



# TOWARDS A NEW PROTOCOL FOR FIELD MEASUREMENTS OF GREENHOUSE GASES FROM WASTEWATER TREATMENT PLANT

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**Abstract.** Emissions into the atmosphere of greenhouse gases (GHGs), i.e., carbon dioxide, methane and nitrous oxide from wastewater treatment plants are of increasing concern in the water industry. In order to produce useful and comparable information for monitoring, assessing and reporting GHG emissions from wastewater treatment plants, there is a crescent need for a general accepted methodology. This paper aims at proposing the first protocol for monitoring and accounting GHG emissions from wastewater treatment plants taking into account both direct and internal indirect emissions focusing on sections known to be major responsible of GHG emissions i.e. oxidation tanks and sludge digestion. The main novelties of the proposed protocol are: (i) direct and indirect internal emissions ascribed to aeration devices which are related each other, (ii) the monitoring of biogas composition in case of anaerobic digestion which affects GHG emissions offset due to biogas valorization systems and (iii) monitoring of non-aerated tanks.

## 1. Introduction

Greenhouse gas (GHGs) emissions from wastewater treatment plants (WWTPs), such as carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O), are of increasing concern in the water industry. Biological processes needed for wastewater treatment have been found responsible for the unintentional generation of GHGs. The quality and quantity of GHGs emitted from a WWTP can significantly vary with the wastewater composition, process configuration, and process control strategies employed. Further, significant efforts have been made in the last years for modelling such emissions. The development of reliable models rely also on the availability of field measurement for supporting the model concept and model calibration.

Throughout the last decade, several efforts have been done in the scientific world to establish protocols for monitoring and accounting N<sub>2</sub>O and CH<sub>4</sub> emissions from WWTPs. Different sampling and measuring techniques have been adopted to better understand GHG emission dynamics. On the basis of the existing protocols for quantifying GHG in other fields, some protocols based on emission factors were proposed (inter alia USEPA, 2007). Later, field measurements were indicated as a key element for improved GHG emission estimations based on site-specific operating parameters and processes (Chandran, 2011). In 2011, the Global Water Research Coalition (GWRC), published two reports (scientific and technical) on N<sub>2</sub>O and CH<sub>4</sub> emissions from WWTP as a result of an extensive monitoring study conducted on real WWTPs in Australia, France, USA and Netherlands, where different protocols for measuring GHG emissions were adopted (GWRC, 2011). In final instance, the Cities Climate Leadership Group and ICLEI Local Governments for Sustainability have proposed algorithms to quantify tN<sub>2</sub>O and CH<sub>4</sub> emissions at WWTP scale (Arikan et al., 2012). These algorithms contain specific plant information and measured data (such as measured volume of digester gas produced per day or measured total nitrogen discharged).

Despite the potentials of the existing resources available in literature for accounting GHG emission from WWTPs, there are still relevant differences between protocols, toolboxes and methods. While agencies and scholars have tried to converge towards standardized protocols to quantify and estimate GHG emissions from WWTPs, these differences reflect the fragmentation of research and regulation on a regional basis. Research, and consequently methodologies and tools, have been developed for specific regulatory needs of a country. In order to improve the usefulness of protocols, the harmonization of the regulatory framework among countries represents a critical need.

Within the research project “Energy consumption and GreenHouse Gas (GHG) emissions in the wastewater treatment plants: a decision support system for planning and management (<http://ghgfromwwtp.unipa.it>) supported by grant of the Italian Ministry of Education, University and Research (MIUR) through the Research Project of National Interest PRIN2012, it has been developed a comprehensive protocol for monitoring and accounting for direct and internal indirect GHG emissions related to treatment steps known to be major sources of GHGs in biological WWTPs. The main novelties of the proposed protocol are: the direct and indirect internal emission ascribed to aeration devices which are linked each other, the monitoring of biogas composition in case of anaerobic digestion which affect GHGs emission offset due to biogas valorization systems and monitoring of non-aerated tanks.

## **2. Classification of GHG emissions**

Focusing on WWTPs, several pathways and processes taking place both within and outside their boundary are responsible for GHG emissions which can be classified as direct, indirect internal and indirect external (Law et al., 2012). These three sources belong to the scopes established by the World Resources Institute and the World Business Council for Sustainable Development in the GHG Protocol Standard to classify emissions (Scope I, Scope II and Scope III, respectively). Direct emissions (also referred to as Scope I emissions) are those produced and discharged into the atmosphere within the WWTP boundary and one of their main contributors are biological processes and sections treating by-products of wastewater treatment (e.g. biogas produced from anaerobic sludge digestion). Indirect internal GHGs emission (also referred to as Scope II

emissions) is a consequence of activities that take place within the WWTPs' boundary, but occurs at sources owned or controlled by another entity. Indirect internal emissions are associated with the consumption of electrical power imported to supply electromechanical devices. Indirect external emissions (also referred to as Scope III emissions) are those related to sources not directly controlled inside the WWTP boundary (e.g. off-site sludge disposal, production of chemicals used in the process, third party transportation, etc.) and are typically excluded from carbon accounting since they are Scope I emissions for other parties.

## **2.1 Direct emissions**

Direct emissions can be substantially attributed to biological processes taking place in the plant for wastewater and sludge treatment and depends on both the production rate of GHGs and the mass transfer rate between the liquid and the gas phase.

Emission from WWTPs to the atmosphere can be classified as:

- volumetric emissions from aerated tanks;
- surface emissions from non-aerated tanks;
- point-source emission (e.g. chimney, biofilter, scrubber);
- diffused emissions and leakages (from pipes and fittings, incidental releases of gases, emission from building not equipped with vacuum system directing the drawn air to a point source emission such as biofilter or scrubber).

## **2.2 Indirect emissions**

WWTPs contribute to GHG emissions also through their energy consumptions required to supply electromechanical devices and buildings. In biological WWTPs energy demand is dominated by aeration that usually is responsible of 45-75% of the total energy consumption (WEF, 2009). Therefore, the monitoring and improvement of oxygen transfer efficiency (OTE) represents the key to minimize indirect internal emissions. However, in order to reduce overall GHG emissions, contribution of direct emission and indirect emission (linked to OTE) must be simultaneous. In fact, merely lowering DO and air flow rate may be beneficial to reduce energy consumption and thus indirect internal emissions, but concurrently can also promote higher production and stripping of N<sub>2</sub>O.

## **3. Proposed protocol**

Referring to Figure 1, the proposed protocol aims to set materials and methods for measuring /estimating the following contribution to GHG emission from WWTPs:

- direct emission of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O from aerated tanks (i.e. oxidation tank, aerobic stabilization tanks and membrane tank, this latter only in case of MBRs);
- direct emission from non-aerated tanks (denitrification, settlers);
- direct emission from biogas valorization or flaring systems (if present);
- indirect internal emission for aeration of both oxidation tank and aerobic stabilization tank.

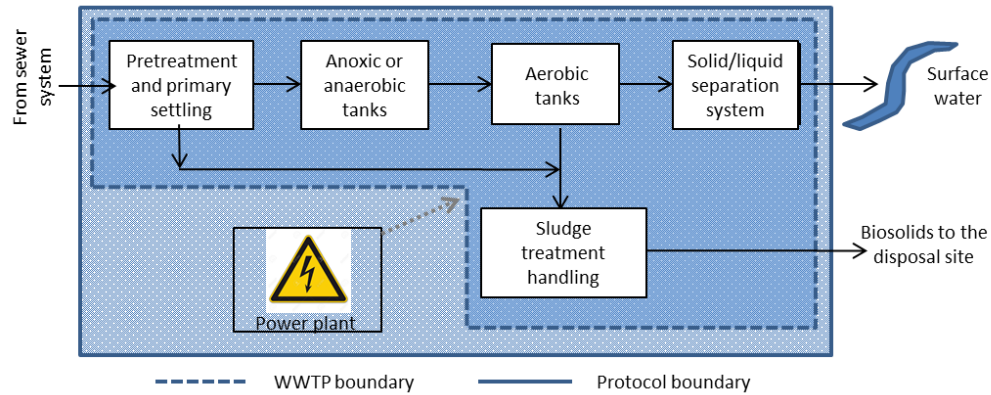


Figure 1. Protocol boundaries.

### 3.1 Estimation of indirect emission due to aerated tanks

The off-gas technique (Redmon et al., 1983) is proposed as method for estimating indirect GHG emissions from aerated tanks (oxidation tanks and aerobic stabilization tanks) using diffused air aeration systems. The layout of the proposed device suitable for such aim is represented in Figure 2.

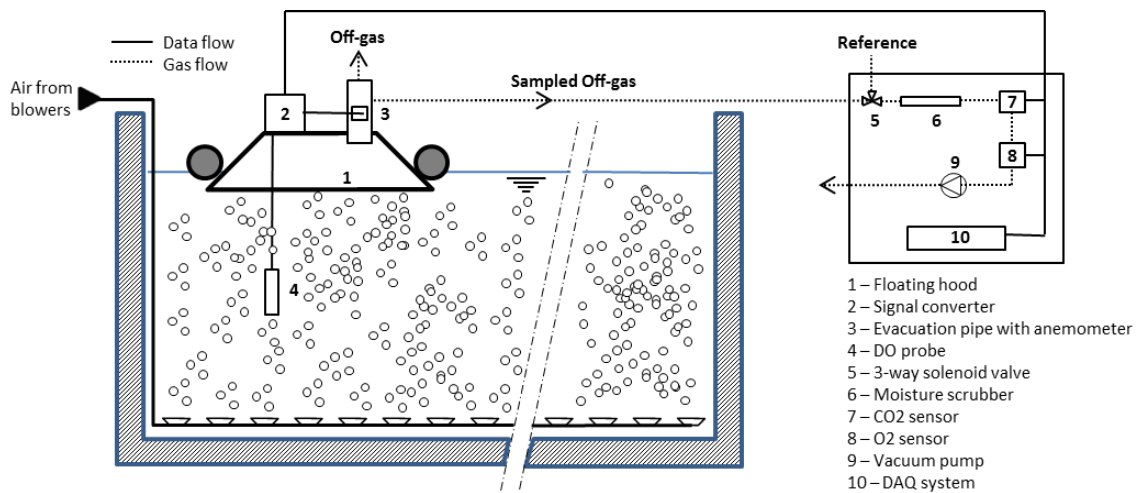


Figure 2. Schematic layout of the off-gas analyzer for measuring OTE in aerated tanks.

A floating hood with a cross-sectional area usually in the range 0,5-1 m<sup>2</sup> captures the off-gas leaving the tank surface and the flow rate ( $Q_{\text{measured}}$ ) is measured by an hot wire anemometer (TSI Air Velocity Transducer 8455 Series). Hoods with larger cross sectional area allow to reduce the points of measure but can pose problems for transportation while cross sectional area lower than 0.5 m<sup>2</sup> could emphasize differences in off-gas flow rate. The system is also equipped with a probe for measuring dissolved oxygen (DO) in the liquid phase (Thermo Scientific AquaSensors RDO Pro-X), required for correcting the OTE to standard conditions (i.e.  $\alpha\text{SOTE}$ ). A portion of 0,27 Nm<sup>3</sup>/h at the of the off-gas is sampled using a volumetric pump and the captured stream is sent to an off-gas analyzer equipped with a PVC column (h=0.255 m, d=0.025 m) filled with silica gel for moisture removal and

specific sensors for analyzing O<sub>2</sub> (Alphasense O2-C2 153600859) and CO<sub>2</sub> (Crestile instruments Model 7911) content. Through a three-way solenoid valve, also the atmospheric air, which we refer to as 'reference', is regularly analyzed and used for OTE calculation. The recorded data allow the calculation of the OTE (under process conditions) and in standard conditions for both new ( $\alpha$ SOTE) and used ( $\alpha$ FSOTE) diffusers (Gori et. al, 2014). The product  $\alpha F$  is the ratio of process to clean water mass transfer coefficients for used diffusers (dimensionless) where  $F = \alpha FSOTE / \alpha SOTE$  is the fouling factor (dimensionless). The estimation of  $F$  is only possible if  $\alpha SOTE$  is measured at the beginning of diffusers' operation. The factor  $F$  is of great concern for GHG emissions for two reasons: i) the erosion in aeration efficiency triggers an increase in air flow to supply the target oxygen delivery to the process, thereby increasing GHG stripping; ii) it makes possible accurate estimations of the increase in power consumption due to diffuser fouling and thus its contribution to the CFP of the plant due to indirect internal emissions.

### 3.1.1 *Materials and methods for sampling and detection*

Concerning the frequency of measurements for estimating OTE in aerated tanks of a WWTP, from 2 to 4 campaigns per year should be carried out in order to appreciate seasonal variations of phenomena affecting the transfer efficiency (i.e. temperature, wastewater characteristics, bower performances, etc.). Monitoring of aeration system efficiency should be carried out on regular basis in order to assess the decay rate of the devices' efficiency (e.g. fouling rate in case of diffusers).

Within a measurement campaign the floating hood is consecutively placed in several position according to a pre-defined sampling grid for monitoring the following parameters: oxygen carbon dioxide content in the off-gas, air flow rate, DO in the liquid phase, water temperature. At least 2% of the aerated tank surface have to covered by the floating device (ASCE, 1997), however it is considered good practice to exceed that value and typical tests are conducted sampling 3-6% of the total area.

Once the mapping of OTE and off-gas flow rate have been carried out, the floating hood is placed in a sampling point and the OTE and DO in the liquid phase are monitored with a frequency in the order of one measure every 20 minutes for a minimum of 24 h in order to appreciate diurnal variation. In case of multiple days monitoring it is preferable to include also weekend.

The mapping of off-gas flow rate over the tank is useful also for estimating the GHGs emission from aerated tanks (see paragraph 3.2).

### 3.1.2 *Assessment of contributions to GHGs' emissions*

The contribution of the aeration system to indirect internal emission of GHG can be calculated through its power demand, energy consumption and the carbon emission intensity for power generation  $k$  (i.e., specific GHG emission per unit energy produced expressed in terms of CO<sub>2</sub> equivalent, kgCO<sub>2,eq</sub>/kWh). In case the power demand and energy consumption of aeration systems is not monitored, it can be estimated using the characteristic curves of electromechanical devices involved in the aeration system (e.g., blowers) but only if air flow-rate is known.

If the air flow rate is not measured, the off-gas method can be used to measure the air flow supplied to the aeration system and its spatial variability, by measuring the air flow exiting the aerobic tanks. In particular, the measured air flow can be normalized for the area covered by the hood and extended in the proximity of each

measurement point so that the whole tank surface is virtually covered.

In case of aeration system using blowers, knowing air flow rate it is possible to derive the actual power ( $P_w$ ) used by blowers with the adiabatic compression formula (Tchobanoglous et al., 2003) and this latter can be used for the estimation of energy consumption and account the blowers contribution to indirect internal emissions:

$$\text{Internal indirect GHG emission (IIE)} \text{ [(kgCO}_{2,\text{eq}}/\text{d})] = \int k \cdot P_w \, dt \quad (8)$$

Depending on the location of the measurement are carried out, using the off-gas technique for monitoring OTE it is possible to estimate the internal indirect emission due to oxidation tank (IIE,OX) and aerobic stabilization tank (IIE,AS).

### **3.2 Estimation of direct emission from aerated tanks**

Estimation of direct emission from aerated tanks requires to monitor both off-gas flow rate and GHG concentration in the off-gas of aerated tanks. Since operating conditions (e.g. DO, COD/N ratio, ammonium concentration) are variable both in time and within process tanks also direct emissions of GHGs are expected to be variable as well. For this reason, unless aerated tanks are covered, the protocol suggest a simultaneous multi-point monitoring of aerated tanks using some floating hoods located in the tank (see Figure 5). Each floating hood is connected to an auto sampler device which automatically switch among different sampling points. The auto sampler is coupled to an instrument for online monitoring of GHGs concentration in the off-gas. In this way, for each floating hood the time profile of GHGs emission can be outlined.

The protocol suggests to locate one floating hood in proximity of the oxidation tank inlet in order to capture GHGs already present in the incoming stream (e.g.  $N_2O$  produced in pre-denitrification tank).

Concerning the measurement of the off-gas air flow rate which necessary to calculate the GHG emissions rate the protocol proposes to use results of the campaign carried out for monitoring previous OTE. It requires that locations of sampling points for estimating GHG emission rate must overlap those for measuring OTE

In case solid-liquid separation in AS systems occurs by means of a membrane (i.e., in MBRs), the additional direct GHG emissions due to the membrane cleaning can be relevant. The protocol proposed in this paper, suggests to separately perform off-gas tests on the membrane tank in order to properly assess its contribution to the overall emission from the WWTP (inter alia, Mannina et al., 2015; Mannina et al., 2016).

#### **3.2.1 Materials and methods for sampling and detection**

GHGs emission from WWTPs is variable over time both on the short term (on an hourly and daily basis) and on the long term (on a seasonal basis and from one year to the next). GHGs emission is variable within process tanks as well, due to variability of both off-gas flow rate and/or GHGs production in the liquid phase.

It is therefore expected that the sampling strategy will influence the emission estimation from such a dynamic process. For example, in the case of  $N_2O$ , whose dynamic is probably the most critical among the three GHGs of interest, the influence of the sampling strategy on the estimation of emissions was deeply discussed by Daelman et al. (2013).

The protocol suggests to carry out from 2 to 4 campaigns per year in order to cover the entire temperature

range that can possibly be encountered and appreciate seasonal variations of phenomena affecting the GHGs emission. Within the single campaign the protocol suggest to adopt an online and high-frequency measurement (in the order of one measure every 10-20 minutes) monitoring of GHGs concentration in the off-gas for a minimum of 24 h up (in order to appreciate diurnal variation) to one week. In case of multiple days monitoring it is preferable to include also weekend samples which contribute significantly to increase the GHGs' emission estimation accuracy (Daelman et al. 2013).

Regarding GHGs techniques for online detection and measuring of GHGs, literature contains a wide range of examples. The protocol suggest the use of the IR analyzer due to its high measurement accuracy and the ease of operation. For example the IR Multi-gas Monitor model 1312/5 (Innova Air Tech Instrument, Airnova, Padua, Italy) detects the concentrations of gas mixtures with a limit of detection of 0.03 ppmv for N<sub>2</sub>O, 0.4 ppmv for CH<sub>4</sub> and 1.5 ppmv for CO<sub>2</sub> at 20°C and 1 atm with a measurement frequency up to 1/80 s. Compensation is provided for temperature fluctuations and water vapor interference, but also other gases known to potentially bias the measurements can be taken into account. However, the elevated concentrations of water vapor that occur in the off-gas leaving a treatment facility tank can still bias the reading and a specific moisture filter needs to be used (e.g silica gel).

The protocol suggests to couple the instrument for GHGs detection (IR or micro-GC) with an auto-sampler thus allowing to continuously and contemporarily monitor several locations within process tanks.

### **3.2.2 Assessment of contributions to GHGs' emissions**

For each GHG, partial pressure registered using online monitoring devices, can be converted to mass flow rate through the product of the concentration and the volumetric gas flow rate. The following emission will be determined depending on the location where the measures are carried out: direct emission of CO<sub>2</sub> (indicated as DE-CO<sub>2,OX</sub> in case of oxidation tanks and DE-CO<sub>2,AS</sub> in case of aerobic stabilization tank); direct emission of CH<sub>4</sub> (indicated as DE-CH<sub>4,OX</sub> in case of oxidation tanks and DE-CH<sub>4,AS</sub> in case of aerobic stabilization tank); direct emission of N<sub>2</sub>O (indicated as DE-N<sub>2O,OX</sub> in case of oxidation tanks and DE-N<sub>2O,AS</sub> in case of aerobic stabilization tank).

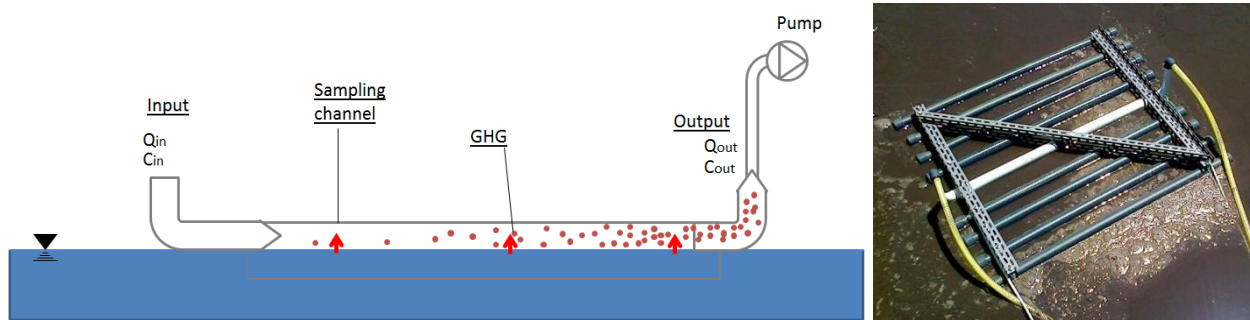
### **3.3 Estimation of direct emission from non-aerated tanks**

The proposed protocol allows also to assess emissions in the case of non-aerated tank emissions by both production inside the tank and wind velocity on the surface. The protocol proposes to assess GHG emissions using a sweeping flux that promotes GHG emissions. It is worth notice that the measured emission is representative only of the condition imposed with the sweeping flux and is not representative in general for all environmental conditions because air velocity on the tank surface is continuously variable with time.

For open non-aerated tanks it was designed a new hood equipped with 8 floats and a central channel open at the bottom in which the sample is guided to flow from one side to the other (Figure 3).

The sampling channel is open at both sides and connected with two hoses. The input hose is open to the atmosphere and must be placed far from the tank surface. The output hose is connected to a vacuum pump with adjustable flow which allow to impose a gas velocity on the surface within the sampling tube. The pump to be used should have a finely adjustable flow and be robust in its function since the flow used to sample is of crucial

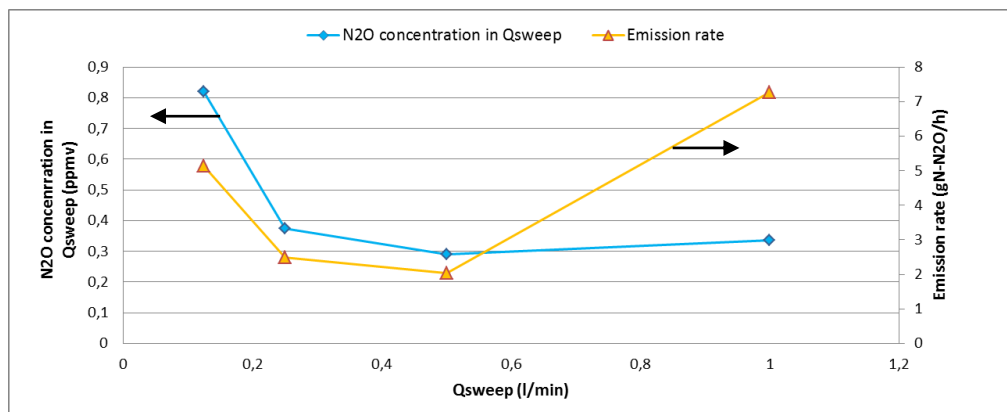
importance in the calculation of the emission flux (e.g. GilAir Plus, 1 - 5000 cc/min, Gilian).



**Figure 3.** Schematic of the working principle of the hood for non-aerated zones

With respect to the off-gas hood, the hood for non-aerated zones covers a much lower surface and sampling from a representative area will take a sensibly longer time. However, the restricted area is a must in order to achieve a renewable sample in a reasonable amount of time even in zones where emissions are very low.

Figure 4 shows results obtained testing the method in the denitrification tank of the plant managed by Cuoiodepur SpA which treats tannery wastewater and urban wastewater. Results show that the  $N_2O$ -N concentration decrease as the  $Q_{sweep}$  increase and at  $Q_{sweep}$  of 500 and 1000 cc/min is approximately the same. Instead, the emission rate, has a minimum for  $Q_{sweep}$  of 500 cc/min and has the highest value with the highest  $Q_{sweep}$ .



**Figure 4.** Trends of  $N-N_2O$  concentration and emission rate vs  $Q_{sweep}$

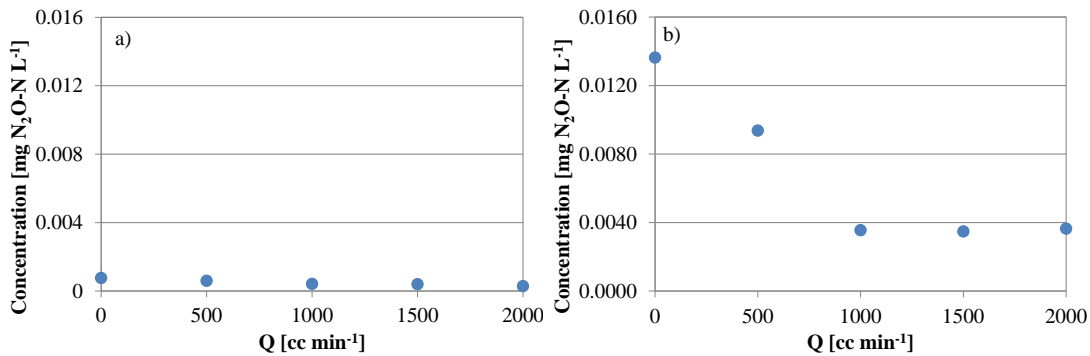
In case of covered non-aerated tanks, a sweeping flow can be applied in the headspace in order to promote GHG emissions. This method was tested on a Membrane Bioreactor pilot plant with a University Cape Town (UCT) configuration equipped with three reactors: anaerobic (volume 62 L), anoxic (volume 102 L) and aerobic (volume 211 L). The solid-liquid separation occurred by means of an ultrafiltration hollow fiber membrane module (PURON®) located inside an aerated tank (36 L). An oxygen depletion reactor allowed the oxygen stripping in



the mixed liquor recycled from the MBR tank to the anoxic one. All the tanks were completely covered equipped with holes for sampling and measurement of air flow rate (Mannina et al., 2015; 2016).

The test was used to evaluate the effect of the sweep air on the  $N_2O$ -N concentration measured in the headspace of the anoxic zone. Indeed, as discussed in literature the mixing gained by the sweep air ensures the collection of a representative gas concentration (Chandran, 2011). Furthermore, the influence of different influent COD/N ratio on the  $N_2O$ -N emission during the denitrification process was also investigated. More precisely, the experimental campaign was carried out according to two main phase: i. COD/N ratio equal to 9.6 ; ii. COD/N ratio equal to 2.6. The main wastewater features as well as operational conditions for each phase can be found in literature (Mannina et al., 2015; 2016).

During the two phases of the experimental campaign, the gas was collected by promoting the gas mixing with sweep air at different flow rate ( $Q_{sweep}$ ). The sampling frequency was established on the basis of the time required for the saturation of the headspace volume. Figure 5 shows the results of  $N_2O$ -N concentration measured at different  $Q_{sweep}$  referring for each phase.



**Figure 5.**  $N_2O$ -N concentration at different  $Q_{sweep}$  for COD/N ratio of 9.8 (a) and 2.6 (b)

By analyzing Figure 5 one can observe that the  $N_2O$ -N concentration (on average) was 1 order of magnitude higher when COD/N was reduced to 2.6, in detail 0.0005 and 0.007 mg  $N_2O$ -N L<sup>-1</sup> were found, respectively for 2.6 and 9.8 COD/N ratio. Such differences should confirm the impact that low COD/N ratio exerts on  $N_2O$  production. Indeed, several studies report similar results. For example, Itokawa et al. (2001) found that when COD/N ratio was below 3.5, nitrous oxide emitted was up to 20-30% of the nitrogen load.

It is worth notice that both in phase 1 and in phase 2, the sweep air induce the same dilution effect, indeed the  $N_2O$ -N concentration at 1000 cc/min was in both cases around the 30% of that at  $Q_{sweep}$  null. At  $Q_{sweep}$  higher than 1000 cc/min the  $N_2O$ -N concentration kept on almost the same value (Figure 5).

### 3.3.1 Assessment of contributions to GHGs' emissions

For each monitored GHG, partial pressure registered using online monitoring devices, can be converted to mass flow rate through the product of the concentration and the volumetric gas flow rate. The following emission will be determined depending on where the measures are carried out. In the calculation of total emission the following symbol will be used for emission from non-aerated tanks: DE-CO<sub>2,NA</sub> for direct emission of CO<sub>2</sub>, DE-CH<sub>4,NA</sub> for direct emission of CH<sub>4</sub> and DE-N<sub>2</sub>O<sub>NA</sub> for direct emission of N<sub>2</sub>O.

### **3.4 Monitoring of liquid phase during the estimation of GHGs emission**

The protocol also set that the monitoring of both direct and indirect GHGs emissions should be accompanied by a monitoring activity carried out on the liquid phase of the investigated tanks.

During the off gas test campaign, the quality of the treated effluent must be monitored. At the inlet and at the outlet of the oxidation tank the concentrations of organic and nitrogen should be assessed. In order to correlate the OTE and the aeration energy consumption, with the overall WWTP performance, the daily average hourly data of the WWTP inlet and outlet should be also assessed.

During the monitoring of the GHGs produced by the denitrification and nitrification tanks, analyses in the liquid phase should be performed in order to carry out the correct mass balance of the gases monitored (see Table 3).

### **3.5 Estimation of GHGs' direct emission from biogas combustion**

With regard to GHG emissions, the presence of H<sub>2</sub> in the biogas is known to be responsible for a higher NO<sub>x</sub> production in the exhausts fumes from the process of biogas conversion to energy. This happens due to an increase of the combustion temperature in the co-generator engine (Park et al., 2011). Therefore, when the biogas combustion takes place within a WWTP, it is strongly suggested to monitor H<sub>2</sub> levels in the biogas, not only to control the state of the anaerobic reactors, but also to prevent potential GHG emissions. Thus, monitoring the biogas composition as well as the biomethane potential (BMP) of the excess sludge (produced by a WWTP) has the advantage of controlling the good behavior of the anaerobic treatment and of assessing the environmental impact of the WWTP in terms of GHG emissions.

In order to estimate direct GHGs emission due to biogas combustion the protocol suggest to measured: BMP of the sludge, percent composition of the biogas to optimize the power production with particular reference to the CH<sub>4</sub>/CO<sub>2</sub> ratio, percentage of H<sub>2</sub> present in the biogas.

In this paper a procedure for the simultaneous detection of H<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub> is presented. Concerning the BMP tests the procedure proposed by Esposito et al. (2012) is suggested.

#### **3.5.1 Materials and methods for sampling and detection**

Monitoring the biogas composition of anaerobic digesters can be carried out using both online and offline sampling. The following techniques can be used for online measurements:

- biogas IR sensors;
- GC-TCD with the gas line connected to the loop and auto-inject function.

The main advantage of online measurements is the possibility to perform continuous monitoring of the process. On the other hand, depending of the technology available, less sensitivity is granted mostly for the H<sub>2</sub> detection. In fact, in the process balance the H<sub>2</sub> indicator could appear only in very low concentrations.

The chromatographic analysis usually requires the installation of at least two instruments (a GC-FID and a GC-TCD/ECD), that operate in different conditions and operate separately for the analysis of CO<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub> respectively. A number of configurations are possible and standardized methods propose the use of different capillary columns and detectors (FID, ECD, TCD, PID) depending on the analytes and the relative concentrations (TangMeng, 2002).

The protocol suggests the use of GC-TCD technique which allows the determination of H<sub>2</sub> as low as 0.05% in the biogas sample.

A 2 m x 1 mm ID micropacked column containing ShinCarbon ST can be used to separate the permanent gases in 10-15 minutes, without cryogenic cooling. Restek's ShinCarbon ST 80/100 mesh is a high surface area carbon molecular sieve (~1500 m<sup>2</sup>/g) which is an ideal medium for separating gases by Gas-Solid Chromatography (GSC).

Normally, the suggested carrier gas for gas analysis is Helium (He), since it is the ideal carrier to enhance sensitivity for most gases given that the TCD detector measures the difference in conductivity between the sample channel and a reference channel where only pure carrier gas flows. However, the He has a conductivity very similar to H<sub>2</sub>, resulting in very low sensitivity for H<sub>2</sub> detection. Also, by using He as carrier, the instrument becomes a bit less sensitive against CO<sub>2</sub>. Being the CO<sub>2</sub> concentration in the biogas samples around 30 to 70% there is no need of high sensitivity for this compound. On the other hand, high sensitivity is essential for H<sub>2</sub> analysis since it is present in much lower concentration (2% maximum). The GC-TCD should be equipped with 400 µL sample loop. The Ar carrier gas pressure should be set at 30 psi in both front and rear reference column. The injector should be set at 50°C and the detector at 120°C.

The described technique could also be used in continuous online mode by collecting the biogas line to the injection loop. An automated system injects the sample each 20 minutes giving in this way a very precise and sensitive response of biogas composition.

### 3.5.2 Assessment of contributions to GHGs' emissions

For each monitored GHG, partial pressure registered using online or offline monitoring devices, can be converted to mass flow rate through the product of the concentration and the volumetric gas flow rate. The following emission will be determined depending on where the measures are carried out:

- direct emission of CO<sub>2</sub> from biogas valorization/flaring: DE-CO<sub>2,BV</sub>;
- direct emission of CH<sub>4</sub> from biogas valorization/flaring: DE-CH<sub>4,BV</sub>.

Monitoring of the biogas composition allows also to calculate a reliable CO<sub>2,eq offset</sub> due to energy recovery from biogas which is proportional to the biogas produced and biogas composition:

$$mCO_{2,eq\ offset} [kgCO_{2,eq}/d] = h_{ER} \cdot h_{BG} \cdot m_{BG} \cdot k$$

where  $h_{ER}$  is the efficiency of the energy recovery unit (-) that can be obtained from field measurement or technical sheet,  $h_{BG}$  is the calorific value of the biogas (kJ/kg<sub>biogas</sub>) which can be calculated from measured CH<sub>4</sub> content of biogas,  $m_{BG}$  is the mass of biogas from field measurement and  $k$  is the local carbon emission intensity for power generation (kgCO<sub>2,eq</sub>/kWh) in the region where the treatment plant is located.

Here we assume that 100% of the CH<sub>4</sub> entering the combustion chamber is fully combusted to CO<sub>2</sub>. The combustion gas can be analyzed in order to assess the real CH<sub>4</sub> oxidation efficiency during combustion.

## 4. Accounting of total GHGs emission and carbon footprint

To determine the total carbon footprint (CFP), all sources must be converted to CO<sub>2,eq</sub> multiplying emission of

N<sub>2</sub>O and CH<sub>4</sub> times their respective GWP (i.e 298 and 25 respectively, IPCC, 2006).

In case of WWTPs with aerobic stabilization, the total CFP can be calculated as follows:

$$\text{Total CFP} = \text{DE-CO}_{2,\text{OX}} + \text{DE-CO}_{2,\text{NA}} + \text{DE-CO}_{2,\text{AS}} + 25 \cdot (\text{DE-CH}_{4,\text{OX}} + \text{DE-CO}_{2,\text{NA}} + \text{DE-CH}_{4,\text{AS}}) + 298 \cdot (\text{DE-N}_{2\text{O},\text{OX}} + \text{DE-N}_{2\text{O},\text{NA}} + \text{DE-N}_{2\text{O},\text{AS}}) + \text{IIE}_{\text{OX}} + \text{IIE}_{\text{AS}}$$

In case of WWTPs with anaerobic stabilization of sludge and biogas valorization system, the total CFP can be calculated as follows:

$$\text{Total CFP} = \text{DE-CO}_{2,\text{OX}} + \text{DE-CO}_{2,\text{NA}} + \text{DE-CO}_{2,\text{BV}} + 25 \cdot (\text{DE-CH}_{4,\text{OX}} + \text{DE-CO}_{2,\text{NA}} + \text{DE-CH}_{4,\text{BV}}) + 298 \cdot (\text{DE-N}_{2\text{O},\text{OX}} + \text{DE-N}_{2\text{O},\text{NA}} + \text{DE-N}_{2\text{O},\text{BV}}) + \text{IIE}_{\text{OX}} + \text{IIE}_{\text{AS}} - m\text{CO}_{2,\text{eq offset}}$$

## 5. Conclusions

Due to the growing awareness on climate change there is a need to quantify greenhouse gases (GHG) from different sources and some governments started to implement regulations that force water authorities to report their GHG emissions.

Throughout the last decade, several efforts have been done in the scientific world to establish protocols for monitoring and accounting N<sub>2</sub>O and CH<sub>4</sub> emissions from WWTPs. Despite the potentials of the existing resources available in literature for accounting GHG emission from WWTPs, there are still relevant differences between protocols, toolboxes and methods. In this paper it has been developed a comprehensive protocol for monitoring and accounting for direct and internal indirect GHG emissions related to treatment steps known to be major sources of GHGs in biological WWTPs. The main novelties of the proposed protocol are: the direct and indirect internal emission ascribed to aeration devices which are linked each other, the monitoring of biogas composition in case of anaerobic digestion which affect GHGs emission offset due to biogas valorization systems and monitoring of non-aerated tanks.

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