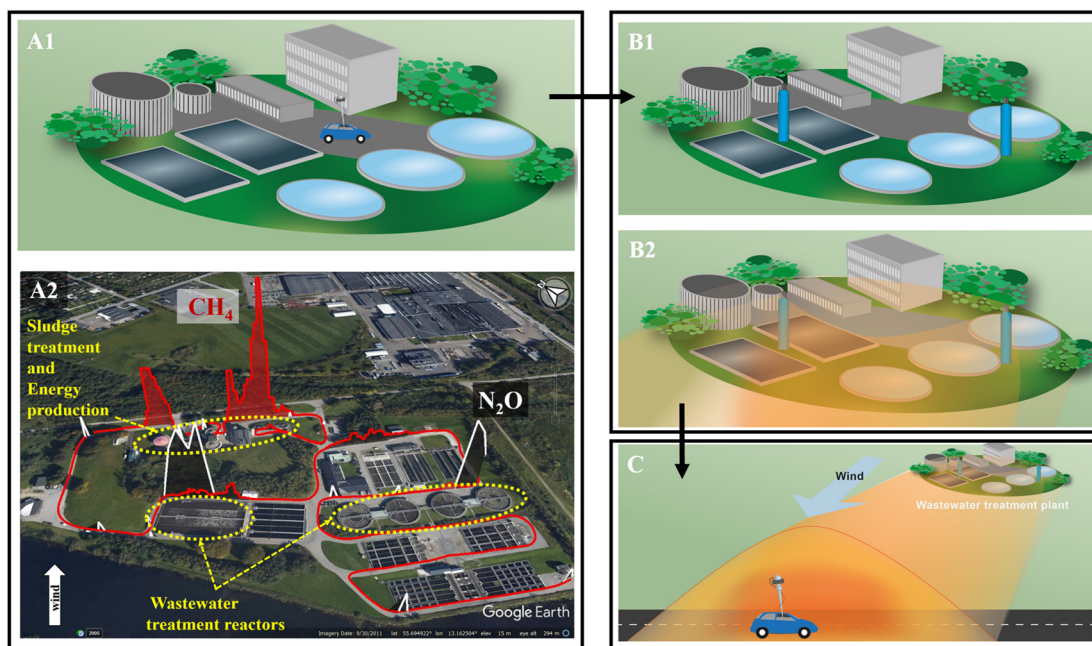


Figure 5.5 Illustration of the tracer gas dispersion method applied at wastewater treatment plants. (a) The initial screening phase with A1 showing on-site measurements of atmospheric concentrations of target and tracer gases and A2 showing an example of on-site screenings performed at Källby (SE) visualized on a Google Earth © image. CH₄ (marked in red) and N₂O (marked in white) concentrations are shown above the background level. The white arrow shows the wind direction. (b) Tracer placement with B1 showing the location of the tracer gas for source simulation and B2 showing the release of the tracer gas into the atmosphere. (c) The quantification phase showing downwind gas concentrations measurement performed along a plume transect. This figure was published in *Science of Total Environment*, Vol number 605–606, Delre A., Mønster J., Scheutz C., Greenhouse gas emission quantification from wastewater treatment plants, using a tracer gas dispersion method, Page Nos 258–268, Copyright Elsevier (2017).

within the same plume traverse, small differences between gas concentrations detected inside and outside the plume. A precision of 0.7, 3.8 and 0.5 ppb when measuring N₂O, CH₄ and C₂H₂, respectively, was found to be sufficient for measuring at WWTPs (Delre, 2018). Reported values of instrument precision are defined as three times the standard deviation of six minutes' constant concentration reading (Delre *et al.*, 2018). The magnitude of the target gas emission rate also influences the success of the quantification, because if the emission rate is too low, the plume cannot be distinguished from the background at a proper measuring distance. In this case, a detection limit can be estimated (Delre *et al.*, 2017). Stable weather conditions produce a lower vertical atmospheric dispersion of gases compared to unstable situations. Thus, stable conditions are usually preferred because this allows better plume definition within a plume traverse. This is mainly relevant for the target gas rather than the tracer gas, because the downwind signal-to-noise ratio of the tracer gas can be improved by increasing the flow rate of the release. Correct tracer placement and consequent proper simulation of the target gas emissions is central when applying the MTDM (Delre *et al.*, 2018; Mønster *et al.*, 2014). As long as the employed analytical instrument can detect the tracer gas, any long-lived atmospheric gas can be used as tracer gas in MTDM application (Delre *et al.*, 2018). However, this statement does not consider price and environmental issues, which could be important constraints in the choice of the tracer gas.

A detailed description of best practice for the application of the MTDM at WWTPs is available in [Delre \(2018\)](#). Like any measurement method, the MTDM has strengths and limitations, which are listed below.

Strengths:

- One skilled operator alone can carry out the measurements;
- Data processing is straightforward when gases are fully mixed;
- Any change in downwind plume description can be instantaneously detected and measurements can be adjusted accordingly;
- Capability to identify main emitting areas, especially if occurring close to ground level;
- Emission quantification is possible even without locating specific on-site emitting sources;
- Identification of possible emission variation within the measurement campaign;
- Potential flexibility of moving the equipment around using different means of transportation.

Limitations:

- Like other ground-based remote sensing methods, emission quantifications are not possible if there are interfering sources of target and tracer gases upwind of the target area;
- Dependence on favourable wind conditions combined with road access;
- Monitoring time is limited to a period when wind blows with favourable conditions;
- Unable to perform long term and continuous monitoring;
- Transport of tracer gas cylinders must comply with specific regulations.

5.3.2 Process-unit quantification of N₂O and CH₄ emissions

Process-unit GHG quantification methods are designed to measure emissions from single process units as opposed to a large whole-of-plant footprint. Plant-wide quantification of emissions is however achievable with these methods, provided that all individual emission sources are quantified separately and aggregated. Process-unit quantification is essential when process specific emissions need to be characterized, for example, for calibration of mechanistic models or to link emissions to the operating conditions of the plant. The development of mitigation measures for GHG emission also requires the identification and quantification of each single source at the plant.

The first N₂O monitoring campaigns at WWTPs were based on grab-sampling methods but due to the large temporal fluctuations in emissions occurring in most cases, the continuous online monitoring methodology is favoured. The floating hood method is the most common approach – among others – to sample the off-gas leaving the surface of activated sludge tanks with bubble aeration. The off-gas stream captured by the hood is usually fed to an online gas analyser for quantification of N₂O or CH₄. This method has also been employed in biofilm-based reactors ([Bollon et al., 2016a, 2016b](#); [Gruber et al., 2020](#); [Vieira et al., 2019](#); [Wang et al., 2016](#)). In activated sludge tanks equipped with surface aerators the liquid-to-gas mass transfer method needs to be adopted, which allows N₂O or CH₄ emissions to be calculated from liquid phase measurements. In covered tanks, continuous or discontinuous off-gas sampling and analyses can be performed directly from the ventilation system. Furthermore, ground-based remote sensing methods (e.g., tracer gas dispersion method) can also be applied for process-unit GHG quantification.

All these measurement approaches are described in [Sections 5.3.2.1 to 5.3.2.4](#). A summary of these methods is given in [Section 5.3.3](#). Finally, [Section 5.3.4](#) provides general recommendations for minimum data requirements.

5.3.2.1 Floating hood

The WERF protocol ([Chandran, 2009](#)) gives guidance on planning and performing an N₂O measuring campaign based on the floating hood method. It was completed by [Chandran et al. \(2016\)](#) notably to

highlight the major considerations for carrying out representative sampling of off-gas emissions. As measuring campaigns have been carried out in previous years by different research groups around the world, additional know-how has been gained that has led to alternative sampling hood designs with adapted flux calculation, novel monitoring approaches in gas and liquid phase, as well as a better understanding of relevant requirements of sampling procedures (e.g., tubing, hood placement, etc.). This section summarizes (with no claim to completeness) the most common options.

Emissions from open surface process units were, most of the time, monitored using floating hoods (also called floating chambers, isolation flux chambers, gas-collecting chambers or closed chambers). They are floating devices that are maintained at a given process-unit position, usually using ropes, to collect and sample the gases emitted at the water-air interface. In some cases, they were also designed to measure the off-gas flowrate. Such devices are floating versions of hoods that are used for measuring emissions from soils or landfill. The first floating hoods were employed to measure volatile organic compounds from wastewater treatment plants (Tata *et al.*, 2003) using a surface emission isolation flux chamber (SEIFC). The SEIFC hood is one of the few devices approved by the United States Environmental Protection Agency (U.S. EPA) and is used in U.S. EPA method EPA/600/8-86/008 (1986) to measure gaseous emission rates from land surfaces. Chandran (2009, 2011) adapted this method for measuring N₂O emissions from biological nutrient removal (BNR) plants, which has resulted in a comprehensive field measurement protocol certified by the U.S. EPA (Chandran, 2009). Although the protocol was specifically developed for SEIFC hoods, many researchers successfully applied the guideline to alternative methods for measuring N₂O and CH₄ emissions from different process units of WWTPs including those operated with advective gas flow (aerated units) and those having a passive liquid surface (non-aerated units). Application examples are provided in Tables 5.1 and 5.2.

While some research teams used commercial hoods (such as SEIFC and AC'SCENT® Flux Hood), many others used custom-built floating hoods. This resulted in a great variety in hood shape (cuboid, half-spherical, cylindrical, etc.), material (stainless steel, aluminium, wood, plastic) and size (surface area covered ranging from 0.03 m² to 2 m²). In most cases, hoods are submersed (by a few centimetres) to prevent lateral movement and introduction of external air. This can be achieved by placing the floating system (e.g., polystyrene float or inner tube) above the bottom of the hood. Since atmospheric carbon dioxide (CO₂) concentration in the off-gas is much higher than that of the atmosphere, its measure in the off-gas can be used to check that no external air enters the measuring loop (Valkova *et al.*, 2020). Despite the variety in hood design, they can be classified into two categories: closed flux chambers and open flux chambers. Figure 5.6 presents the basic scheme of the most common configurations of open and closed flux chambers.

5.3.2.1.1 Closed flux chambers

The basic principle of closed flux chambers is to isolate a given surface area from the atmosphere, thus allowing for the accumulation of the gas inside the hood over time. The emission rate is then determined by the change in gas concentration over time. Gas mixing is usually achieved by installing a fan inside the hood or by recirculating the gas flow between the hood and the GHG analyser (Figure 5.6a and b). If the chamber is operated without a gas flow (without recirculation) it could be referred to as a “static chamber”, otherwise, it is a “dynamic chamber”. This technique was originally developed to measure gas emissions from natural soils where surface emissions are controlled by diffusion (Monster *et al.*, 2019). Likewise, it was successively applied to measure GHG emissions from non-aerated unit processes of WWTPs, such as equalization tanks (Masuda *et al.*, 2015), anoxic and anaerobic tanks (Mello *et al.*, 2013; Ren *et al.*, 2013; Wang *et al.*, 2011; Yan *et al.*, 2014), primary and secondary settlers (Caniani *et al.*, 2019; Czepiel *et al.*, 1993, 1995; Masuda *et al.*, 2015; Ren *et al.*, 2013; Wang *et al.*, 2011; Yan *et al.*, 2014) and sludge storage tanks (Oshita *et al.*, 2014; Ren *et al.*, 2013). Build-up of high concentrations in the hood is not recommended as it may reduce the emission rate during the course of the experiment which would result in underestimating the actual emission rate

Table 5.1 Examples of floating hoods employed in advective flow conditions.

Reference	Process unit	GHG	Method	Floating hood			Mixing	$Q_{g,hood}$	Gas line
				Type/shape	Material	Area (m ²)			
Benckiser <i>et al.</i> (1996); Sümer <i>et al.</i> (1995)	AS	N ₂ O	OFC	Cuboid	PVC	0.24	Perforated plates	Measured	
Kimochi <i>et al.</i> (1998)	AS	N ₂ O	OFC	Cuboid				Q reactor	
Ahn <i>et al.</i> (2010); Chandran (2011)	AS	N ₂ O	OFC	1		0.13	He	He mass balance	P, T
Desloover <i>et al.</i> (2011)	PN, AS	N ₂ O, CH ₄	OFC	Lindvall hood, Cuboid	Al	0.864	Air	Measured	T
Aboobakar <i>et al.</i> (2013a); Aboobakar <i>et al.</i> (2013b)	AS	N ₂ O, CH ₄	OFC	2		0.34		Q reactor	
Ren <i>et al.</i> (2013)	AGC, AS	N ₂ O, CH ₄	CFC	1	SST	0.13		-	
Mello <i>et al.</i> (2013)	AS	N ₂ O	OFC	Funnel attached to a pipe	Plastic	0.071		Gas circulation	Q reactor
Rodriguez-Caballero <i>et al.</i> (2015); Rodriguez-Caballero <i>et al.</i> (2014)	AS	N ₂ O, CH ₄	OFC	3	SST	0.13		Q reactor	O ₂ conc.
Brotto <i>et al.</i> (2015)	AS	N ₂ O	OFC	Funnel attached to a pipe	PVC	0.071	No	Q reactor	
Masuda <i>et al.</i> (2015)	AS	N ₂ O, CH ₄	OFC		PVC	0.196		Q reactor	
Marques <i>et al.</i> (2016)	AS	N ₂ O	OFC	3	SST	0.13		Q reactor	
Bollon <i>et al.</i> (2016a); Bollon <i>et al.</i> (2016b)	BAF	N ₂ O	OFC	Cuboid	Wood	1.6	No	Measured	
Duan <i>et al.</i> (2020); Pan <i>et al.</i> (2016a)	AS	N ₂ O	OFC	Modified hopper tank	Plastic	0.22	No	Measured	P, T
Yang <i>et al.</i> (2016)	PN/A	N ₂ O	OFC	Cuboid		0.81	Fan	Q reactor	

<i>Wang et al. (2016)</i>	BAF	N ₂ O	OFC	Half spherical	0.0314	No	Fan	Not clear	T, liquid level
<i>Bellandi et al. (2017)</i>	AS	N ₂ O	OFC	Different chambers	0.35–2			Measured or estimated	
<i>Ribeiro et al. (2017)</i>	AS	N ₂ O	OFC	PVC	0.05			Measured	
<i>Spinelli et al. (2018)</i>	AS	N ₂ O	OFC	Different chambers	0.125–0.457			Q reactor	
<i>Caniani et al. (2019)</i>	AS	N ₂ O	OFC	Complex shape	0.7			Measured	
<i>Vieira et al. (2019)</i>	BAF	N ₂ O	OFC	3				Q reactor	
<i>Tauber et al. (2019)</i>	AD	CH ₄	OFC/ CFC	Lindvall hood/Cuboid	1	Air/No	No/Gas circulation	Measured	P, T
<i>Gruber et al. (2020)</i>	AS, BAF	N ₂ O	OFC	Triangular top and cuboid body	1			Q reactor	

The italics indicate the elements calculated from information provided in the scientific paper or manufacturer's technical documentation: 1: Commercial "SEIFC", half circular top and cylindrical body; 2: Commercial hood provided with the N-Tox nitrification toxicity monitoring system (Water Innovate, UK); 3: Commercial "AC-SCENT® Flux Hood", half circular top and cylindrical body.

AD: anaerobic digester; AGC: aerated grit chamber; Al: aluminium; AS: activated sludge; BAF: biologically active (or aerated) filter; CFC: closed flux chamber; GC: grit chamber; HDPE: high density polyethylene; He: helium; OFC: open flux chamber; PN: partial nitrification; PN/A: partial nitrification/anammox; P: pressure; PP: polypropylene; PVC: polyvinyl chloride; SST: stainless steel; T: temperature.

Table 5.2 Examples of floating hoods employed in passive liquid surface conditions.

Reference	Process unit	GHG	Method	Floating hood			Gas line			
				Type/shape	Material	Area (m ²)		Sweep/tracer gas	Mixing	Q _{g, hood}
Czepiel <i>et al.</i> (1995); Czepiel <i>et al.</i> (1995)	SET	N ₂ O	CFC	Cuboid	Al			Gas circulation	-	T
Kimochi <i>et al.</i> (1998)	AS	N ₂ O	OFC	Cuboid			Ar		Mass balance	
Ahn <i>et al.</i> (2010); Chandran (2011)	AS	N ₂ O	OFC	1		0.13	He, Air	Gas circulation	Mass balance	P, T
Desloover <i>et al.</i> (2011)	Anammox, AS	N ₂ O, CH ₄	OFC	Lindvall hood / Cuboid	Al	0.864	Air	-	Measured	T
Ren <i>et al.</i> (2013); Wang <i>et al.</i> (2011)	IPS, SET, AS, SCT	CH ₄	CFC	1 (probably)	SST	0.13		Gas circulation	-	T
Mello <i>et al.</i> (2013)	AS	N ₂ O	CFC	Custom-made	PVC	0.045			-	
Rodriguez-Caballero <i>et al.</i> (2015); Rodriguez-Caballero <i>et al.</i> (2014)	AS	N ₂ O, CH ₄	OFC	2	SST	0.13	Air		Mass balance on oxygen	
Oshita <i>et al.</i> (2014)	SCT	N ₂ O, CH ₄	CFC	Cylindrical	PVC	0.15			-	T
Yan <i>et al.</i> (2014)	SET, AS	N ₂ O, CH ₄	CFC	Cylindrical	SST	0.14		Gas circulation		T
Mikola <i>et al.</i> (2014)	SET, AS	N ₂ O	OFC	Truncated cone		0.15			=flow of the analyser	
Masuda <i>et al.</i> (2015)	ET, DT, SET	N ₂ O, CH ₄	CFC		PVC	0.16			-	
Marques <i>et al.</i> (2016)	AS	N ₂ O	OFC	2					=flow of the analyser	
Bellandi <i>et al.</i> (2017)	AS	N ₂ O	OFC	Modified Lindvall hood			Air		=flow of the analyser	
Duan <i>et al.</i> (2020)	AS	N ₂ O	OFC	Modified hopper tank	Plastic	0.22			=flow of the analyser	P, T
Caniani <i>et al.</i> (2019)	SET	N ₂ O	CFC	Complex shape	SST	0.7	Air	Gas circulation	Measured	

The italics indicate the elements calculated from information provided in the scientific paper or manufacturer's technical documentation.1: Commercial "SEIFC", half circular top and cylindrical body, 2: Commercial "AC'SCENT® Flux Hood", half circular top and cylindrical body.
 Al: aluminium; Ar: argon; AS: activated sludge; CFC: closed flux chamber; DT: disinfection tank; ET: equalization tank; He: helium; IPS: influent pump station; OFC: open flux chamber; P: pressure; PVC: polyvinyl chloride; SCT: sludge concentration tank; SET: settler; SST: stainless steel; T: temperature.

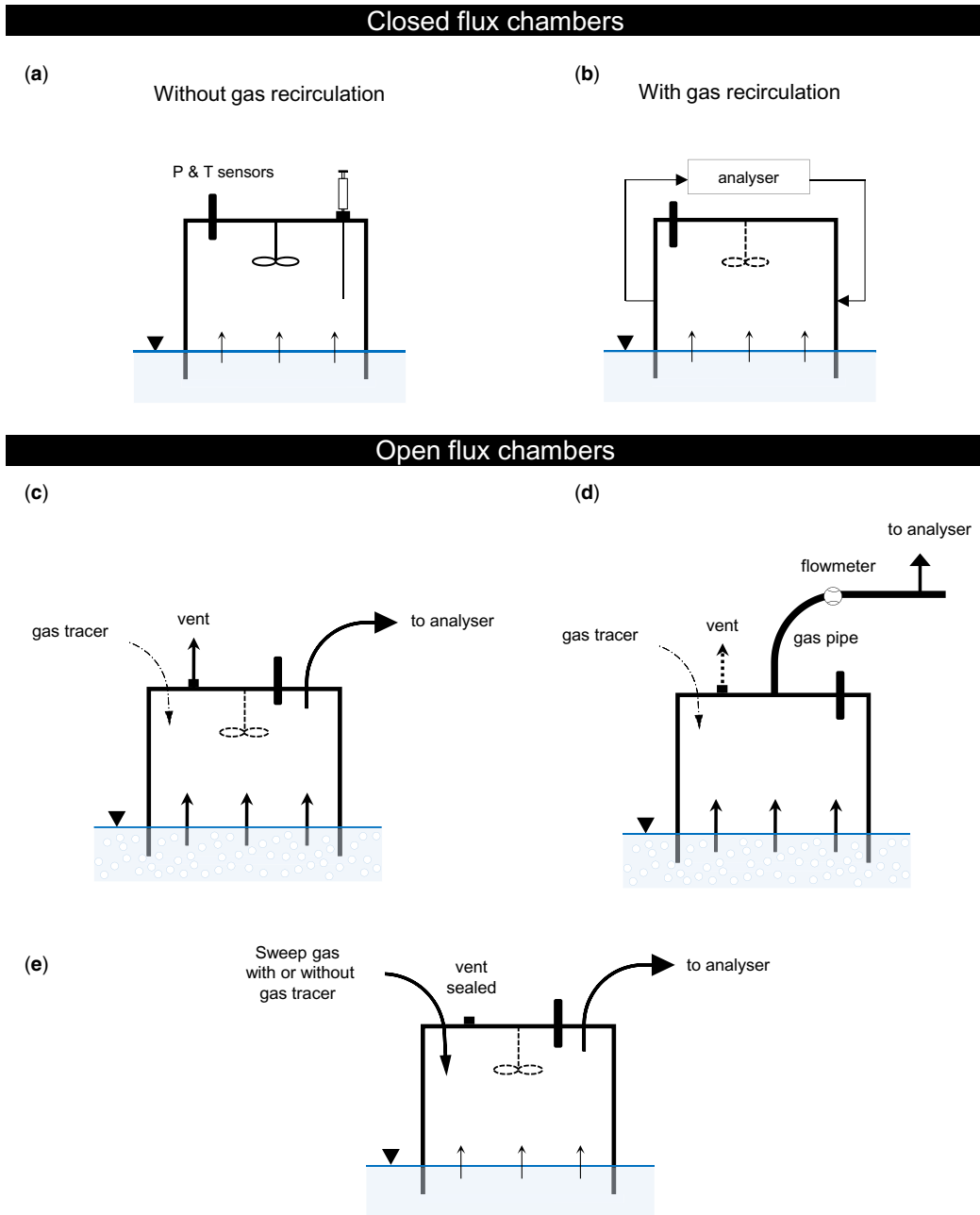


Figure 5.6 Most common hood configurations. Dotted elements are optional.

(Gao and Yates, 1998). To avoid it, short sampling times were applied (generally less than half an hour) and fresh air was introduced in the hood in between two sampling rounds. In most cases, a manual sampling was performed but it is possible to design fully automated devices (Filali *et al.*, 2017; Oshita *et al.*, 2014; Pavelka *et al.*, 2018).

5.3.2.1.2 Open flux chambers

The open flux chambers (also referred as “dynamic chambers”) are fitted with tubes and vent ports allowing headspace gas to escape from the hood and/or the introduction of a sweep gas into the hood (Figure 5.6c–e and a photo of an example in Figure 5.7). In aerated zones or tanks, the off-gas sample to be analysed can be directly extracted from the hood, usually at a constant flowrate that is much lower than the gas flowrate entering the hood to avoid negative pressure built-up (Figure 5.6c). The excess gas is exhausted from the hood through vents. The SEIFC and AC'SCENT[®] flux hoods are designed on this principle. The alternative configuration (Figure 5.6d) would be to let the off-gas escape through a large pipe and direct a small portion of the off-gas to the analyser. The dimensions of the pipe are also very variable ranging from 25 mm to 100 mm (Bollon *et al.*, 2016a, 2016b; Duan *et al.*, 2020; Gruber *et al.*, 2020; Pan *et al.*, 2016a; Spinelli *et al.*, 2018). This configuration is convenient because it allows, with some caution, measurement of the off-gas flow rate.

In non-aerated zones or tanks (Figure 5.6e), a flow of sweep gas can be applied to enhance an effective gas flow through the flux chamber (Ahn *et al.*, 2010; Caniani *et al.*, 2019; Chandran, 2011; Kimochi *et al.*, 1998; Rodriguez-Caballero *et al.*, 2014, 2015). As sweep flow rate was evidenced to influence the estimated emission rate of several compounds in dynamic flux chambers (Gao and Yates, 1998; Prata *et al.*, 2018), some researchers applied a wind-tunnel-type, namely the Lindvall hood (Lindvall *et al.*, 1974), that allows better control of gas velocities inside the hood. In this hood, the sweep gas (usually ambient air) is introduced in a directional way to simulate the action of the wind on the sampled surface (Capelli *et al.*, 2013). It was applied by Desloover *et al.* (2011) to measure N₂O and CH₄ emissions from a full-scale partial nitrification and anammox process. Bellandi *et al.* (2017) applied a modified version to measure N₂O from anoxic zones of two activated sludge plants.



Figure 5.7 Floating hood (configurations C and E in Figure 5.6) and associated equipment for measuring off-gas flowrates and off-gas concentrations. Photos courtesy of Dr. Maite Pijuan (ICRA Catalan Institute for Water Research). These figures were published in *Journal of Cleaner Production*, Vol number 212, A. Ribera-Guardia, L. Bosch, L. Corominas, M. Pijuan, Nitrous oxide and methane emissions from a plug-flow full-scale bioreactor and assessment of its carbon footprint, Page Nos 162–172, Copyright Elsevier (2019) and in *Science of the Total Environment*, Vol number 493, A. Rodriguez-Caballero, I. Aymericha, M. Poch, M. Pijuan, Evaluation of process conditions triggering emissions of green-house gases from a biological wastewater treatment system, Page Nos 348–391, Copyright Elsevier (2014).

Prior to concentration measuring, the gases sampled are usually conditioned to remove moisture and/or other gases (such as CO₂) that might interfere with the target gas measurement. Depending on the duration of the monitoring campaign, conditioning methods with different degrees of sophistication can be used. They include the use of condensation moisture traps, silica gel and sodium hydroxide traps or conditioning units (membranes and coolers/condensers).

In the case of grab sampling, gaseous concentrations were mainly measured by gas chromatography equipped with an electron-capture detector (N₂O) and with a flame ionization detector (CH₄). When a continuous sampling was applied, concentrations were mainly measured using optical techniques including non-dispersive infrared spectroscopy (NDIR) and Fourier transform infrared spectroscopy (FTIR). In some cases, photo-acoustic spectroscopy (Desloover *et al.*, 2011) and Clark-type N₂O gas sensors (Marques *et al.*, 2016) were used. More details on the analytical methods for measuring N₂O concentration can be found in Rapson and Dacres (2014).

The spatial variability of the emissions was investigated by sampling different positions of the process units either sequentially (Aboobakar *et al.*, 2013a, 2013b; Ahn *et al.*, 2010; Caniani *et al.*, 2019; Oshita *et al.*, 2014; Rodriguez-Caballero *et al.*, 2014) or (almost) simultaneously using a multi-hood system (Bellandi *et al.*, 2017; Duan *et al.*, 2020; Gruber *et al.*, 2020; Pan *et al.*, 2016b). In the last case, an automated valve system is used to direct the off-gas captured from the individual hoods to the analyser at a short interval time (usually of few minutes). Recently, an automated, wireless and self-moving floating hood “LESSDRONE” was developed within the project LESSWATT (LIFE16 ENV/IT/000486). The automatic positioning of the hood is managed by global positioning system (GPS). In addition to GHG emissions monitoring, the device was designed to allow the real-time monitoring of the oxygen transfer efficiency.

Depending on the flux hood method employed, different approaches were used to estimate the surface emission rate. The surface emission rate $M_{g,hood}$ (kg/(m²*d)) from the closed flux chamber is determined by the change in concentration of the targeted GHG over time ($dC_{g,hood}/dt$, kg/(m³*d)) with reference to the headspace volume (V_{hood} , m³) and surface area of the hood (A_{hood} , m²) using Equation (5.5):

$$M_{g,hood} = \frac{V_{hood}}{A_{hood}} \times \frac{dC_{g,hood}}{dt} \quad (5.5)$$

Unlike closed flux chambers, open flux chambers require determination of the off-gas flowrate ($Q_{g,hood}$, m³/d) to estimate the surface emission rate (Equation (5.6)). The latter was determined following three main methods described below.

$$M_{g,hood} = \frac{Q_{g,hood} \times C_{g,hood}}{A_{hood}} \quad (5.6)$$

- (1) The off-gas flowrate during aeration can be directly measured from the gas pipe of the floating hood after closing any other vent port, according to configuration D in Figure 5.6. For a proper measurement of the flowrate, care must be taken to maintain the pressure under the hood close to that of atmospheric pressure. A way to do so would be to regulate the gas extraction rate while monitoring the pressure. When steady state conditions are achieved, the emission flowrate ($Q_{g,hood}$) is estimated to be equal to the extraction flowrate and it can subsequently be measured using a gas flowmeter. This is the typical approach employed for measuring the off-gas flowrate in oxygen transfer testing (ASCE, 1997). As the flowrate can only be measured punctually using this method, a correlation between $Q_{g,hood}$ and the total off-gas flowrate of the tank is established to allow quantification of the surface emission flux continuously (Bollon *et al.*, 2016a).

Pan *et al.* (2016a) suggested another option allowing for a continuous monitoring of the flowrate. The basic difference between this and the previous method is that the hood

is submersed by 100mm to 150 mm, to avoid any leakage of the gas from the sides, which generates a slight over pressure (1.0–1.5 kPa) under the hood. Continuous monitoring and recording of pressure in the gas line are performed to correct $Q_{g,hood}$ accordingly. In the case of the Lindvall hood, the off-gas is exhausted from a vent port on which a gas flowmeter can be installed. The emission rate is estimated considering the dilution of the off-gas with the sweep gas ($Q_{g,sweep}$) according to Equation (5.7). If ambient air is used as the sweep gas, regular measurements of ambient N_2O and/or CH_4 concentrations ($C_{g,sweep}$) should be performed.

$$M_{g,hood} = \frac{Q_{g,hood} \times C_{g,hood} - Q_{g,sweep} \times C_{g,sweep}}{A_{hood}} \quad (5.7)$$

- (2) The second method employed is known as the “tracer method” which was proposed by Chandran (2009) and applied to the SEIFC hood having a configuration close to that shown in Figure 5.6c (in aerobic zones) and Figure 5.6e (in anoxic zones). The method can be applied only discontinuously during the measurement campaign, the determined off-gas flowrate escaping the hood needs to be linked to the aeration flowrate to capture fluctuations. Briefly, a tracer gas (helium) with a given concentration ($C_{g,He}$) is introduced into the hood at a known flow rate ($Q_{g,He}$). Helium concentration in the exhaust gas from the hood ($C_{g,He-hood}$) is measured using a field gas chromatograph equipped with a thermal conductivity detector. The difference in concentration due to the dilution by the off-gas can be used to calculate the flux. In non-aerated zones, a sweep gas at a known flowrate ($Q_{g,sweep}$) is introduced to enhance an effective gas flow through the hood as explained above. $Q_{g,hood}$ can be computed using Equation (5.8) (in aerated zones $Q_{g,sweep} = 0 \text{ m}^3/\text{d}$).

$$Q_{g,hood} = \frac{Q_{g,He} \times (C_{g,He} - C_{g,He-hood})}{C_{g,He-hood}} - Q_{g,sweep} \quad (5.8)$$

The surface emission rate at the hood location ($M_{g,hood}$) can be extrapolated to a given zone i ($M_{g,i}$) of the process unit assuming that the off-gas concentration and emission rate measured with the hood were uniform over that zone (Equation (5.9)).

$$M_{g,i} = M_{g,hood} \times \frac{A_i}{A_{hood}} \quad (5.9)$$

where A_i is the surface area of the zone i (m^2).

The total emission rate of the process unit ($M_{g,total}$, kg/d) can be computed considering the contribution of the different sampled zones (Equation (5.10)). Caution must be taken when defining these sampling zones as they can greatly affect the estimated emission rate.

$$M_{g,total} = \sum_{i=1}^n M_{g,i} \times A_i \quad (5.10)$$

- (3) An alternative method consists in estimating the total off-gas flowrate of the tank using a gas mass balance for nitrogen and argon gas over the activated sludge tank and considering the intake airflow rate of the blower and the off-gas composition leaving the aerated tank (Valkova et al., 2020). The intake air flowrate can be calculated based on rotation frequency and manufacturer’s data. The rotation frequency of the air blower drive motors can be measured and logged with an electricity analyser with a one-minute time lag. This method requires that in the system “blower/tank” the blower (or the group of blowers) provides air to exclusively one single activated sludge tank. If this is not the case, the aeration rate sent to the tank needs to be

accurately measured on site. It can be noted that surface extrapolation is not required with this method because the concentration measured in one or more hoods is referred to the calculated total off-gas airflow rate of the tank. Thereby, uncertainties induced by insufficient spatial sampling of $Q_{g,hood}$, that could be encountered with the two previous methods, are avoided.

The floating hood method was applied to many different process units of the plants ranging from the influent pumping station to the disinfection unit (Tables 5.1 and 5.2). Basically, it can be applied to sample the off-gas of any process unit, in which a part of the water surface, the interphase where the gas-liquid mass transfer takes place, can be covered with the hood. It is difficult to use on process units equipped with surface aerators where aeration is achieved through dispersing water in the air (cf. Section 5.3.2.2). Severe foaming and turbulence can complicate gas collection and hood placement. Hoods are easy to build and relatively simple to deploy onsite. In most cases, the floating hood method does not require specialized skills (depending on the associated measurement system) but requires a good understanding of the operation of the studied process unit to properly design the measurement campaign. Its main strength relies on online and continuous quantification of spot specific emissions, concurrently with monitoring of the plant's operating conditions. Thus, it is highly appropriate when a deep understanding of the triggers of GHG emissions is sought. Additionally, it allows spatial variability in emissions across different zones of the process units to be quantified. A whole-site GHG emission quantification, as with ground-based remote sensing methods, is not achievable.

In the absence of comparative studies, it is difficult to assess which hood method (e.g., open or closed flux chamber, with or without tracer and sweep gas, small or large) can provide higher accuracy for estimating GHG emissions. It is likely that the universal hood does not exist, as its design should be adapted to the experimental conditions, which are by definition site specific. Nevertheless, this section summarizes typical pitfalls when designing and measuring GHG emissions using flux hoods. Additionally, it provides some recommendations for best measurement practice.

5.3.2.1.3 Passive liquid surfaces

In passive liquid surfaces it is believed that the main concern is that the conditions inside the hood do not resemble critical features of the atmospheric flow to which the water surface is exposed in the absence of the hood, such as the boundary layer structure or surface currents and waves (Prata *et al.*, 2018). In closed flux chambers, excessive gas accumulation may alter the diffusional flux, resulting in non-linear gas concentration accumulation curves (Mønster *et al.*, 2019). In that case, it is recommended to select the linear part of the curve (i.e., the starting points from the hood's closure time) to avoid underestimating the emission rate (Pavelka *et al.*, 2018). The duration of the hood closure and the number of samples to collect should be adjusted accordingly on site. Adequate gas mixing must be achieved inside the hood. Spherical shaped hoods are believed to offer the best gas mixing conditions as they lack dead zones. Otherwise, mixing can be enhanced by placing a fan/blower inside the hood, recirculating the headspace gas in a closed loop or applying a flow of sweep gas (open flux chambers). Ideally, the gas mixing achieved inside the hood should be close to wind speed at the water surface level (Caniani *et al.*, 2019). When applying a sweep gas, caution must be taken to ensure that the concentration of the diluted off-gas can still be measured accurately.

5.3.2.1.4 Advective flow conditions

In advective flow conditions, previous work comparing a custom-made, large hood (cuboid) and the SEIFC hood types indicated that hood size and design do not significantly impact N₂O measurements assuming they are properly vented to prevent pressure build-up (Porro *et al.*, 2014). Similar conclusions were reached in the study of Spinelli *et al.* (2018). The authors recommended avoiding the use of fixed hoods (instead of floating hoods) because they showed higher gas compression phenomena in the headspace due to the variation of the water level inside the hood. Thus, it is recommended to fit the hood with adequate vent ports (in number or in size) and to monitor and record the pressure under

the hood to correct the off-gas concentration (and the flowrate) accordingly if needed (Chandran *et al.*, 2016). Finally, the volume of the hood should be selected with regard to the gas retention time under the experimental conditions, the dynamics of the process unit investigated and the subsequent use of the collected data. If the gas is conditioned using moisture traps, silica gel columns or condensers, one must consider the additional gas retention time resulting from the introduction of this type of device.

The site-specific measurement plan should address floating hood placement depending on the reactor configuration, operating conditions and the objectives of the measurement campaign. If the reactor presents spatial gradients in concentrations of dissolved oxygen, nitrogen species or biomass along the reactor path (due to its design or to bad mixing), emissions should be sampled at different positions of the reactor to achieve a coherent estimation of the emission rate. In most cases, the positions of the hood (or hoods) are chosen so as to sample zones with contrasting operating conditions (e.g., beginning, middle and end of a plug flow reactor). When using the SEIFC hood, Chandran *et al.* (2016) recommend sampling at least two positions per aerated zone to address any variability in gas fluxes that may result from variations in mixing or flow patterns therein. The study of Caniani *et al.* (2019) is one of the few to fix a quantitative coverage criterion of 2% of the total aerated tank surface in accordance with oxygen transfer measurement practices (ASCE, 1997). In that respect, large hoods offer the advantage of covering a greater surface area and thus provide a better averaging of emissions in a given zone (Porro *et al.*, 2014). On the other hand, small hoods are lighter and thus easier to move around for measuring many different positions and/or lanes.

If not measured in the hood, the off-gas flowrate was estimated considering either a homogenous gas distribution over the surface of the aerated tank (or an aerated zone of it) or a variable gas distribution approximated according to the aerator density in the relative zone. Depending on the tank configuration and design, these assumptions can be a source of great error. Thus, it is recommended to measure both off-gas concentration and flowrate to estimate the local emission rate. Additionally, data from the plant's air flowmeters need to be checked against the calculated intake airflow rate of the air blowers.

5.3.2.2 Liquid-to-gas mass transfer estimation method

N₂O and CH₄ emissions in WWTPs derive from generation processes in the liquid phase. The determination of N₂O and CH₄ transferred from the liquid phase serves as a feasible approach to estimate their emissions to the atmosphere. The liquid-to-gas mass transfer estimation method has been mostly applied to quantify N₂O emissions in WWTPs. The transfer rate of N₂O and CH₄ across the gas-liquid interphase (dC/dt) is governed by the N₂O or CH₄ gas-liquid transfer coefficient ($K_{L\alpha}$) as well as the respective gas and liquid concentrations. The mass transfer of N₂O, CH₄ as well as other soluble gases such as O₂, can be described by Equation (5.11) (Holley, 1973):

$$dC/dt = K_{L\alpha} * (C_{l,eq} - C_{l,t}) - r \quad (5.11)$$

where dC/dt is the dissolved gas concentration in the bulk liquid with time (gN/(m³*d)), $K_{L\alpha}$ is the volumetric mass transfer coefficient (d⁻¹), r is the uptake rate of the studied substance per unit volume per unit time (gN/(m³*d)), $C_{l,t}$ is the dissolved gas concentration in the bulk liquid at time t (gN/m³), $C_{l,eq}$ is the dissolved gas concentration at the liquid-gas boundary, which is assumed to be in equilibrium with the gas phase as given by Henry's law, calculated by using the unitless Henry's coefficient (H) and the gas concentration (C_g): $C_{l,eq} = C_{g,eq}/H$, (gN/m³).

When the substance uptake rate is zero, the initial dissolved gas concentration ($C_{l,0}$) at time 0 ($t = 0$) and the dissolved gas concentration at time t ($t = t$), can be calculated as Equation (5.12):

$$\frac{C_{l,t} - C_{l,eq}}{C_{l,0} - C_{l,eq}} = e^{-K_{L\alpha} * t} \quad (5.12)$$

Therefore, the amount of N₂O or CH₄ emissions (M_t) during the period from $t = 0$ to $t = t$ through liquid gas transfer can be estimated by Equation (5.13):

$$M_t = V * \int_{t_0}^{t_1} K_L a_{(t)} * (C_{l,(t)} - C_{l,eq}) dt \quad (5.13)$$

The estimation of N₂O or CH₄ emissions requires measurements of N₂O and CH₄ liquid concentrations and their volumetric mass transfer coefficient. Online monitoring of liquid N₂O concentrations can be carried out in a WWTP using a modified Clark electrode N₂O probe (Figure 5.8). By comparing the liquid N₂O probe monitoring with simultaneous gas chromatograph analysis of the off-gas, studies have demonstrated the accuracy of liquid N₂O probe monitoring in WWTPs (N₂O gas concentration in the range of 0–1000 ppm) (Baresel *et al.*, 2016; Marques *et al.*, 2016; Myers, 2019). Nevertheless, it should be noted that the liquid N₂O probe is sensitive to disturbances and should be used with care. The electrode N₂O probe requires relatively frequent calibration to ensure accurate measurement, and has an expected life time of 4–6 months (manufacture information). Temperature variation could affect the response of the liquid concentration measurement and thus require corrections to be applied (Marques *et al.*, 2016).

Online probes for dissolved CH₄ are currently not widely employable with wastewater, therefore grab sampling needs to be applied. In this case the concentration of dissolved CH₄ can be measured using the headspace method for gas chromatography as described in Section 5.2.2.

Compared with N₂O or CH₄ liquid measurement, the determination of $K_L a$ is more challenging. There are three approaches proposed to determine the volumetric N₂O mass transfer coefficient: theoretical, empirical and oxygen proximity.



Figure 5.8 Dissolved N₂O probes with protective cover (left), and measurement controller (right). Photo courtesy of Dr. Adrian Oehmen (The University of Queensland).

5.3.2.2.1 Theoretical method

With simultaneous measurement of N_2O concentrations in the gas and liquid phase, the $K_L a_{N_2O}$ can be theoretically calculated as Equation (5.14). The equation is derived from the two-film derivation with the assumption that the activated sludge basin is well-mixed with no vertical stratification of dissolved N_2O concentrations. Such an assumption allows a simplified integration with regard to time from the bottom to the surface of the basin (Myers, 2019).

$$C_g = C_{g,in} * e^{-\frac{K_L a * V_L}{H * Q_A}} + H * C_{l(t)} * \left(1 - e^{-\frac{K_L a * V_L}{H * Q_A}}\right) \quad (5.14)$$

where C_g is the gas N_2O concentration (gN/m^3), $C_{g,in}$ is the gas N_2O concentration in the aeration bubbles at the bottom of the aeration basin (gN/m^3), V_L is the volume of bulk liquid (m^3), Q_A is the aeration air flowrate (m^3/d), and H is the unitless Henry's coefficient.

At steady state when the changes of dissolved N_2O concentration can be assumed negligible, Equation (5.14) can be simplified and written as Equation (5.15).

$$K_L a = \frac{Q_A * C_g}{V_L * (C_{l,eq} - C_{l(t)})} \quad (5.15)$$

5.3.2.2.2 Empirical method

The empirical determination of $K_L a$ was proposed by Foley *et al.* (2010) based on field and laboratory measurements of liquid and off-gas N_2O . Air flow and depth correction were considered in the determination, as shown in Equation (5.16).

$$K_L a = \left(\frac{H_R}{H_L}\right)^{-0.49} * 34500 * (\nu_g)^{0.86} \quad (5.16)$$

where H_R is the depth of the field reactor (m), H_L is the depth of the lab stripping column applied in Foley *et al.* (2010), which is 0.815 m, and ν_g is the superficial gas velocity of the field reactor ($m^3/(m^2*d)$), calculated as air flowrate (Q_A) divided by aerated area (A).

5.3.2.2.3 Oxygen proximity method

The third $K_L a$ determination approach is based on Higbie's penetration model (Equation (5.17)) (Higbie, 1935). In this model, when two gases share similar low solubilities and diffusivities, the $K_L a$ of one gas can be estimated by measuring the $K_L a$ of the other gas under the same conditions.

$$K_L a_{N_2O} = K_L a_{O_2} * \sqrt{\frac{D_{N_2O}}{D_{O_2}}} \quad (5.17)$$

where D_{N_2O} is N_2O molecular diffusivity in water ($1.84 \times 10^{-9} m^2/s$ at $20^\circ C$), and D_{O_2} is O_2 molecular diffusivity in water ($1.98 \times 10^{-9} m^2/s$ at $20^\circ C$).

Oxygen transfer is critical to wastewater treatment and therefore often monitored in WWTPs. The $K_L a$ for O_2 can be quantified by the in-situ oxygen uptake rate (OUR) method, or by the off-gas method (ASCE, 1997). The off-gas method is based on a gas-phase mass balance, which requires the use of a suitable gas analyser for determining the oxygen concentration and hoods to collect the off-gas. Due to the wide availability of dissolved oxygen (DO) monitoring in WWTPs, and the more straightforward experimental procedure, the in-situ OUR method is more commonly used. The in-situ

OUR method uses the in-situ OUR, and liquid O₂ concentrations ($C_{l(t)}$) to determine the $K_L a_{O_2}$, as described in Equation (5.18) (Moutafchieva *et al.*, 2013). Note that the determination will require online or continuous monitoring of the DO concentrations for a period of time.

$$\frac{dC}{dt} = K_L a_{O_2} * (C_{l,eq} - C_{l(t)}) - \text{OUR} \quad (5.18)$$

When the direct online/continuous measurement of DO is not feasible, $K_L a_{O_2}$ can still be obtained by oxygen balance analysis, enabling the subsequent estimation of N₂O emissions. In particular, for aeration basins with mechanical aeration systems, such as surface aerators, wastewater is disrupted at the surface to allow the mass transfer of oxygen. In close proximity to the surface aerator there is a high liquid-gas transfer rate while the continuous/online measurement of liquid O₂/N₂O concentration is practically challenging. The turbulent mixing of mechanical aerators creating fast flowing low buoyancy waters presents an unacceptable health and safety risk for measuring the liquid oxygen concentrations. The direct quantification of $K_L a_{O_2}$ or $K_L a_{N_2O}$ in the intensive aeration area is difficult.

Ye *et al.* (2014) proposed an oxygen balance analysis approach to obtain the $K_L a_{O_2}$ in the intensive aeration area. An illustration of the oxygen balance, chemical oxygen demand (COD) and total Kjeldahl nitrogen (TKN) oxidation is shown in Figure 5.9. The oxygen consumption for the entire plant ($M_{O_2 \text{ tot}}$) is due to the oxidation of COD ($M_{O_2 \text{ COD tot}}$) and TKN ($M_{O_2 \text{ TKN tot}}$) (Equation (5.19)). The oxygen consumption for COD and TKN oxidation can be solved by Equations (5.20) and (5.21), respectively (Ye *et al.*, 2014). Note that CH₄ emission from total COD loss is ignored in the COD balance (Figure 5.9), due to the fact that methanogens can hardly grow with the frequent exposure to oxygen in the aerobic reactor. With the oxygen consumption obtained, the $K_L a_{O_2}$ can be solved using

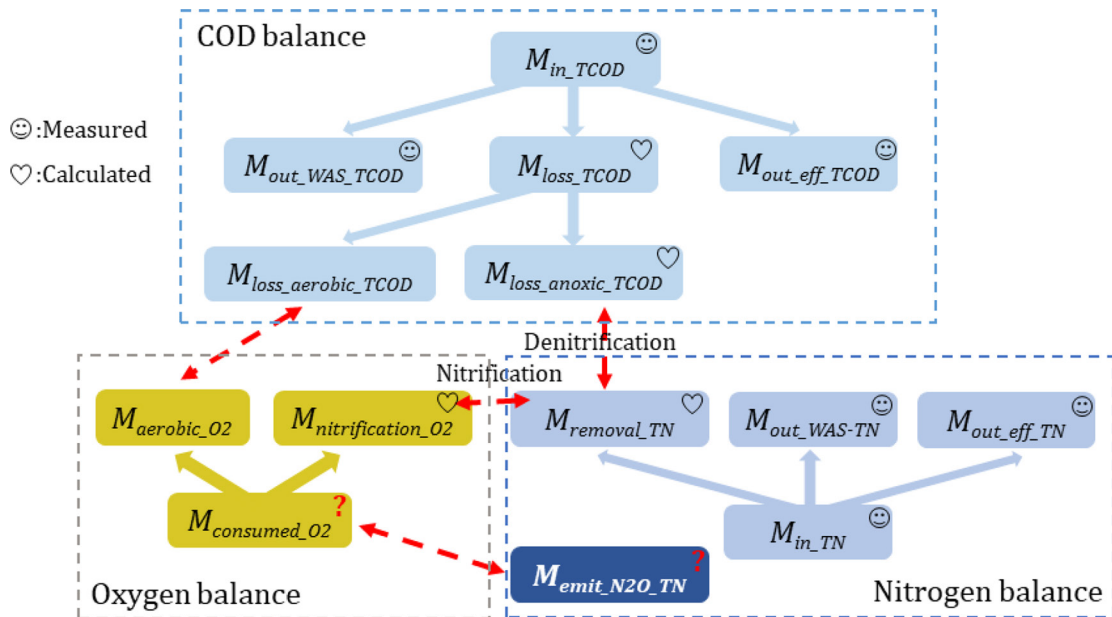


Figure 5.9 Simplified illustration of the methodology to determine the N₂O volumetric transfer coefficient via oxygen mass balance analysis.

Equation (5.13). The $K_L a_{N_2O}$ for the surface aerator area can be calculated using Equation (5.17), and the N_2O emission from the surface aerator area is subsequently obtained using Equation (5.13).

$$M_{O_2\text{tot}} = M_{O_2\text{CODtot}} + M_{O_2\text{TKNtot}} \quad (5.19)$$

$$M_{O_2-\text{COD}-\text{tot}} = \int_{t_0}^{t_1} \left[\begin{array}{l} Y_A * [Q_{\text{inf}}(t) * S_{\text{inf-TKN}}(t) - Q_{\text{eff}}(t) * S_{\text{eff-TKN}}(t) - Q_{\text{WAS}}(t) * X_{\text{WAS-TN}}(t)] + \\ Q_{\text{inf}}(t) * S_{\text{inf-COD}}(t) - Q_{\text{eff}}(t) * S_{\text{eff-COD}}(t) - Q_{\text{WAS}}(t) * X_{\text{WAS-COD}}(t) \\ - 2.86 * [Q_{\text{inf}}(t) * S_{\text{inf-TKN}}(t) + Q_{\text{inf}}(t) * S_{\text{inf-NO}_3}(t) - \\ Q_{\text{eff}}(t) * S_{\text{eff-TKN}}(t) - Q_{\text{eff}}(t) * S_{\text{eff-NO}_3}(t) - Q_{\text{WAS}}(t) * X_{\text{WAS-TN}}(t)] \end{array} \right] dt \quad (5.20)$$

$$M_{O_2-\text{TKN}-\text{tot}} = \int_{t_0}^{t_1} [Q_{\text{inf}}(t) * S_{\text{inf-TKN}}(t) - Q_{\text{eff}}(t) * S_{\text{eff-TKN}}(t) - Q_{\text{WAS}}(t) * X_{\text{WAS-TN}}(t)] * 4.33 dt \quad (5.21)$$

where $Q_{\text{inf}}(t)$ is the daily influent flow rate into the reactor (m^3/d), $Q_{\text{eff}}(t)$ is the daily effluent flow rate from the bioreactor (m^3/d), $Q_{\text{WAS}}(t)$ is the daily waste activated sludge from plant (wet tonne solids/d), $S_{\text{inf-TKN}}(t)$ is the average TKN concentration in the influent ($\text{g N}/\text{m}^3$), $S_{\text{eff-TKN}}(t)$ is the average TKN concentration in the effluent ($\text{g N}/\text{m}^3$), $S_{\text{inf-COD}}(t)$ is the average COD concentration in the influent ($\text{g COD}/\text{m}^3$), $S_{\text{eff-COD}}(t)$ is the average COD concentration in the effluent ($\text{g COD}/\text{m}^3$), $S_{\text{inf-NO}_3}(t)$ is the average nitrate concentration in the influent ($\text{g N}/\text{m}^3$), $S_{\text{eff-NO}_3}(t)$ is the average nitrate concentration in the effluent ($\text{g N}/\text{m}^3$), $X_{\text{WAS-COD}}(t)$ is the COD concentration in the waste sludge ($\text{g COD}/\text{g wet solids}$), $X_{\text{WAS-TN}}(t)$ is the total N concentration in the waste sludge ($\text{g N}/\text{g wet solids}$), and Y_A is the autotrophic yield ($\text{g COD}/\text{g N}$).

The mass transfer approach has been applied in WWTPs with different configurations, as summarized in Table 5.3. The mass transfer approach has wide applicability to varying process-unit configurations. It can be applied to any process unit with liquid gas transfer. The mass transfer approach is practically straightforward. It doesn't need the surface area of the investigated process unit to be covered. Therefore, the monitoring configuration is relatively simple. Minimal maintenance is required when moving around different locations. It doesn't necessarily need continuous online monitoring of liquid N_2O concentrations. With options of grab sampling analysis, this method is operator-friendly and incurs relatively low costs. It is particularly suitable for continuous aeration systems at steady state.

However, some limitations of this method should be noted. Firstly, similar to the chamber method, the mass transfer method has a small footprint. Monitoring one location is hardly representative of the overall N_2O emissions of a process unit. Multiple representative monitoring locations must be chosen. Secondly, while grab sampling is feasible to estimate N_2O emissions, the accuracy of the results is questionable. The N_2O liquid concentration in the grab samples analysis needs to be representative. The quantification is based on the assumption that the bioreactor is operated under steady state conditions, which may not be valid. With grab samples, the potentially significant N_2O emission dynamics cannot be captured, so the measured concentration may not be representative of the overall dynamic concentrations. Thirdly, wastewater characteristic changes could also affect the accuracy of mass transfer estimation. For example, increased wastewater salinity could encourage the stripping of N_2O from the liquid phase (Kosse *et al.*, 2017). Finally, considering the dynamic nature of mass transfer with aeration and environmental conditions, using a single representative $K_L a$ is inherently problematic. A dynamic $K_L a$ should be obtained with simultaneous online measurements. The oxygen proximity method provides opportunities for simultaneous determination of the dynamic $K_L a$ for estimating N_2O emissions. This will require further investigation.

Table 5.3 Examples of mass transfer methods employed in estimating GHG emissions in WWTPs, ranked by publication date.

Reference	BNR configuration	GHG	Aeration system	Monitoring frequency	K _L a estimation Method	Remarks
Foley <i>et al.</i> (2010)	AAO, MLE, Oxidation ditch, Johannesburg and SBR	N ₂ O	Diffused aeration	Grab samples	Empirical method and oxygen proximity method	N ₂ O emissions from 7 full-scale WWTPs were quantified based on the mass transfer approach with grab samples. Bioreactors were assumed to be working at near steady-state conditions
Ye <i>et al.</i> (2014)	Oxidation ditch	N ₂ O	Mechanical aeration: surface aerators	Grab samples for liquid N ₂ O analyses	Oxygen proximity method with oxygen balance analysis	The N ₂ O emissions from a surface aerator area were quantified with the mass transfer method. K _L a was estimated by plant-wide oxygen balance analysis.
Mampaey <i>et al.</i> (2015)	SHARON® SBR	N ₂ O	Gas stripping device	Online gas phase analyser	Theoretical method	A continuous flow of reactor liquid goes through a stripping vessel and the gas concentration in the stripped gas is continuously monitored. This allows liquid phase N ₂ O or CH ₄ concentration determination by gas phase measurements.
Pan <i>et al.</i> (2016b)	Sludge drying lagoon	CH ₄	No aeration	Grab samples	Oxygen proximity method with COD balance analysis	The mass transfer approach can also be applied to quantify CH ₄ emissions from sludge drying lagoon.
Marques <i>et al.</i> (2016)	SBR	N ₂ O	Diffused aeration	Online liquid and gas measurement	Theoretical method	K _L a for anoxic zones was calculated based on the dynamic emissions measured by the N ₂ O gas and liquid sensors.
Baresel <i>et al.</i> (2016)	AAO	N ₂ O	Diffused aeration	Continuous monitoring for two months	Empirical method	Calculated emissions by mass transfer method had good agreement with measured emissions in the off-gas ventilation system from the covered process.
Blomberg <i>et al.</i> (2018)	Anoxic/oxic	N ₂ O	Diffused aeration	Continuous monitoring for 14 days	Empirical method	The mass transfer of N ₂ O was built into a mathematical model to predict N ₂ O emissions.
Myers (2019)	Anoxic/oxic	N ₂ O	Diffused aeration	Continuous monitoring for two weeks	Theoretical, empirical and oxygen proximity methods	Compared the accuracy of the three K _L a _{N₂O} determination approaches in a full-scale WWTP. Simultaneous N ₂ O off-gas concentrations were monitored to validate the liquid-gas transfer model. The findings suggested that the trends of N ₂ O emissions can be reliably modelled. Of the three K _L a _{N₂O} estimation approaches, the oxygen proximity method can best describe the real N ₂ O gas concentrations.

AAO: anaerobic/anoxic/oxic; MLE: modified Ludzack-Ettinger; SBR: sequencing batch reactor; SHARON®: Single reactor system for High activity Ammonium Removal Over Nitrite.

5.3.2.3 Ground-based remote sensing methods

The layout of the investigated WWTP is an important constraint when applying a ground-based remote sensing method for GHG emission quantifications from a specific process unit. All ground-based remote sensing methods must be applied at a suitable distance from the target emitting area, which should generate an atmospheric plume distinguishable from any other GHG source inside the WWTP.

The mobile tracer gas dispersion method (MTDM) is the only ground-based remote sensing method that has been used for quantifying CH₄ and N₂O emissions from specific process units. Thanks to a specific plant layout, the MTDM was applied on-site at WWTPs (Delre *et al.*, 2017; Samuelsson *et al.*, 2018). Although the inverse dispersion modelling method (IDMM) has never been applied at WWTPs, it could be potentially used for quantifying CH₄ emissions from the sewage sludge treatment area. The literature reports several studies quantifying CH₄ emissions from biogas plants, using the IDMM (Flesch *et al.*, 2011; Groth *et al.*, 2015; Hrad *et al.*, 2014, 2015; Reinelt *et al.*, 2017). Biogas plants have structures and technologies which are very similar to those used for sludge treatment in WWTPs. However, the WWTP layout could be a constraint.

5.3.2.4 Measurements in covered process-units

Process-unit emission measurements of N₂O and CH₄ can be readily employed in covered tanks where the off-gas is extracted and treated prior to its release into the environment. A part of this off-gas stream can be withdrawn and fed to an online gas analyser, as performed in the work of Daelman *et al.* (2012), Carlsson and Lindblom (2015) and Kosonen *et al.* (2016). According to the goal of the measurements, also grab sampling and analysis with GC would be a suitable approach. At fully-covered WWTPs where the off-gas of most components of the plant is constantly withdrawn, a plant-wide quantification can be achieved with this approach. Thanks to the ease of collecting the off-gas samples from the venting pipes, covered activated sludge tanks are suitable candidates to perform long-term measurements. On the other hand, one limitation of the method is its inability to measure spatial variability within a tank, which is essential to identify “hotspots” and hence develop targeted mitigation measures.

By this method, besides the analytical determination of the GHG concentration in the off-gas, the accurate measurement of the off-gas flow rate in the venting pipes is essential. If no online flowmeters are installed, different portable measurement devices such as a hot wire anemometer (Daelman *et al.*, 2012) or a Pitot tube static anemometer (Valkova *et al.*, 2020) can be applied to measure the airflow velocity. Proper calibration and probe positioning inside the off-gas pipe during the measurement need to be ensured. It is also recommended to continuously monitor the operation of the off-gas ventilators on the basis of power consumption data.

The quantification method assumes that the headspace in the covered tank is fully mixed and no airstream short-circuits occur. In order to exclude this, parallel comparative short-term measurements using a floating hood, which can be introduced under the tank covers, are recommended.

Additionally, a static version of the tracer gas dispersion method can be applied where process units are enclosed and indoor air is collected in a ventilation system (Samuelsson *et al.*, 2018). Samuelsson *et al.* (2018) reported a successful application of the static tracer gas dispersion method (STDM) for quantification of N₂O and CH₄ emission rates from the ventilated duct in the building where digestate dewatering and sludge thickening occurred. The STDM deploys a static analytical instrument, as previously reported for CH₄ emission quantifications from leachate wells at landfills (Fredenslund *et al.*, 2010). In the reported measurements, the tracer gas was released in the enclosed ventilated duct upstream of a fan, which facilitated proper mixing of tracer and target gases at the end of the duct, where the air intake of the gas analyser was located. Emission rates of the target gases were calculated by slightly modifying Equation (5.4), whereby, instead of plume integration, the ratio of the two gases was used. Although the hereby reported application of the STDM is limited to process units enclosed

in buildings with ventilation system, it can be performed disregarding weather conditions and for a long period of time.

5.3.2.5 Point monitoring of CH₄ leakages

Sources of CH₄ emissions from WWTPs can also be derived from leakages in the biogas valorization system (fugitive emissions). Point monitoring approaches such as a portable flame ionization detector (FID) and an infrared gas imaging camera with an absorption filter within a specific wavelength range (e.g., GasFindIR-camera FLIR GF320) have been used to identify gas leakages at biogas plants (Liebetrau *et al.*, 2013; Reinelt *et al.*, 2017) and can be applied also to anaerobic digesters of WWTPs (Tauber *et al.*, 2019). These methods have a limited spatial and temporal resolution for gas emissions and the application can be difficult for areas with restricted access. After localization, the accessible leakage spots can be encapsulated in a flexible enclosure made, for example, of a gas tight foil, equipped with an input and output pipe and a blower to produce a constant air flow through the enclosed volume as described in Liebetrau *et al.* (2013). The quantification of the CH₄ leakages can be then performed similarly as for Lindvall hoods (see Section 5.3.2.1). Depending on the accessibility of the leakage point, the static chamber method may also be used (Tauber *et al.*, 2019). A method to quantify operational CH₄ emissions from pressure relief valves of biogas plant digestors is described in Reinelt and Liebetrau (2020).

5.3.3 Recommendations for selecting the measurement method

Table 5.4 summarizes (with no claim to completeness) the currently available and most commonly applied methodologies for the quantification of direct N₂O and CH₄ emissions at full-scale WWTPs. The methodologies, their strengths and limitations, and instrumental requirements, as well as some general remarks are presented. Among the ground-based remote sensing methods, the MTDM is considered in this overview, since this is the sole method for plant-wide quantification that has been successfully applied at WWTPs to date.

This overview emphasizes that a universally recommended quantification method does not exist, whereas the choice of the suitable method is mainly dictated by the specific goals of the survey as well as by individual local requirements. Moreover, some objectives can require bottom-up or top-down approaches where the application of more than one method is required. The intention of this section is to provide general recommendations for researchers and practitioners interested in measuring N₂O and CH₄ emissions at full-scale WWTPs. In this context, the most common goals of GHG quantification are:

- Quantification of the overall GHG emissions for a given WWTP to comply with GHG emission protocols/inventories and/or to provide consolidated data for carbon footprint analyses within life cycle assessment (LCA) studies.
- Development of mitigation strategies for direct GHG emissions at WWTPs:
 - Approach 1: Estimation of the N₂O and/or CH₄ emissions for a given WWTP and changing sets of conditions (e.g., operation, load, temperature) with the aim of linking emissions to operational parameters and plant performance in, for example, regression analysis.
 - Approach 2: Calibration and validation of N₂O and/or CH₄ mechanistic models to understand potential generation and emission pathways and be able to accurately describe observed emissions.

When quantification of a WWTP overall GHG emission is the main objective of the survey, plant-wide quantification can be, in many cases, the most suitable approach. When specific local conditions hamper the application of these methods, a bottom-up approach can be followed, by identifying and quantifying the largest emitters at process-unit level and then summing up the single sources. In this case, however, unknown emission sources will remain undetected.

Table 5.4 Comparison of different GHG emissions quantification methodologies for WWTPs.

Methodological approach	Measurement method	Strengths	Limitations	Equipment ¹	Remarks
Plant-wide quantification ²	Mobile tracer gas dispersion method	On-site screening can identify the major source of GHG emissions. Quantification of the overall GHG emissions, thus reducing the potential overlook of individual on-site emission sources.	Emission quantification is not possible if the facility has an upwind source of the target GHG, which overlaps the target plume. Unable to perform long term and continuous monitoring.	A mobile analytical platform equipped with fast-responding and sensitive gas analyser, a GNSS ⁵ device, and flow control system from the tracer gas cylinders. The literature reports successful applications using gas analysers with the following features: CH ₄ frequency 0.06–2 Hz CH ₄ precision ³ : 2.6–3.8 ppb N ₂ O precision ³ : 0.7–21.1 ppb C ₂ H ₂ precision: 0.3–4.2 ppb CH ₄ detection: interval 0–20 ppm N ₂ O detection: interval 0–400 ppm C ₂ H ₂ detection: interval 0–500 ppb	Minimal detectable emission is related to analytical instrument, size of the target source, weather conditions and measurement distance. Therefore, minimum detectable emission rate is site, time, and equipment specific.
Process-unit quantification	Floating hood	Can investigate the dynamics and spatial variability of GHG emissions. Can establish the links between GHG emission and the nitrogen removal process. Can identify GHG production sources. Relatively straightforward implementation	Relatively small foot-print, challenging to extrapolate to large areas. Unsuitable for surface aeration systems (e.g., surface aerators).	For low N ₂ O conc. range: Detection interval: N ₂ O 0–50 ppm Detection limit: 0.05 ppm Precision: 1% of reading—For high N ₂ O conc. range: Detection interval: N ₂ O 0–1000 ppm Detection limit: 1 ppm Precision: 1% of full-scale ⁴ —For CH ₄ : Detection interval: CH ₄ 0–500 ppm Detection limit: 0.3 ppm Precision: 1% of reading	The most common approach for N ₂ O quantification, spatial variations however could cause uncertainties for large scale quantification. Other portable sensors can also be mounted to simultaneously measure the wastewater treatment operational parameters, providing opportunities to link operational conditions to the GHG emissions.
	Liquid-to-gas mass transfer method	Suitable for treatment plants with surface aeration systems. Grab samples or online measurement can be carried out.	The investigated system needs to be well defined and in steady state to allow accurate mass balance analysis. Relatively small foot-print, challenging to extrapolate to large areas.	Liquid N ₂ O sensor: Detection range: 0–14 mg N/L; Detection limit: 28 µg N/L.	The N ₂ O liquid measurement is sensitive to temperature variations and has a relatively long response time (<20 or <45 s depending on the sensor type). This method can link oxygen consumption, N ₂ O and CH ₄ emissions together.
	Mobile tracer gas dispersion method	Quantification of the GHG emissions from the entire target process unit.	The same as plant-wide quantification.	The same as plant-wide quantification.	The same as plant-wide quantification

¹Mentioned detection interval and detection limit are manufacturers' specifications.

²Only methods currently applied to full-scale WWTPs were considered.

³Precision in detecting specific gas is given as three times the standard deviation of six minutes' constant concentration reading (Samuelsson *et al.*, 2018). Acetylene (C₂H₂) is the most commonly used tracer gas.

⁴Precision definition: 1% of full-scale accuracy means that the maximum absolute error of the analyser by measuring a constant concentration is no more than 0.01 times the full-scale value of the analyser (in this case 1000 ppm).

⁵GNSS: global navigation satellite system.

When the focus of the quantification survey is to develop mitigation strategies to reduce GHG emissions at the plant, much deeper insights into the generation and emissions pathways are essential. For this purpose, the process-unit approaches can provide the required information for developing mechanistic model or regression analyses linking operational and emission data. The selection of the suitable method for process-unit quantification will be dictated in many cases by the typology of the targeted process unit itself (in some cases also by the targeted GHG), taking into account the strengths and limitations of each method.

Some examples referring to the most common applications of GHG quantification at WWTPs are given as follows:

Example 1: Decrease the Carbon Footprint of the WWTP.

Possible approach (top-down):

- (1) Perform plant-wide quantification and carbon footprint evaluation of the plant. If direct N₂O and/or CH₄ emissions are shown to be contributing significantly to the plant carbon footprint, further investigation will be carried out to quantify emissions from process units.
- (2) On-site quantification to identify the largest emission sources applying either ground-based remote sensing or hood methods.
- (3) Undertake a long-term study to investigate spatial-temporal dynamics using hoods and liquid sensors and establish links with process parameters and/or implement a model. After having optimized the investigated process towards lower GHG emissions, the generated mitigation potential can be eventually verified by performing new plant-wide measurements.

Example 2: Estimation of N₂O and/or CH₄ emissions for GHG inventories.

Possible approach:

- (1) Perform plant-wide quantification of N₂O and CH₄ emissions for different sets of local conditions (e.g., at differing loading conditions and/or water temperature) to generate average values on a yearly basis.
- (2) Bottom-up: if largest emitters are already known, process-unit quantification can be used as well and the single sources can be integrated. In this case, unknown emission sources remain undetected. A long-term approach is recommended.

Ultimately, specific local factors such as WWTP design and operation, technical staff resource availability, monetary resources, analytical capacity, and equipment/instrument availability can play a significant role in selecting the quantification method as well as in developing the sampling plan. Therefore, these additional constraints need to be carefully evaluated in the decision-making process to ensure they do not hamper the fulfilment of the measurement goals.

5.3.4 Recommended data requirements

The aim of this section is to provide additional practical guidance for the implementation of measurement campaigns to quantify direct N₂O and CH₄ emissions at full-scale WWTPs. The main objective focuses on the minimum data requirements (in terms of quality and quantity) and duration of a measurement campaign. The minimum data requirements strongly depend on the measurement goals (e.g., GHG inventory versus GHG emission modelling) and will be influenced by several factors such as the site layout, accessibility of sampling points and resources availability (human and monetary) for the campaign.

Multiple factors can impact the accuracy of the estimation of GHG emissions and GHG emission factors of WWTPs. The most relevant of these are summarized in [Figure 5.10](#). Beside issues related to the method implementation and analytical uncertainty, the chosen sampling strategy as well as the plant data availability and quality are of significant concern and need to be thoroughly considered. Plant data are not only essential to compare GHG emissions to influent loads, they also provide

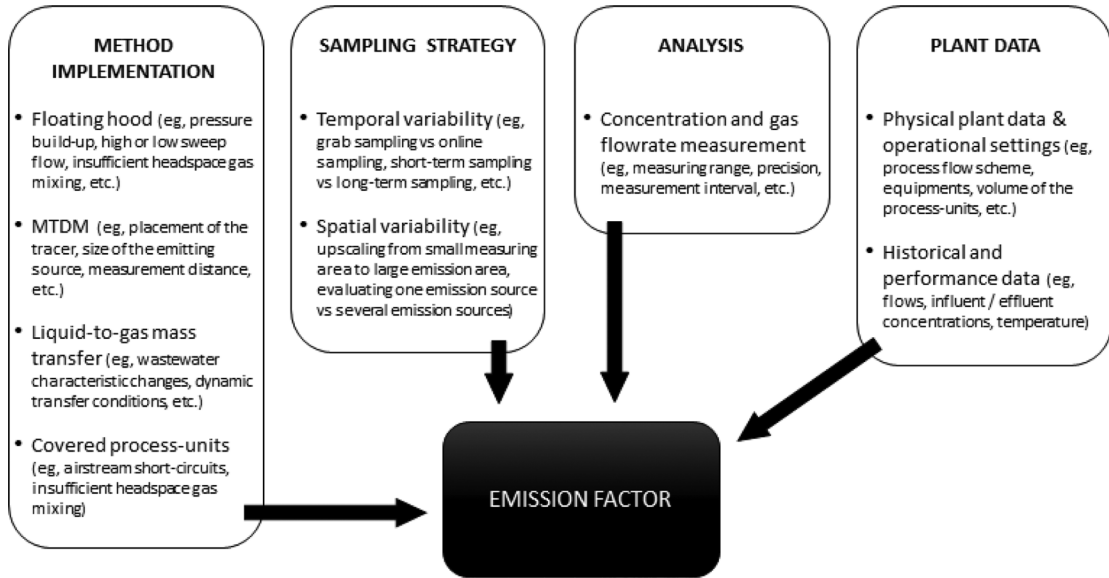


Figure 5.10 Potential sources of errors impacting the estimation of GHG emission factors at WWTPs.

the basis for developing a sound field sampling plan and define the number and duration of the measurement campaigns. Although some protocols (Chandran, 2009; Chandran *et al.*, 2016) provide an overview of the data requirements for the preliminary WWTP assessment and complementary data requirements accompanying off-gas measurements, the design of a GHG quantification campaign remains a challenging task. In general, it can be said that good knowledge of the plant and process unit operation is essential and GHG assessments should be performed in cooperation with the plant operators.

For a preliminary assessment of the GHG emissions, a straightforward grab sampling approach can be carried out to provide an order-of-magnitude estimate of GHG emissions from the sampled location. Discrete samples can be taken for offline analysis of liquid GHG concentrations. Together with the estimated K_La , the emission rates of GHGs can be calculated by the liquid-to-gas mass transfer estimation method (as presented in Section 5.3.2.2). Grab sampling is particularly suitable for continuous aeration systems where the dynamics of K_La are less significant. Due to the spatio-temporal variability of GHG emissions (especially N_2O), this can only serve as a preliminary assessment of the sampled location. Since production and emission of N_2O and CH_4 can occur temporally and/or spatially independently from each other, selection of the sampling locations should reflect this pattern.

In the majority of cases, the minimum number of operating parameters that need to be monitored during the quantification campaign is dictated by the measurement goals. While daily influent load (daily average) and plant removal performance are usually sufficient for GHG emission inventories, more data are needed to establish correlations between the operating conditions and emissions or for model calibration. With regard to the key parameters to be monitored, it is possible to distinguish between those that are essential to estimate N_2O and CH_4 emissions (e.g., plant flows, aeration air flow, nitrogen loading, etc.) and those that influence production/emission pathways (e.g., concentrations of dissolved oxygen, nitrogen species, biomass concentration, sludge age, etc.). The reader interested in data analysis and reconciliation methods is advised to read the procedure proposed by Rieger *et al.* (2013). Additionally, when modelling is targeted, the frequency of the plant data acquisition needs to be increased from composite samples (24-hour average concentrations) that would be suitable for

inventories/quantification, to higher resolution sampling (in most cases, online sensors are used). To better correlate N₂O emissions with the influent pollutant load, the 24-hour window for the calculation of the daily N₂O flux should be the same as that for the daily composite influent samples of the WWTP (Valkova *et al.*, 2020).

Owing to the plurality of quantification methodologies, (1) the floating hood method for N₂O emission quantification in activated sludge tanks and (2) plant-integrated GHG emission quantification were chosen as exemplary applications in this section for further discussion. Although the focus is upon these specific applications, general recommendations can also be extrapolated for other quantification methods.

5.3.4.1 Floating hood method for N₂O emission quantification

Spatial variability of GHG emissions was shown to be significant in tanks having spatial gradients of dissolved oxygen/nitrogen species concentrations or different aeration strategies along a lane. Regardless of the objective (inventories or modelling), zones with contrasted conditions should be sampled more intensively, preferably applying multiple floating hoods, as suggested by several authors (Bellandi *et al.*, 2017; Duan *et al.*, 2020; Gruber *et al.*, 2020; Pan *et al.*, 2016a). In the case of modelling, it is also recommended to sample and analyse the bulk liquid at the proximity of the hoods during the course of the monitoring period. Tanks exhibiting complete mixing conditions during aeration do not usually require multiple zone sampling. The variability of emissions between different parallel lanes also needs to be addressed. Differences in key performance indicators (e.g., effluent concentrations, sludge production, energy consumption) can be important indicators of uneven influent loading, leading to differing N₂O emissions (Gruber *et al.*, 2020).

The minimal duration of sampling should cover the diurnal variability of the load (24 h), which also corresponds to the maximum hydraulic retention time of most BNR technologies. However, in practice, a week of sampling including the weekend is advised to capture the temporal variability of N₂O and link it with the operating conditions of the plant.

If the plant treats a proportion of industrial waste, measurement should comprise periods where this load is added to the urban wastewater. If the plant is located in a tourist area, with significant variations in the load over a year, the sampling plan should comprise high and low loading periods. To account for the seasonal variability of GHG emissions, several short-term monitoring campaigns, for example, three to four per year, can be performed. The sampling protocol should cover periods with typical plant loadings and performance (base line) as well as periods with contrasting nitrification and denitrification capacities. Historical plant performance data can help with identifying these periodic patterns.

5.3.4.2 Plant-wide GHG emission quantification

The number of measurement campaigns should properly describe the emissions over one year. To date, no study has investigated the sufficient number of measurement campaigns and the suitable timing of measurements along one year. One quantification per season could be a good compromise in most cases. However, different plants require tailored sampling strategies according to the features of the process units. This is the case for WWTPs where biosolids are stored on site and seasonally applied on land, exhibiting higher GHG emissions when the biosolid storage is full.

The minimum number of plume traverses performed in a single quantification campaign could be set to 10. However, longer measurement campaigns would give the chance to gather potential GHG emission dynamics. In any case, the measurement campaign should last for a period that includes the entire process cycle of specific technologies used at the plant. For example, in WWTPs performing biological nitrogen removal, the N₂O emission quantification should last for a complete cycle of the nitrification/denitrification phases.

Detailed guidelines on how to best perform a measurement campaign, from design to application and data processing, are reported by Delre (2018).

5.4 CONCLUSIONS AND PERSPECTIVES

In the past two decades, the full-scale quantification of N₂O and CH₄ emissions from sewers and WWTPs has been significantly improved. Advances in analytical detection techniques have supported the development and application of plant-wide quantification approaches, capturing the entire emission spectrum of WWTPs, along with sources that were usually overlooked. Moreover, the upgrade from grab sampling towards online monitoring by process-unit applications has contributed to a better understanding of the mechanisms governing the production and emission pathways of both N₂O and CH₄. To estimate N₂O or CH₄ emissions from activated sludge tanks equipped with surface aerators, a tailored methodological approach was implemented. All these methodological improvements are key factors to developing effective mitigation strategies for urban water systems.

Despite the improvements, quantifying GHG in sewers and WWTPs still remains a challenging task. Current quantification methods can only partially depict the high spatio-temporal variability of GHG emissions, which are strongly influenced by environmental and process conditions in sewers and WWTPs, respectively. Extensive sampling of plants and long-term monitoring are necessary to capture the complexity of the targeted systems, thus requiring a significant input of resources on site. However, the improved data quality and quantity achieved through sound sampling and measurement protocols have helped to identify process parameters that trigger GHG emissions and refine models that are able to describe GHG emission profiles from sewers and WWTPs. To further support these achievements, future measurement campaigns at full-scale WWTPs should employ tailored measurement approaches aiming to link emissions to process parameters or performance indicators that can be monitored with less effort. With regard to inventory protocols, such established links would allow estimations of GHG emission intensity based on process data, replacing the current applied fixed and generic emission factors. In addition to this, application of full-scale quantification of GHG emissions will continue to be essential to identify emission sources and to verify the effectiveness of mitigation strategies. Analytical and methodological developments in this field should provide more accurate and resource friendly quantification approaches.

With regard to sewers, current available methods are not yet capable of capturing the complexity of these systems due to their geographical extension and highly varied conditions. However, the combination of measurements in selected hotspots with mathematical modelling of GHG production is a viable solution to obtain estimations of full-network emissions.

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NOMENCLATURE

∅	Diameter
AD	Anaerobic digester
Al	Aluminium
Ar	Argon
AS	Activated sludge
BAF	Biologically active (or aerated) filter
BNR	Biological nutrient removal
CFC	Closed flux chamber
CH ₄	Methane
DT	Disinfection tank
ET	Equalization tank
FTIR	Fourier transform infrared spectroscopy
GC	Grit chambers
HDPE	High density polyethylene
He	Helium
IPS	Influent pump station
NDIR	Non-dispersive infrared spectroscopy
N ₂ O	Nitrous oxide

OFC	Open flux chamber
P	Pressure
PE	Polyethylene
PN/A	Partial nitrification/anammox
PN	Partial nitrification
PP	Polypropylene
PVC	Polyvinyl chloride
SCT	Sludge concentration tank
SEIFC	Surface emission isolation flux chamber
SET	Settler
SST	Stainless steel
T	Temperature
WERF	Water Environment Research Foundation
UNFCCC	United Nations Framework Convention on Climate Change
U.S.EPA	United States Environmental Protection Agency
WWTP	Wastewater treatment plant

