TOWARDS A REDUCTION OF GREENHOUSE GAS EMISSION FROM WASTEWATER TREATMENT PLANTS: A NEW PLANT WIDE EXPERIMENTAL AND MODELLING APPROACH

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Abstract. The increasing interest in greenhouse gas (GHG) emissions from wastewater treatment plants (WWTPs) has led to the development of new tools for their design and management. Studies about gas emissions show that the sewer collection and the wastewater treatment plant are anthropogenic GHG potential sources, so they contribute to the climate change and air pollution. A wastewater treatment plant receives wastewater from sewers and, while produces treated water for discharge into surface water, emits the three major greenhouse gases, CO_2, CH_4, and N_2O, during the treatment processes, and additional amounts of CO_2 and CH_4 from the energy demands (Bani Shahabadi et al., 2009). Indeed, energy consumption can be considered as an indirect source of GHGs. Greenhouse-gas emissions are generated by water-line and sludge-line processes and by the on-site combustion of biogas and fossil fuels for energy generation. GHGs may also be produced during sludge disposal or reuse (transportation and degradation of remaining biosolids off-site), off-site energy production and off-site chemicals production. In recent years, increasing attention is given to the assessment of N_2O emissions from WWTPs. N_2O is a powerful greenhouse gas that is almost 300 times stronger than CO_2. Nevertheless, the source and magnitude of N_2O are relatively unknown and the knowledge is still incomplete. This paper presents the first results of an ongoing research project aiming at setting-up an innovative mathematical model platform (Decision Support System—DSS) for the design and management of WWTPs. The project is constituted by four research units (UOs) and its final goal is to minimize, by means of this platform, the environmental impact of WWTPs through their optimization in terms of energy consumptions and pollutants, sludge and GHG emissions.

1. Introduction

The research developed so far on the evaluation of GHG emissions from WWTPs is fragmented and can be subdivided into two types: experimental and modelling (Bani Shahabadi et al., 2009). The experimental investigations have been focused on both the development of measurement techniques and acquisition of GHG data, which are used in order to understand the mechanisms of formation and emission of these gases (Ahn et al., 2010).

Despite the efforts undertaken so far at the international level, from an in-depth literature review on the project main field, it comes out that there are some important aspects that require further studies. In particular, there is the lack of criteria for the design and management of WWTPs through integrated approaches that include GHGs. Moreover, the absence of extensive data base of measures of GHGs in terms of both temporal and spatial distribution (i.e., acquired on different WWTPs), for encoding GHG behaviour in the yield process and also for assessing the GHG temporal variability during the year, can be observed in the literature. These extensive databases are also essential for the development and application of robust and reliable mathematical models. Other important issues that need to be investigated concern: the lack of standard protocols for measuring emissions, that can allow the comparison of the data obtained in various WWTPs; the identification of appropriate mitigation measures, which are based on process control, aimed at reducing GHG emissions; the evaluation of the modelling uncertainty in order to quantify the potential error in the information "predicted" through the models and the development of models that are characterized by combined (i.e., complex and simplified) approaches.

Finally, N_2O emission from wastewater treatment plants (WWTPs) represents a frontier of Research that still requires to be crossed. N_2O emissions primarily occur in aerated zones owing to the fact that the main contributors are active stripping and ammonia-oxidizing bacteria, rather than heterotrophic denitrifiers. Indeed, despite during the last years efforts have been done to better understand the key elements on the N_2O production/modelling, several questions remain scarcely understood (Caniani et al., 2015). In terms of process knowledge, several studies have been performed to identify the key operating factors or the influent features mostly affecting the N_2O production (Stenström et al., 2014; Wu et al., 2014). However, these studies have been mainly performed on conventional activated sludge (CAS) systems. Therefore, the results are difficult to be transferred into the behaviour WWTP where advantage technology is applied (e.g., membrane bioreactors – MBR, or moving bed biofilm reactors – MBBR). In terms of N_2O modelling, the use of plant-wide mechanistic dynamic models versus the model complexity still represent a controversial research topic (Mannina et al., 2016a).

In this paper, we present the key methodological features and the preliminary results of an ongoing project aiming at developing an innovative simulation platform for the design and management of WWTPs. Such a platform is aimed at reducing the energy consumption and pollutant/residue emissions (namely, residual pollutants in the effluent, sludge and GHGs). The main objective of the project is the development of a decision support system that will allow reducing GHGs as well as other emissions from WWTPs.

2. Description of the research project

The activities and the results presented here belong to the project "Energy consumption of GreenHouse Gas

(GHG) emissions in wastewater treatment plants: a decision support system for planning and management", which is supported by grant of the Italian Ministry of Education, University and Research (MIUR), and, started in 2014 and will end in 2017. The main aim of developing an innovative mathematical platform (Decision Support System—DSS) for the design and management of WWTPs will be achieved by performing experimental and modelling activities (Caniani et al., 2015).

The aim of experimental activities is to identify design and operational variables that have an important role both in energy consumption and GHG production, while maintaining an high quality of liquid effluents as required by the Water Framework Directive 2000/60/EC. Furthermore, from the modelling point of view, the project aims at setting up, for each specific treatment unit that take place in both water and sludge line, a detailed and a simplified mathematical model that is able to describe, under dynamic conditions, the main physical/chemical/biological processes including GHGs emissions occurring in a WWTP. Complex and simplified mathematical models will then be integrated to set up a DSS. Both single treatment units and their interactions are being analysed. Particular care is dedicated to the energy consumptions and emissions. A specific protocol for assessing the emissions from the different treatment units has been set up (Gori et al., 2015). An innovative mathematical model platform for the design and management of WWTPs is going to be set up (Figure 1) to achieve the main goal of the project. As shown in Figure 1, the decision support system will be implemented by using the results of the simple (inner circle of Figure 1) and detailed modelling (outer circle of Figure 1) of the biological processes.
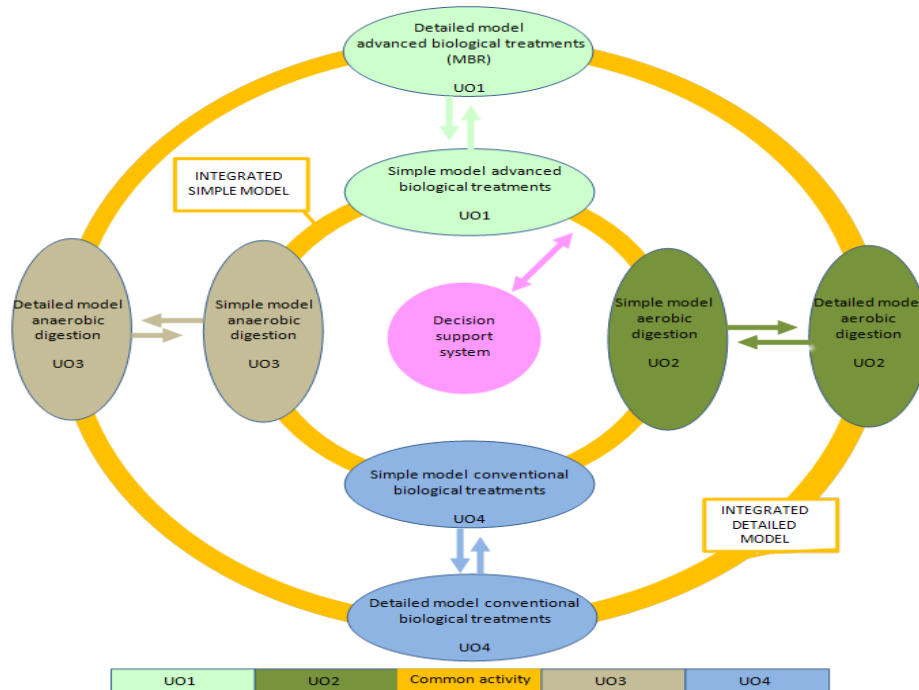

Figure 1. *Integrated model layout of the WWTP with indication of the contribution provided by each research unit (UO) (Caniani et al., 2015).*

2.1. Activities of the Research Units

Four research units (UOs) are working on the: University of Palermo (UO1), University of Basilicata (UO2), University of Cassino and Southern Lazio (UO3) and University of Florence (UO4).

In detail, the objective of UO1 is the study of the chemical/physical/biological phenomena of the water line of the advanced wastewater treatment systems, through designing, building and operating an MBR plant at pilot scale aimed at removing nutrients. The pilot plant is monitored in order to analyse the influence of wastewater compositions (domestic and industrial), operative conditions (*i.e.*, sludge age, hydraulic retention time, *etc.*) and pilot plant configurations (Denitrification-Nitrification-MBR; UCT-MBR; moving bed biofilm reactor—MBR; *etc.*) for GHG emissions. A complex mathematical model, based on the Activated Sludge Model (ASM), has been implemented in order to properly simulate biological process as well as physical phenomena. Furthermore, the UO1 will also implement empirical simplified models that should be characterized by a good reliability and an easier implementation.

The UO2 has designed, built and operated a pilot scale plant in order to deepen the chemical/physical/biological phenomena of thickening and aerobic digestion more effectively. A monitoring campaign of the qualitative and quantitative characteristics of the sludge and operating parameters of a full-scale treatment plant is also in progress. Data gathered from experimental activities are collected in a database in order to increase knowledge concerning the influence of management parameters on GHG emissions from aerobic treatment of sludge and to develop and calibrate an ASM type model.

The UO3 has linked the operative conditions of the anaerobic digestion (sludge age, sludge concentration, retention time) and the quality of the reactors feed, to the biogas production, energy recovery and GHGs emission. The UO3 gives essential information for operating the wastewater treatment line which greatly affects the quality of the anaerobic digestion feed and, in turn, affects the biogas and methane production and thus the GHGs emission of WWTPs. Activities of the UO3 are carried through both experimental and modelling approaches. Data gathered from experimental activities are collected for setting up a database in order to increase knowledge and develop models (both detailed and simplified) able to properly predict the observed phenomena.

The UO4 developed a detailed protocol for the measurement of oxygen transfer efficiency from processes units and for GHG measurement. This protocol has been proposed as a standard and is one of the results of the project. The has carried out experimental activities on both conventional and innovative plants, with particular attention to the influence of operative conditions on GHGs emissions.

3. Materials and Methods

3.1. Experimental activities

3.1.1. The pilot plant and the sampling campaign of UO1

An University Cape Town (UCT) membrane bioreactor (MBR) pilot plant was monitored according to two different configurations (I and II) (Figure 2).

Configuration II represents an integrated fixed film activated sludge (IFAS) MBR system. For both configurations, the pilot plant consisted of anaerobic (volume 62 L), anoxic (volume 102 L) and aerobic (volume 211 L) compartments according to the UCT scheme. The solid-liquid separation phase was achieved by means of an ultrafiltration hollow fibre membrane module (PURON® Triple bundle Demo Module; nominal pore size 0.03 μm, membrane area 1.4 m^2), located inside a dedicated aerated compartment (MBR tank, 36 L). An oxygen

depletion reactor (ODR) allowed oxygen removal in the mixed liquor recycled from the MBR tank to the anoxic tank (Q_{RAS}). The membrane was periodically backwashed (every 9 min for a period of 1 min) by pumping a volume of permeate back through the membrane fibres from the Clean In Place (CIP) tank. During the II configuration operation the anoxic and aerobic compartments were filled with suspended carriers (Amitech s.r.l.) with a 15 and 40% filling fraction respectively, corresponding to a net surface area of 75 and 205 m^2 m^{-3}, respectively. For both configurations, the influent flow rate was set equal to 20 L h^{-1} (Q_{IN}).The anaerobic, anoxic, aerobic and MBR reactors were equipped with specific covers that guaranteed gas accumulation in the headspace to perform the gas sampling. The pilot plant was monitored for 100 days according to the configuration I and for 251 days according to the configuration II. During the operation of the configuration I the influence of the C/N ratio (C/N = 10 and C/N = 5) on the N_2O emission and on the plant performance was investigated (Mannina et al., 2016b). During the operation of the configuration II the influence of several operating conditions and influent features on the N_2O emission and on the plant performance was investigated. More specifically the following operating conditions were investigated: C/N ratio (C/N = 10, C/N = 5 and C/N = 2.5); sludge retention time (SRT) (SRT = indefinite; SRT = 30 days; SRT = 15 days) and the air flow rate for membrane fouling mitigation. During the pilot plant operation (for both configurations) samples were withdrawn in order to analyse the performance of the system in terms of COD, N and P removal. Furthermore, nitrous oxide (N_2O) dissolved in the liquid phase and in the gas samples was analysed. N_2O concentration was measured by using a Gas Chromatograph (Thermo Scientific™ TRACE GC) equipped with an Electron Capture Detector.
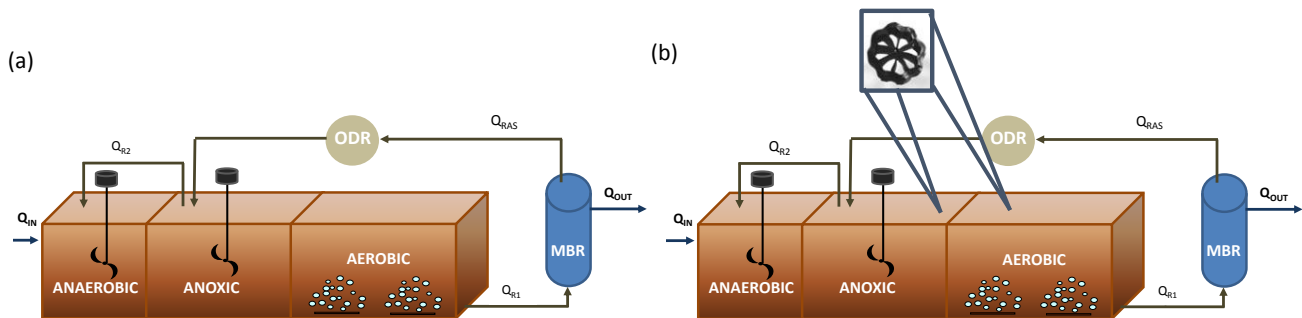

Figure 2. *Layout of the UCT-MBR pilot plant according to the configuration I (a) and configuration II (b). Where: Q_{IN} = influent wastewater; Q_{R2} = mixed liquor recycled from the anoxic to the anaerobic tank; Q_{R1} = mixed liquor recycled from the aerobic to the MBR tank; Q_{RAS} = Recycled sludge from the MBR to the anoxic tank; Q_{OUT} = effluent permeate flow rate; ODR = Oxygen Depletion Reactor.*

3.1.2. The pilot plant and the full scale sampling campaign of UO2

Figure 3 shows a simplified drawing of the pilot apparatus used for the aerobic digestion experimentation, which was a cylindrical aerated tank connected to the off-gas apparatus.

A 10L reinforced polyethylene tank was equipped with an aeration system, supplying an air flow rate of 0.05 m^3h^{-1}. Furthermore, a mixer was introduced to avoid the settling of sludge particles and, at the same time, to ensure a well - mixed system without anoxic dead zones during aeration periods.
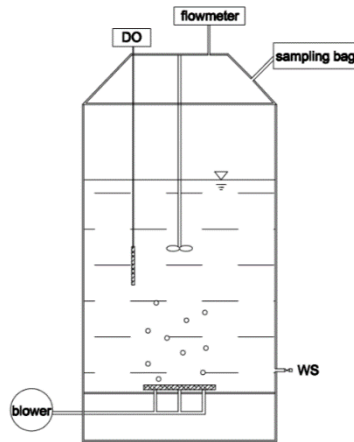
Figure 3. *Simplified drawing of the pilot apparatus (DO=Dissolved Oxygen; WS=Wasted Sludge)*

The pilot digester was firstly fed with 6L of activated sludge from the secondary settler underflow of a full-scale WWTP and, subsequently, 0.06L of the same sludge were introduced for each testing day to compensate the same discharged amount. A 30-days monitoring campaign was carried out. The first ten days were dedicated to reaching the equilibrium conditions for a conventional aerobic digestion and the remained days to complete the process, assuming 20 days as sludge retention time (SRT).

In order to monitor the performance of the pilot digester, analysis of the influent and discharged sludge were performed, regarding the concentration of chemical oxygen demand (COD), total suspended solids (TSS), volatile suspended solids (VSS), ammonium (NH_4^+), nitrites ($N-NO_2^-$), and nitrates ($N-NO_3^-$). Table 1 shows the results of these analysis, reporting an average value of the the values of influent and discharged sludge characteristics at the beginning and at the end of the digestion process, respectively.

Table 1. *Sludge characteristics (all values are expressed in mg/l)*

	COD	TSS	VSS	NH_4^+	$N-NO_2^-$	$N-NO_3^-$
Influent sludge at first day test	6,141.2	10,720	8,2	2.3	1.1	132.9
Discharged sludge after 20 days	5,130.5	6,780	4,045	3.0	1.8	277.5

A 50.9 percent decreasing in VSS concentration and a 36.7 percent decreasing in TSS concentration were observed, respectively, after 20 days, which are values closer to the literature range for well performed systems (38 - 50 per cent in VSS and 30 - 50 per cent in TSS, Metcalf and Eddy, 2003).

Furthermore, knowing that the quantity of produced GHG mainly depends on the characteristics of the incoming wastewater, analysis on the wastewater influent in the reference full - scale plant were performed.

The monitoring of the aerobic digestion (AeD) of a full scale WWTP was also carried out. The municipal WWTP under study is located in a small village in Southern Italy and serves 15,000 population equivalents (with a wastewater flow of approximately 3,750 $m^3 d^{-1}$) and treats organic matter and nitrogen with a Modified Ludzak-Ettinger (MLE) configuration. The off-gas measurements were performed during a monitoring campaign lasted

for three-days.

Analyses of influent and effluent, regarding the concentrations of chemical oxygen demand (COD), total suspended solids (TSS), ammonium (NH_4^+), nitrites (NO_2^-) and nitrates (NO_3^-) were performed on the days of testing.

Both the aerobic bioreactor and AeD were monitored using the off-gas technique described in the following section 2.1.4 in order to evaluate aeration efficiency and CO_2 and N_2O emissions.

Analyses of the influent and effluent of the oxidation tank were necessary in order to investigate treatment efficiency and GHG emissions. Therefore, the concentration of chemical oxygen demand (COD), ammonium (NH_4^+), nitrites (NO_2^-) and, nitrates (NO_3^-) were measured on the day of off-gas test (Day 1) as summarized in Table 2.

Table 2. *Characteristics of the influent and effluent from the oxidation tank.*

tests		2:00 PM	3:00 PM	4:00 PM
Total COD (mg/l)	influent	675	1448	2051
	effluent	9420	10220	11860
Total COD (mg/l)	influent	82	180	202
	effluent	231	91	281
TSS (mg/l)	influent	366	1230	1640
	effluent	10140	9680	8600
NH4+ (mg/l)	influent	55.62	44.95	50.74
	effluent	34.46	35.9	43.51
N-NO3- (mg/l)	influent	0.86	0.27	0.01
	effluent	0.2	0.36	0.003
N-NO2- (mg/l)	influent	0	0	0.1
	effluent	0	0	0

Regarding the AeD, due to the presence of surface aerators, only the GHG emissions were monitored, without measuring the aeration efficiency.
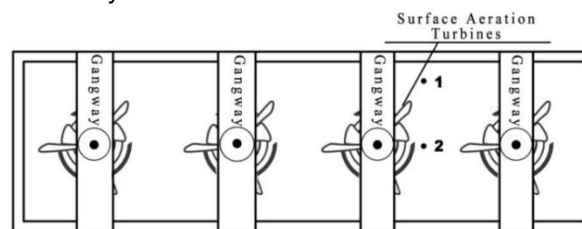

Figure 1. *Sampling points of the aerobic digestion tank*

The off-gas hood was used to collect the exhaust gas in the hood headspace but due to the presence of surface aeration, there was no relevant off-gas flow rate leaving the liquid surface and was impossible to collect

gas samples immediately. Therefore, the floating hood was positioned in one location with all available connections closed except one that was connected with a Teflon tube. In order to measure the relative pressure increase (ΔP as increasing in water height in the tube, mm) inside the hood, and thus the relative flux of the gases leaving the liquid volume, a portion of the Teflon tube, with a diameter d of 3 mm, was siphon shaped and filled with water.

3.1.3. Batch tests and measures conducted by UO3

Different sludge types, collected from several CAS (Conventional Activated sludge) and MBR real scale treatment plants, were concentrated by settling for two hours. After this time, the supernatant was discharged and the thickened sludges were therefore characterized by gravimetry in terms of TS-VS according to EPA standard Methods (1684). Once thickened aliquots of each sludge were subjected to the extracellular polymeric substances (EPS) extraction as described by Frølund et al. (1996). Dowex marathon C (Sigma-Aldrich) was chosen as Cation Exchange Resin (CER). Once extracted, the EPS composition was defined in terms of Carbohydrate (CH) (Dubois et al., 1956), Uronic acids (UA) (Blumenkrantz & Asboe-Hansen, 1973; Kintner III & Van Buren, 1982), Proteins (PR) (Lowry et al., 1951) and humic substances (HA) (Frølund et al., 1996).

Biomethanation batch tests (BMTs) (Pontoni et al., 2015), were conducted, after thickening, on 400 mL of each tested sludge. BMTs were performed in triplicate on a small scale under controlled and reproducible conditions in a 1,000 mL glass bottle GL 45 (Schott Duran, Germany). Each bottle was sealed with a 5 mm silicone disc that was held tightly to the bottle head by a plastic screw cap punched in the middle (Schott Duran, Germany). All digesters were immersed up to half of their height in hot water bath at a constant temperature of 308 K. Methane production was measured periodically by water displacement method after leaving the biogas bubbling in an inverted 1,000 mL glass bottle containing a strongly basic solution (12% NaOH) in order to trap the CO_2 present in the biogas. The methane measurement was stopped once the daily biogas production was lower than 1% of the total BMP. The results are expressed in NmL/gVS as specific methane potential (SMP). Dewaterability was evaluated by Specific Resistance to Filtration (SRF) as described elsewhere (Pontoni et al., 2015b) and Capillary Suction Time (CST). CST was determined by means of a Triton (UK) standard CST apparatus using a 18 mm diameter funnel on standard CST paper according to APHA standard method 2710G (APHA, 1998).

3.1.4. The off-gas analyser developed by UO4

An off-gas analyser setup (**Errore. L'origine riferimento non è stata trovata.**) was designed for measuring aeration efficiency of submerged aeration systems and full scale direct GHG emissions in the form of N_2O, CO_2 and CH_4 biologically generated and/or stripped from activated sludge (AS) oxidation tanks (Gori et al., 2016).

The gas stream leaving the liquid tank is captured by a floating hood and a hot wire anemometer (8455 Series, TSI) measures the flow rate. A small fraction (1 l/min) of the gas captured is spilled by a vacuum pump and directed to the analyser. A desiccator unit performs the first conditioning of the gas sample in order to remove water vapour. The spilled air flow is then circulated inside a zirconium oxide fuel cell (AMI Model 65, Advanced Micro Instruments, USA) to measure oxygen partial pressure. Ambient air was sampled by means of a three-way valve at the start and end of each experiment as reference for the efficiency evaluation. Dissolved oxygen (DO) is also measured in the mixed liquor.

The coupling of off-gas analysers and portable micro gas chromatograph (CG) units allowed us high-resolution online measurements of GHGs with concurrently oxygen transfer efficiency measurements. The GHG partial pressure can be converted to emission rates once the off-gas flow rate is known.
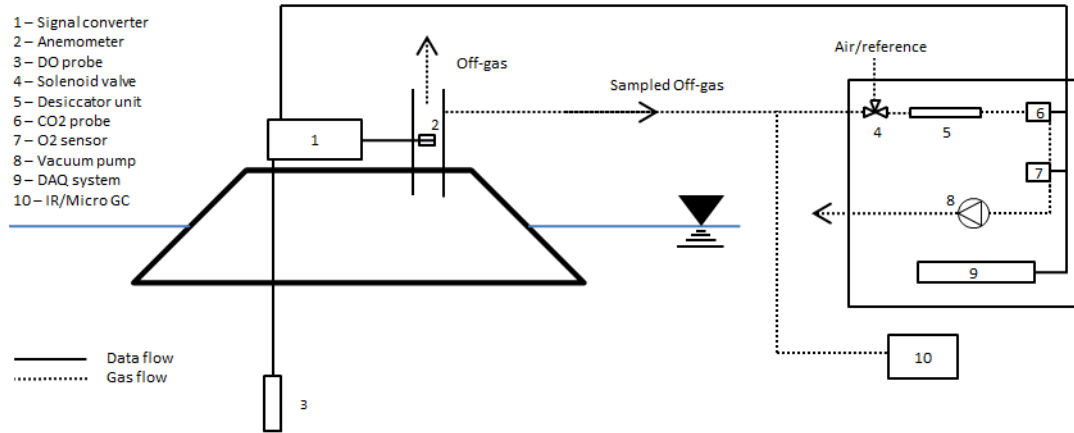

1 – Signal converter
2 – Anemometer
3 – DO probe
4 – Solenoid valve
5 – Desiccator unit
6 – CO2 probe
7 – O2 sensor
8 – Vacuum pump
9 – DAQ system
10 – IR/Micro GC

Figure 5. *Scheme of the off-gas analyser setup (Gori et al., 2016)*

When the humidity is stripped out of the gas stream, only the knowledge of the CO_2 content is necessary in order to calculate the actual mass fraction of oxygen. With this purpose, the CO_2 content of both the ambient air and the off-gas stream was measured with a photo-acoustic infrared gas analyser (X-Stream, Emerson). Knowing the CO_2 content of the gas stream, the partial pressure of oxygen and its ratio with inerts were calculated using Equation 1 and 2.

$$MR_{o/i} = \frac{Y_r}{1 - Y_r - Y_{CO_2 r}}$$

(1)

$$MR_{og/i} = \frac{Y_{og}}{1 - Y_{og} - Y_{CO_2 og}}$$

(2)

where $MR_{o/i}$ and $MR_{og/i}$ represent the molar ratio of oxygen to inerts in the inlet and off-gas respectively. Y_r and Y_{og} are the mole fractions of water vapor in the inlet and off-gas, while $Y_{CO_2 r}$ and $Y_{CO_2 r}$ are the mole fractions of CO2. Finally, the oxygen transfer efficiency (OTE) can be calculated with Equation 3 accounting for the dynamic CO_2 content in the off-gas. Finally, a standardized value of oxygen transfer efficiency can be calculated for both new (αSOTE) and used (αFSOTE) diffusers with Equation 4.

$$OTE = \frac{(O_{2,in} - O_{2,out})}{O_{2,in}}$$

(3)

$$\alpha SOTE = OTE \cdot \frac{C_{S20}^*}{(\beta \cdot C_{S_T}^* - C_i)} \cdot \theta^{(20-T)}$$

(4)

$$\alpha = \frac{\alpha SOTE}{SOTE}$$

(5)

$$F = \frac{\alpha FSOTE}{\alpha SOTE}$$

<div align="right">(6)</div>

where $O_{2,in}$ and $O_{2,out}$ are respectively the ratios of oxygen in the gas stream going in and out of the aerated tank; θ: is the dimensionless temperature correction factor (1.024, for fine pore diffusers); β: is the dimensionless coefficient that takes into account the wastewater salinity (calculated on the basis of total dissolved solids content); $C_{S_{20}}^*$: is the DO at saturation at 20°C (mg/l); $C_{S_T}^*$: is the DO at saturation at the operating conditions (mg/l); C_i: is the time-dependent DO in the tank (mg/l); α: is the ratio of process to clean water mass transfer coefficients for new diffusers (dimensionless); F: is the fouling factor of used diffusers (dimensionless); SOTE: is the oxygen transfer efficiency at standard conditions in clean water (%).

The contribution of the aeration system to internal indirect emissions of GHG can be calculated through its power demand, energy consumption and the carbon emission intensity for power generation. 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. 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.

3.2. Modelling activities

3.2.1. Mathematical modelling activities of UO1

An Activated Sludge Model (ASM) divided into two sub-models (biological and physical) was set-up. The biological sub-model involves: 16 biological processes (aerobic and anoxic); 19 state variables, which include dissolved N_2O and CO_2 (S_{N2O} and S_{CO2}, respectively) and 68 model factors. The nitrogen removal process is described as a two steps nitrification and four steps denitrification processes. With this regard, the autotrophic biomass is modelled as ammonia-oxidizing biomass (X_{AOB}) and nitrite oxidizing biomass (X_{NOB}). Regarding the denitrification process four corrections factors for the heterotrophic anoxic growth rate have been introduced. Specifically, factors related to the reduction from S_{NO3} to S_{NO2} (μ_{g2}), S_{NO2} to S_{NO} (μ_{g3}), S_{NO} to S_{N2O} (μ_{g4}) and S_{N2O} to S_{N2} (μ_{g5}) have been considered. The biological model takes into account the influence of the salinity both for the autotrophic and heterotrophic biomass. The model has been applied to the pilot plant described before, which was cyclically filled with real saline wastewater according to the fill-draw-batch operation. The model was calibrated by adopting a specific protocol based on extensive field dataset. The dataset was acquired during a previous experimental campaign (Mannina et al., 2016c).

3.2.2. Mathematical modelling activities of UO3

The proposed mathematical model is based on differential mass balance equations for the substrate and the product. A single substrate has been taken into account (Organic matter, considered as COD), the overall rate of the whole anaerobic digestion process has been hypothesized to be equal to the hydrolysis rate of the complex macromolecules. In particular, a modified version of surfaced based kinetic (SBK) approach has been used.

The mathematical model is constituted by the following system of ordinary differential equations:

$$\frac{dS}{dt} = -K_{sbk}a^* \frac{S}{K_S + S}$$

(7)

$$\frac{dP}{dt} = \sigma K_{sbk}a^* \frac{S}{K_S + S}$$

(8)

$$\frac{dX}{dt} = \sigma K_{sbk}a^* \frac{S}{K_S + S}$$

(9)

where:

S is the complex organic substrate mass [M];

P is the products [L^3];

X is the microbial biomass [M];

K_{sbk} = disintegration kinetic constant [M L^{-2} T^{-1}];

K = like half saturation constant [M].

n = order of the reaction.

σ = stoichiometric coefficient.

a^* = mass-specific disintegration surface area [L^2];

According to Esposito et al., 2011, assuming that all organic solid particles have the same spherical shape and initial size and they are progressively and uniformly degraded in all directions from the outside towards the inside, the a* can be determined as follows:

$$a^* = \frac{3}{\mu R}$$

(10)

where:

μ is the density, while R is the organic solid particles radius, assumed time dependent in according with the following expression:

$$R = R_0 - K_{sbk} \frac{t}{\mu}$$

(11)

4. Results and discussion

4.1. Main results of UO1

4.1.1. N$_2$O emissions

For sake of conciseness, the main results related to the N$_2$O emission for each pilot plant configuration will be here presented and discussed. A synthesis of the experimental results of the UO1 is reported in Figure 6. In particular, such results are related to the N$_2$O concentration in the off-gas withdrawn from the anaerobic, anoxic, aerobic and MBR tanks. By analysing data reported in Figure 6a, it is possible to observe that low C/N values

promote an increase of the N_2O-N concentration. Indeed, the average value of N_2O-N concentration at C/N = 5 is on average of one order of magnitude greater than the case of C/N = 10. Such a result is likely due to the limited heterotrophic activity at low carbon value. Regarding the configuration II (Figure 6b), the average value of N_2O-N concentration increases with the decreasing of the SRT. Such a result, mainly evident at SRT = 15 days, is likely due to the decrease of the autotrophic biomass which leads to the increase of N_2O during the nitrification process.
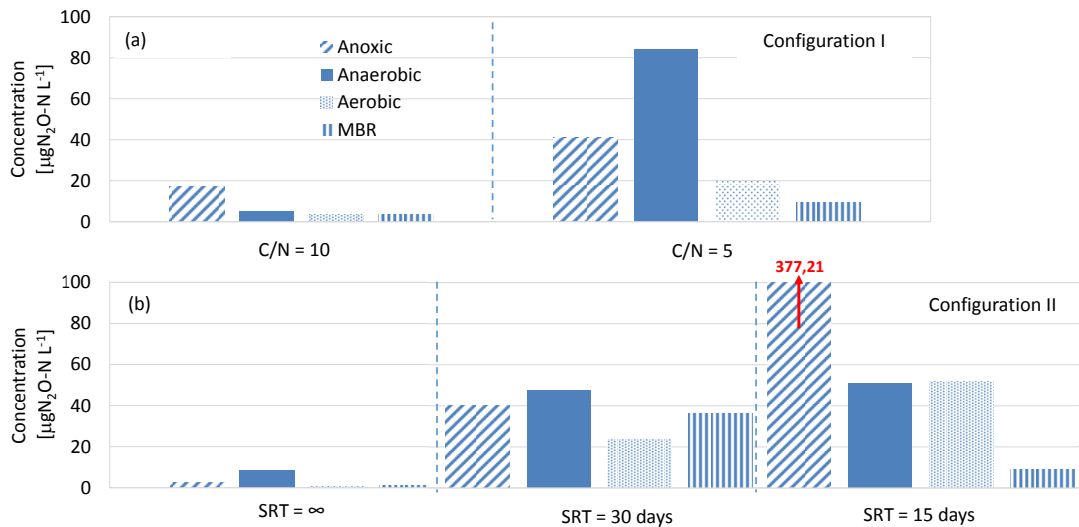
Figure 6. *Average N_2O-N concentration in the off-gas withdrawn from the anaerobic, anoxic, aerobic and MBR tanks for the configuration I (a) and II (b) for the different investigated operating conditions.*

4.1.2. *Mathematical modelling – calibrated model and uncertainty*

In Figure 7 some results related to the model application are reported in terms of N_2O both in liquid and off-gas phases. Data reported in Figure 7 show that the uncertainty band width (as average difference between 95% and 5% percentile) changes with the model outputs in the different plant sections (e.g., greater for $S_{GHG,N2O,1}$ and $S_{N2O,2}$). Such a result is mainly due to the fact that some model outputs entail different level of complexity in terms of involved phenomena in the different plant sections. Moreover, the variation of some factors could make more uncertain the N_2O production in a certain section due to the overlapping effects of different processes. By analysing data in Figure 7, it is possible to observe that for the model outputs for which a greater number of measured data was available ($S_{GHG,N2O,1}$ and $S_{GHG,N2O,2}$) a more accurate model prediction can be obtained. Indeed, for $S_{GHG,N2O,1}$ and $S_{GHG,N2O,2}$ only the 7% and the 12% of the measured data lays outside the band width.

In Figure 7 the cumulative distribution function (CDF) of calibrated, measured, 5th and 95th percentiles for $S_{GHG,N2O,1}$ (a), $S_{N2O,1}$ (b), $S_{GHG,N2O,2}$ (c) and $S_{N2O,2}$ (d) are reported.

Such a result is of paramount interest, suggesting that long extensive data base are required to set up accurate model and to reduce the model uncertainty associated with the model predictions. Indeed, the 60% and the 46 % of the measured data lays outside the band width for $S_{N2O,1}$ and $S_{N2O,2}$, respectively. More precisely, the measured data lower than 0.01 mgN L^{-1} and 0.025 mgN L^{-1} lays outside the band for $S_{N2O,1}$ and $S_{N2O,2}$,
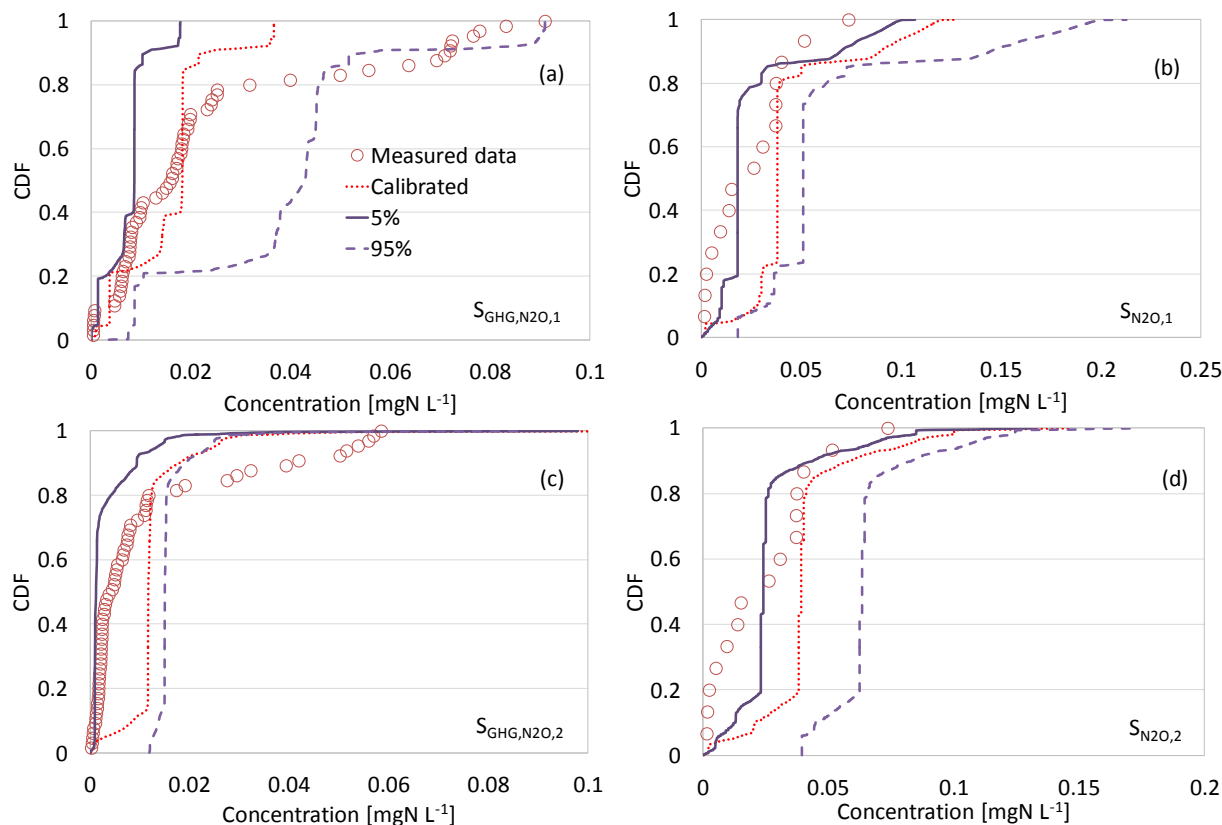
respectively.

Figure 7. *CDF related to the measured data, calibrated model, 5% and 95% percentiles for $S_{GHG,N2O,1}$ (a), $S_{N2O,1}$ (b), $S_{GHG,N2O,2}$ (c) and $S_{N2O,2}$ (d)*

4.2. Main results of UO2

Figure 8 shows the N_2O concentration in the off-gas withdrawn from the pilot scale aerobic digester and NH_3 concentration in the reactor (Caniani et al, 2015). At the beginning of the experiment, during the first three days, N_2O emissions were low and showed little variation ranging from 0.136 to 0.344 ppm, concentrations comparable with that emitted in an activated sludge reactor (Butler et al., 2009). N_2O concentration in the off-gas increases with the increase of sludge stabilization. COD/N ratio in the reactor seems to have an effect on N_2O emission (Figure 8a). As already found in the literature for the activated sludge process (Desloover et al., 2012), during nitrification, a relatively low COD/N ratio is the main parameter leading to N_2O production. If we compare N_2O concentration in the off-gas and NH_3 concentration in the sludge (Figure 8b), we can observe that N_2O increase with the decrease of NH_3, suggesting that nitrification plays an important role in N_2O emissions during aerobic digestion.

Concerning the measure carried out on a full scale WWTP, as expected, the results show that the emissions from the aerobic digestion are smaller than those from AS mainly because of low off-gas flow rates due to the installation of surface turbines instead of submerged diffusers, which provide a lower stripping effect.

Total $CO_{2,eq}$ emissions are summarized in Table 3 and compared with literature data.
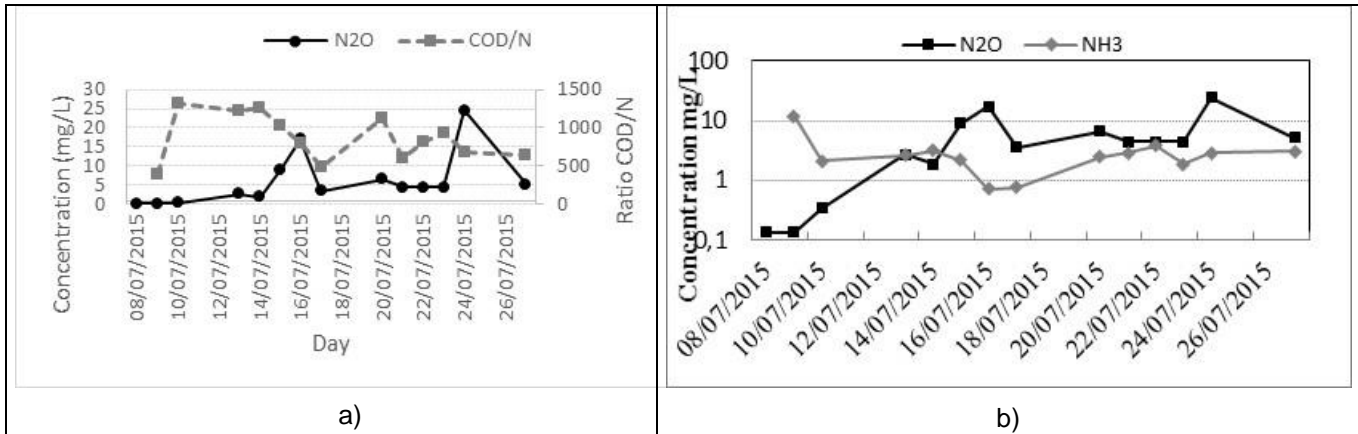
Figure 8. *a) N₂O concentration in the off-gas of the aerobic digester and COD/N ration in the reactor; b) N2O concentration in the off-gas of the aerobic digester and NH3 concentration in the reactor (Caniani et al., 2015).*

Table 3. *Total plant CFP (all values in kgCO$_{2,eq}$/ kgbCOD) and comparison with literature data*

	From electricity generation	From organic matter oxidation	From N$_2$O	Total CO$_{2,eq}$ emissions	Plant CFP
AS	0.26	0.14	0.007	0.407	0.47
AeD	0.063	3·10^{-10}	4·10^{-9}	0.063	
Gori *et al.* 2013	0.6	0.6 from AS 0.4 from AeD	0.1	-	1.7
Corominas *et al.* 2010	0.524	0.376 from AS 0.389 from AD	0.384 from AS	-	1.673

Values reported in Table 3 show that the net energy power generation contributes to about the 69% of the total emissions, confirming that aeration systems are the main contributors. As showed in Table 3, in Gori *et al.* (2013), the specific amount of CO$_2$ emitted from AS and AeD due to the direct transformation of biodegradable organic matter has been calculated, considering the aeration using fine bubble diffusers in both AS and AeD tank. Referring to a temperature of 20°C and to a sludge retention time of 10 days, the direct CO$_2$ emissions from AS and AeD were about 0.60 kg$_{CO2}$/kg$_{bCOD}$ and 0.40 kg$_{CO2}$/kg$_{bCOD}$, respectively. The N$_2$O contributed to a total amount of CO$_2$ equivalent equal to 0.1 kg$_{CO2}$/kg$_{bCOD}$, while the corresponding total CO$_2$ from electricity generation is 0.6 kg$_{CO2}$/kg$_{bCOD}$. In Gori *et al.* (2013), the specific CO$_2$ emissions from AS in two selected municipal WWTPs varied between 0.293 to 1.174 kg$_{CO2}$/kg$_{bCOD}$, The differences were due to the COD fractionation and also depended on the presence of the primary clarifier. The emissions calculated by Corominas et al., 2010, are comparable with the results in Gori et al. (2013), whereas they are higher than those calculated in this study.

The N$_2$O emission fraction was computed by normalizing the flux to the daily influent Total Kjeldahl Nitrogen, as reported by Chandran (2011). Considering an average value of the influent NH$_4^+$ of 52.4 mg/l from the data measured during the monitoring, the value obtained for the emission fraction is 0.00032 kg$_{N2O-N}$/kg$_{NH4-N}$,

corresponding to 0.032%. The obtained value is inside the range indicated by Chandran (2011) for AS, nevertheless closer to its lower bound. This is not because the plant is designed and managed towards a low-emissions configuration, but most probably because many anoxic zones are generated in the aerobic tank due to the poor performance of the aeration system. N_2O could be produced by autotrophic or heterotrophic denitrification, although metabolic activity seems not to be so elevated. Moreover, one possibility is that N_2O production takes place in the liquid phase and it is not stripped in the gas phase due to coarse bubbles and low aeration efficiency. As a matter of facts, the daily rate of N_2O emitted from the aeration tank is 70 g_{N2O}/d that is a value typical obtained for anoxic tanks, as shown for example by Ahn et al. (2010) for a Modified Ludzack - Ettinger (MLE) configuration.

4.3. Main results of UO3

The main results of the experimental campaigns conducted are summarized in Table 4 (Pontoni et al., 2015; Pontoni et al., 2016).

Table 4. *Specific Methane Production of the tested sludge*

Sludge	SMP (NmL/gVS)
CAS1	304
CAS2	342
CAS3	350
MBR1	244
MBR2	186
MBR3	277
MBR4	242

It is noticeable how all tested sludges have a quite high BMP potential, generally being higher in CAS sludge, but not negligible in MBR case. Hence MBR sludge is not to be considered stabilized yet and if not properly disposed, might cause direct emissions of methane (up to 277 ml CH4/gVS) and CO_2 (around 40-60 % of the SMP). Concerning the sludge filtration, a wide variance is found among the studied samples, thus meaning that the dewatering properties depend more from the operational parameters than from the plant configuration (CAS or MBR). Figure 9 confirms this result, showing a linear correlation between SRF and EPS in the sludge (Pontoni et al., 2016).

A very well fitting linear correlation has been found for EPS concentrations and SRF values, reflecting a dominant effect of the EPS on the rheological properties of the sludge. It is important to underline that the tested sludges come from different plants operating with different technologies and operational parameters. If this trend will be confirmed by further experiments with a wider number of sludges, the total EPS concentration could be a parameter to predict the sludge dewatering behavior, or vice versa, the SRF value could give information about the total EPS content in the sludge.
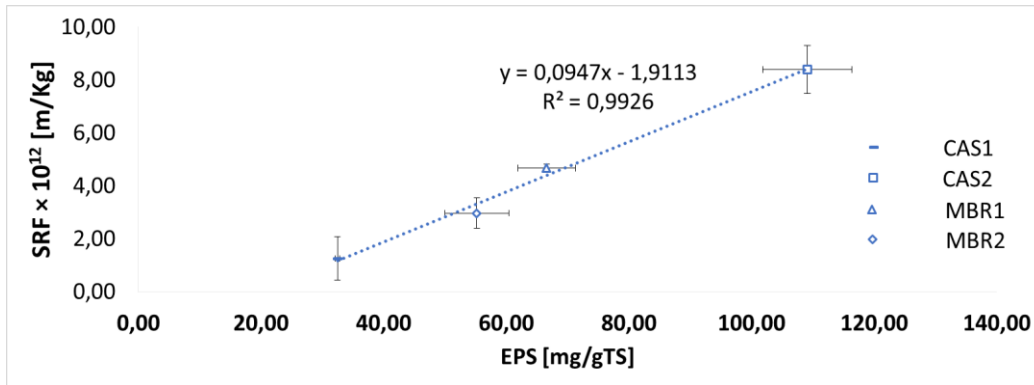
Figure 9. *Linear correlation between the EPS concentration and SRF in the sludge*

4.4. Main results of UO4

4.4.1. Monitoring aerators fouling and aging, optimizing the schedule of diffusers cleaning/substitution

A measurement campaign carried out in two parallel aerobic tanks equipped with EPDM membrane fine bubble diffusers allowed to verify the great potential of the off-gas measurements for optimizing aeration devices and potentially reducing energy requirements in WWTPs. In Figure are reported the results from the two parallel aerobic tanks, one equipped with new diffusers and the other with aged diffusers. Measures were carried out along the length of each aerobic tank (plug-flow design) in twelve locations (Gori et al., 2016).
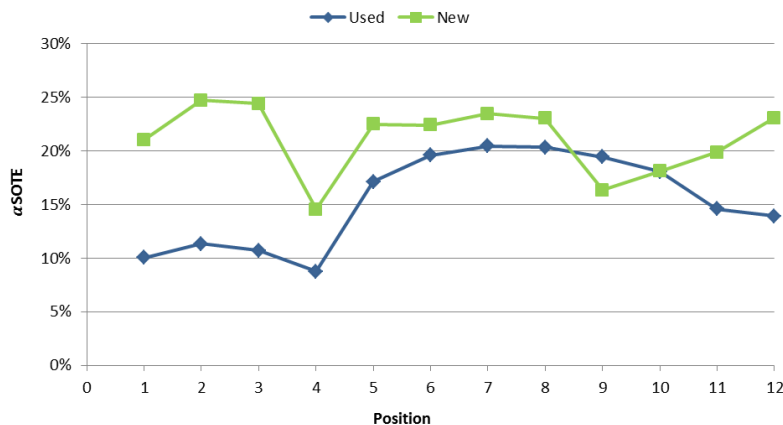

Figure 10. *Effect of diffuser aging on aeration efficiency performances: comparison of OTE results along the length of a plug-flow reactor equipped with used (dots) and new (squares) membrane disc air diffusers (Gori et al., 2016).*

A consistent difference in terms of αSOTE between new and aged diffusers was observed. Interestingly, it was possible to conclude that, only due to the fouling of the diffusers, more than double (117%) of the energy, and therefore of operational costs, was needed to provide similar conditions in the tank equipped with aged diffusers as compared to the tank using new diffusers.

4.4.2. Effects of influent composition and dynamics on direct emissions

Large differences in N_2O emissions (Figure and Figure) were observed among different WWTPs, but also within the same plant with the fluctuation of the incoming load. These results are in accordance with the

literature, confirming the inadequacy of the use of emission factors and the need of a suitable tool for direct and indirect emission assessment (Gori et al., 2016).

The off-gas exiting the aerobic tanks of two WWTPs (one located in Italy and one in The Netherlands), was monitored for a number of days along with plant process dynamics in order to understand the extent and origin of N$_2$O emissions. The Italian plant is a conventional activated sludge (CAS) system characterized by 12 parallel plug flow bioreactors (90x6x15m) with pre-denitrification and aerated in the second half of their length. The wastewater is usually of very low strength as it is heavily diluted by surface water infiltration. The Dutch WWTP is a modified-UCT layout for nitrogen and phosphorous removal, employing a carrousel type bioreactor with concentric rings for alternating anaerobic, anoxic and aerobic conditions.

The two plants differ mostly for influent composition and this seems to be the major responsible causing the one-fold difference in emission factor. The aeration tank of the Italian WWTP emits 0,027 g N$_2$O-N for each gram of N entering the plant, while the Dutch WWTP emission factor is 0.25 g N-N2O/N. Both plants treat municipal wastewater but the Italian plant suffers from dilution due to groundwater infiltration in the sewer (Gori et al., 2016).
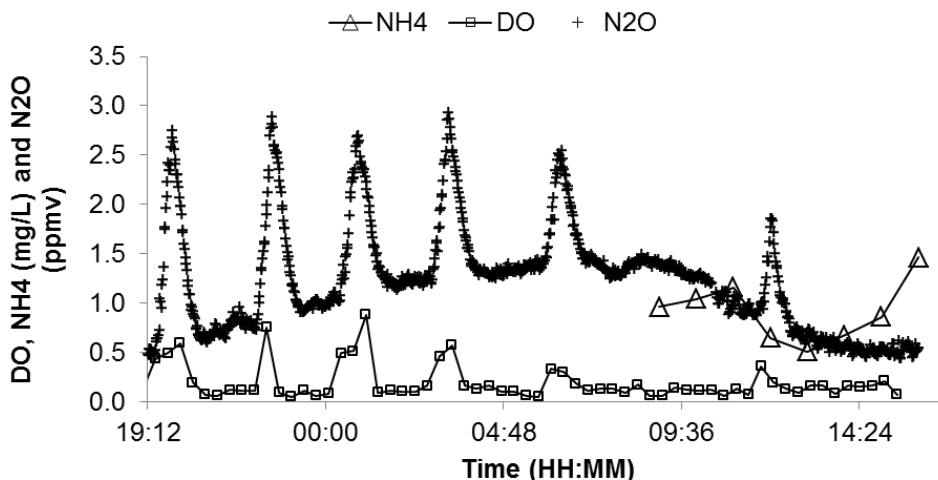

Figure 11 – *N$_2$O concentrations in the off-gas of a WWTP in Italy (Gori et al., 2016)*
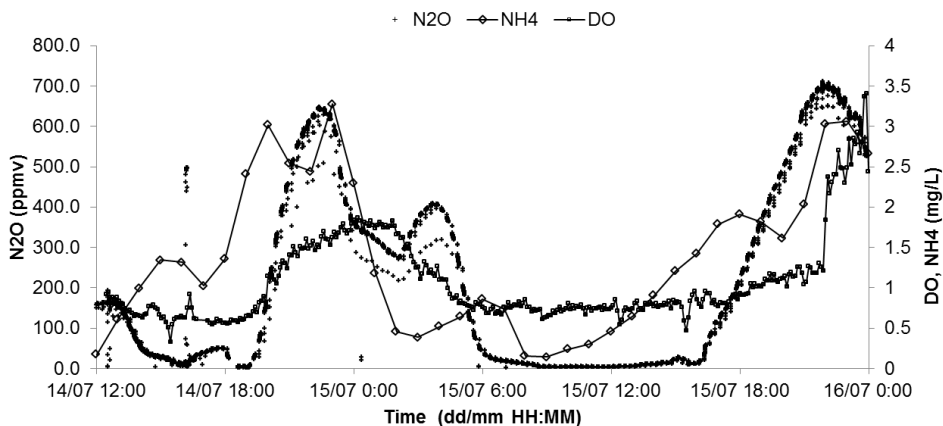

Figure 12. *N$_2$O concentrations in the off-gas of a WWTP in The Netherlands (Gori et al., 2016).*

5. Conclusion

The traditional main goal of a WWTP - to meet effluent standards for receiving water body protection - has to broaden its scope to include the reduction of GHGs. Therefore, that there is a need to address GHG emissions for an integrated WWTP management system. Although GHG emissions from WWTPs are nowadays of concern, the source, magnitude and mechanism for production (mainly for N_2O) are relatively unknown and further investigation is needed (Caniani et al., 2015). The aim of experimental activities is to identify design and operational variables that have an important role both in energy consumption and GHG production, while maintaining an high quality of liquid effluents (Caniani et al., 2015).

During the future final phase of the project, the collected database of measurements and the results of the simple and detailed modelling of the biological processes will allow us to implement the decision support system for the design and management of WWTPs by reducing the environmental impact in terms of both energy costs and emissions. The platform could be used both for conventional and advanced biological treatments.

Acknowledgments

References

[1]   Ahn, J.H.; Kim, S.; Park, H.; Rahm, B.; Pagilla, K.; Chandran, K. N_2O emissions from activated sludge processes, 2008–2009: Results of a national monitoring survey in the United States. Environ. Sci. Technol. 2010, 44, 4505–4511.

[2]   Bani Shahabadi, M.; Yerushalmi, L.; Haghighat, F. Impact of process design on greenhouse gas (GHG) generation by wastewater treatment plants. Water Res. 2009, 43, 2679–2687.

[3]   Butler, M.D., Wang, Y.Y., Cartmell, E., Stephenson, T. Nitrous oxide emissions for early warning of biological nitrification failure in activated sludge. Water Research. 2009, 43, 1265-1272.

[4]   Caivano M.; Saluzzi F.; Caniani D.; Masi S.; Mannina G. Development of an aerobic digestion model for the assessment of greenhouse gases production (AeDMG1): Calibration and validation. In Proceedings of the EuroMed 2015, Palermo, Italy, 10–14 May 2015.

[5]   Caniani, D., Esposito, G., Gori, R., Mannina, G. Towards A New Decision Support System for Design, Management and Operation of Wastewater Treatment Plants for the Reduction of Greenhouse Gases Emission. Water, 2016, 7, 5599-5616.

[6]   Capodici, M., Mannina, G., Torregrossa, M., 2015. Wasted activated sludge dewaterability: a comparative evaluation of sludge derived from CAS and MBR systems. Proceedings of the EuroMed Conference 2015:

Desalination for Clean Water and Energy, Palermo, Italy, 10–14 May 2015.

[7]   Chandran K. Protocol for the measurement of nitrous oxide fluxes from biological wastewater treatment plants. *Methods in Enzymology*, Volume 486, Chapter 16, 2011.

[8]   Chen, Z., Zhang, W., Wang, D., Ma, T., Bai, R. 2015. Enhancement of activated sludge dewatering performance by combined composite enzymatic lysis and chemical re-flocculation with inorganic coagulants: Kinetics of enzymatic reaction and re-flocculation morphology. Water Research, 83, 367-376.

[9]   D'Acunto, B., & Frunzo, L. (2011). Qualitative analysis and simulations of a free boundary problem for multispecies biofilm models. Mathematical and Computer Modelling, 53(9), 1596-1606.

[10] D'Acunto, B., Esposito, G., Frunzo, L., & Pirozzi, F. (2011). Dynamic modeling of sulfate reducing biofilms. Computers & Mathematics with Applications, 62(6), 2601-2608.

[11] D'Acunto, B., & Frunzo, L. (2012). Free boundary problem for an initial cell layer in multispecies biofilm formation. Applied Mathematics Letters, 25(1), 20-26.

[12] Desloover, J., Vlaeminck, S.E., Clauwaert, P., Verstraete, W., Boon, N. Strategies to mitigate N2O emissions from biological nitrogen removal systems. Curr. Opin. Biotechnol. 2012, 23, 474–482.

[13] D.J. Batstone, J. Keller, I. Angelidaki, S.V. Kalyuzhnyi, S.V. Pavlostathis, A. Rozzi, et al. Anaerobic digestion model no.1, Rep. No. 13 IWA Publishing, London (2002) p. 74

[14] Esposito, G., Frunzo, L., Panico, A., & Pirozzi, F. (2011). Modelling the effect of the OLR and OFMSW particle size on the performances of an anaerobic co-digestion reactor. Process Biochemistry, 46(2), 557-565.

[15] Esposito, G., Frunzo, L., Giordano, A., Liotta, F., Panico, A., & Pirozzi, F. (2012). Anaerobic co-digestion of organic wastes. Reviews in Environmental Science and Bio/Technology, 11(4), 325-341.

[16] Gori R., Giaccherini F., Jiang L.M., Sobhani R., Rosso D. Role of primary sedimentation on plant-wide Energy recovery and carbon footprint. Water Science & Technology, 68.4, 2013.

[17] Gori, R.; Bellandi, G.; Caretti, C.; Dugheri, S.; Cosenza, A.; Laudicina, V.A.; Morici, C.; Esposito, G.; Pontoni, L.; Caniani, D.; et al. Greenhouse gases from wastewater treatment plant: Towards a new protocol for field measurements. In Proceedings of the Euromed 2015 Desalination for Clean Water and Energy Cooperation among Mediterranean Countries of Europe and the MENA Region, Palermo, Italy, 10–14 May 2015.

[18] Gori, R., Bellandi, G., Caretti, C. Experience, progresses and perspectives of off-gas testing in wastewater treatment: from aeration efficiency towards CFP assessment. Proceedings of SIDISA 2016, Roma, June 19-23 2016.

[19] Mannina, G., Ekama, G., Caniani, D., Cosenza, A., Esposito, G., Gori, R., Garrido-Baserba, M., Rosso, D., Olsson, G. Greenhouse gases from wastewater treatment - A review of modelling tools. Science of the Total Environment, 2016a, 551-552, 254-270.

[20] Mannina, G., Capodici, M., Cosenza, A., Di Trapani, D. Carbon and nutrient biological removal in a University of Cape Town membrane bioreactor: Analysis of a pilot plant operated under two different C/N ratios. Chemical Engineering Journal, 2016b, 296, 289-299.

[21] Mannina, G., Morici, C., Cosenza, A., Di Trapani, D., Odegaard, H. Greenhouse gases from sequential batch membrane bioreactors: A pilot plant case study. Biochemical Engineering Journal, 2016c, 112,114-122.

[22] Mattei, M. R., Frunzo, L., D'Acunto, B., Esposito, G., & Pirozzi, F. (2015). Modelling microbial population dynamics in multispecies biofilms including Anammox bacteria. Ecological Modelling, 304, 44-58.

[23] Ng, H.Y., Hermanowicz, S.W. 2005. Membrane bioreactor operation at short solids retention times: performance and biomass characteristics. Water Research, 39(6), 981-992.

[24] Pontoni, L., D'Alessandro, G., D'Antonio, G., Esposito, G., Fabbricino, M., Frunzo, L., Pirozzi, F. 2015. Effect of anaerobic digestion on rheological parameters and dewaterability of aerobic sludges from MBR and conventional activated sludge plants. in: Chemical Engineering Transactions, Vol. 43, pp. 2311-2316.

[25] Pontoni, L., Fabbricino, M., Frunzo, L., Pirozzi, F., Esposito, G. 2016. Biological Stability and Dewaterability of CAS and MBR Sludge. Desalination and Water Treatment. (in press) doi: 10.1080/19443994.2016.1153904.

[26] Sanders, W. T. M., Geerink, M., Zeeman, G., & Lettinga, G. (2000). Anaerobic hydrolysis kinetics of particulate substrates. Water Science and Technology, 41(3), 17-24.

[27] Stenström, F., Tjus, K., la Cour Jansen, J. Oxygen-induced dynamics of nitrous oxide in water and off-gas during the treatment of digester supernatant. Water Sci. Technol. 2014, 69, 84–91.

[28] Wu, G., Zheng, D., Xing, L. Nitritation and N_2O Emission in a Denitrification and Nitrification Two-Sludge System Treating High Ammonium Containing Wastewater. Water, 2014, 6, 2978-2992.