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Article

Towards A New Decision Support System for Design, Management and Operation of Wastewater Treatment Plants for the Reduction of Greenhouse Gases Emission [†]

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Abstract: The increasing attention paid to the environment has led to a reduction in the emissions from wastewater treatment plants (WWTPs). Moreover, the increasing interest in the greenhouse gas (GHG) emissions from WWTPs suggests that we reconsider the traditional tools used for designing and managing WWTPs. Indeed, nitrous oxide, carbon dioxide and methane can be emitted from wastewater treatment, significantly contributing to the greenhouse gas (GHG) footprint. The reduction of energy consumption as well as GHG emission are of particular concern for large WWTPs which treat the majority of wastewater in terms of both volume and pollution load. Nowadays, there is an increasing need to develop new tools that include additional performance indicators related to GHG emissions and energy consumption as well as traditional effluent quality parameters.

Energy consumption, in fact, can be considered as an indirect source of GHGs. This paper presents the development of an ongoing research project aiming at setting-up an innovative mathematical model platform for the design and management of WWTPs. The final goal of the project by means of this platform is to minimize the environmental impact of WWTPs through their optimization in terms of energy consumptions and emissions, which can be regarded as discharged pollutants, sludge and GHGs.

Keywords: decision support system; wastewater treatment plants (WWTPs) integrated modeling; greenhouse gas (GHG) emissions

1. Introduction

In recent years, studies about greenhouse gas (GHG) emissions show that wastewater treatment plants (WWTPs) are anthropogenic GHG potential sources, contributing to climate change and air pollution [1]. The reduction of energy consumption as well as monitoring and reduction of GHG emission are of particular concern for large WWTPs which treat the majority of wastewater in terms of both volume and pollution load. WWTPs produce the three major GHGs [2]: carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), from both wastewater and sludge treatment lines, and additional amounts of CO_2 and CH_4 from the energy demands. GHGs are also produced during sludge disposal or reuse (transportation and off-site degradation of biosolids) and off-site production of energy and chemicals.

The estimation of GHG emissions from WWTPs has been traditionally based on the classification between on-site (direct and indirect) emissions and off-site (indirect) emissions. The first are due to liquid and solid treatment processes: aerobic substrate utilisation (CO_2), biomass decay (CO_2) and biological nitrogen removal processes (CO_2 and N_2O); stripping of dissolved gases (CH_4) in dewatering unit [3] as well as biogas/fossil fuel combustion for energy recovery/generation. The latest are due to the production of electricity required for pumping, aeration, heating and mixing, production and transportation of fuel and chemicals, as well as transportation, reuse and disposal of solids, and degradation of remaining constituents in the effluent [2].

In the recent past, increasing attention is given to the assessment of N_2O emissions from WWTPs. Indeed, N_2O is a powerful greenhouse gas that is almost 300 times stronger than CO_2, for an atmosphere residence time of 100–120 years. N_2O emissions from WWTPs represent the 3% of the global emission from every source and it is the sixth most important contribution [4]. 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. Nevertheless, the source and magnitude of N_2O are relatively unknown and the knowledge is still incomplete [5,6]. The quantity and distribution of N_2O produced is variable and depends on the characteristics of the incoming wastewater, the technologies used and the operating conditions of WWTPs.

Mathematical models can be a valid aid for the quantification of GHG emissions from WWTP.

The mathematical models to assess GHG emissions from WWTPs can be classified as: empirical models, simplified models and complex mechanistic models [7]. Mechanistic dynamic models have been demonstrated to have the advantages to estimate GHG emissions by considering effective plant design and operating conditions as well as variability of the influent wastewater [2,8,9]; A new trend in GHGs emission modeling of WWTPs is to develop models able to describe the behavior of the entire WWTP, including both water and sludge lines. In a plant-wide modeling approach, a WWTP is considered as a unit, where the water line and the sludge line are linked together and operated and controlled taking into account all the interactions between the processes [10].

The research developed so far on the evaluation of GHG emissions from WWTPs is fragmented and can be subdivided into two types [2]: experimental and modeling. 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 [11].

At the same time, two international research groups under the umbrella of the International Water Association (IWA) have been set up: the Benchmark Simulation model [12] and the Greenhouse gas emission. The main objective of the research groups is two-fold: deepening the aspects related to the setting up of a standard modeling tool for WWTPs to be used at an international level and deepening the knowledge concerning the assessment of GHG emissions from WWTPs. Both groups have highlighted the need to converge research efforts towards the implementation of integrated approaches in the design and management of WWTPs, in order to minimize emissions.

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:

Lack of criteria for the design and management of WWTPs through integrated approaches that include GHGs;

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 behavior in the yield process and also for assessing the GHG temporal variability during the year. These extensive databases are also essential for the development and application of robust and reliable mathematical models;

Lack of standard protocols for measuring emissions, that can allow the comparison of the data obtained in various WWTPs;

Identification of appropriate mitigation measures, which are based on process control, aimed at reducing GHG emissions;

Evaluation of the modeling uncertainty in order to quantify the potential error in the information "predicted" through the models and development of models that are characterized by combined (*i.e.*, complex and simplified) approaches.

In this paper, we present the key methodological aspects of a 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. Basic Principles of Greenhouse Gas (GHG) Emissions Assessment at Plant-Wide Scale

The main elements of the wastewater treatment scheme are outlined in Figure 1, which shows two different solutions to perform solid liquid separation: secondary settler (conventional biological treatment) or membrane bioreactor (MBR). Regardless of the employed plant scheme, processes occurring both in the water line (primary settling, biological treatment and solid-liquid separation) and in the sludge line (thickener, sludge digestion and dewatering) contribute directly or indirectly to the GHG emission.

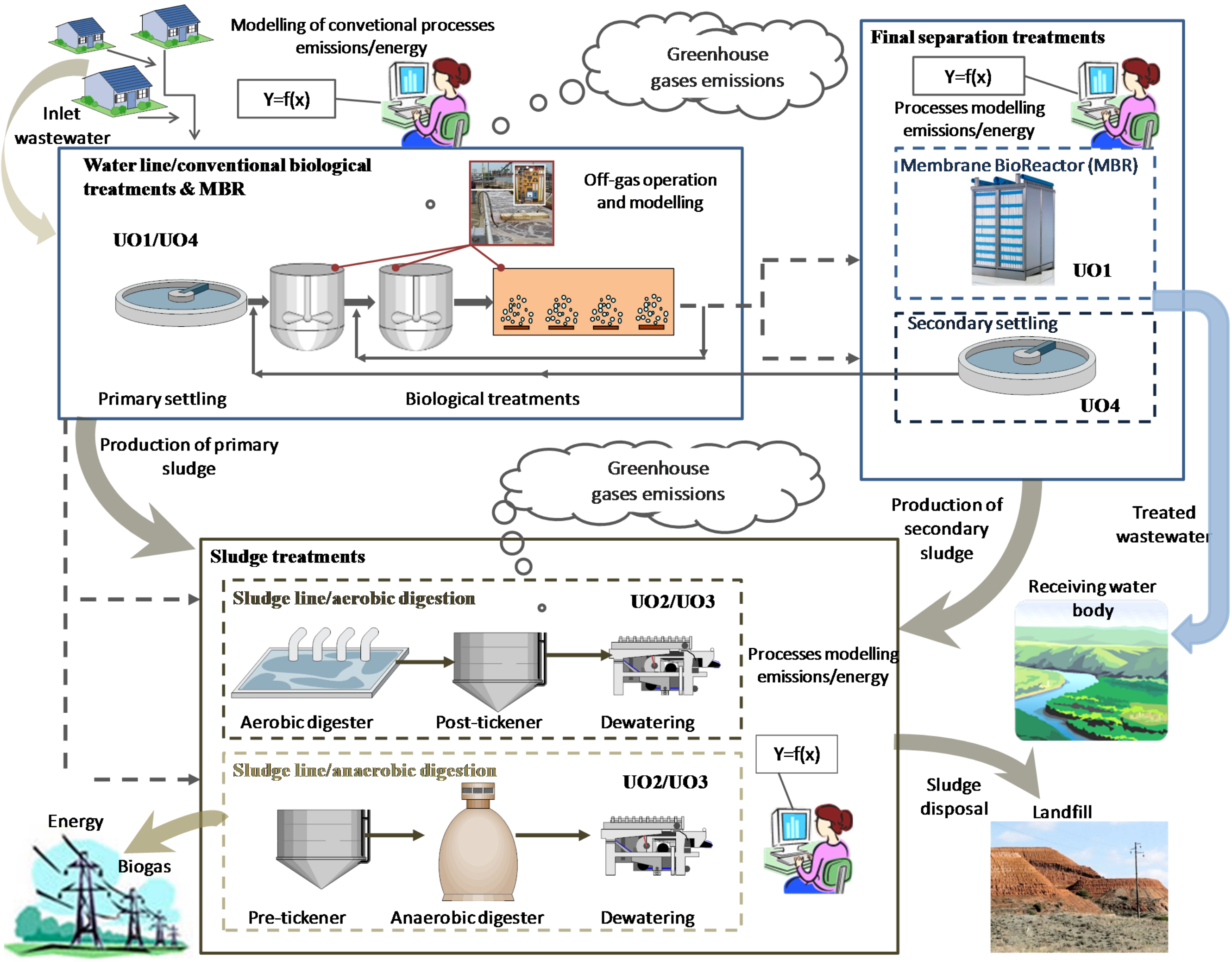


Figure 1. Schematic overview of wastewater treatment plants (WWTPs) having different final separation treatment and sludge treatment processes with the indication of the main sources of greenhouse gas (GHG) emissions.

2.1. CO_2 and Nitrous Oxide Emissions

CO_2 is directly produced during wastewater treatment using both aerobic and anaerobic biological processes. In the first case, organic compounds are oxidized into CO_2 and other metabolites and accompanied by cell growth, while in the second case, organic matter is transformed into biogas (CO_2 and CH_4 in proportions of 30%–40% and 60/70% *v*/*v*, respectively). This short-cycle CO_2 is considered negligible in terms of greenhouse effect [5]. However, fossil organic carbon was found in the influent of WWTPs and related direct fossil CO_2 emissions from oxidation of activated sludge may vary with the wastewater composition and treatment configuration [1]. Further, indirect CO_2 emission is associated to energy production.

Czepiel *et al.* [13] show that 90% of the N_2O emission occurs from the activated sludge compartments, 5% from the grit tanks and 5% from the sludge storage tanks. N_2O emissions from the activated sludge compartments are related to the processes associated with the biological nitrogen removal [5,6]. N_2O can be produced both during nitrification and denitrification processes [5]. Indeed, during nitrification, N_2O is formed during the chemical decomposition of intermediates, such as hydroxylamine and nitrite. N_2O is also produced during the incomplete oxidation of NH_2OH because of formation of nitrosyl radical (NOH). Moreover, N_2O is an intermediate in the denitrification pathway. N_2O is produced (as with denitrification) as an intermediate of reactions by nitrifiers heterotrophic bacteria. Under aerobic conditions, heterotrophic nitrifiers produce much more N_2O per cell than autotrophic nitrifiers. The pathway of nitrification, called nitrifier denitrification, in which the oxidation of NH_3 to NO_2^- is followed by the reduction of NO_2^- to N_2O and N_2, without NO_3^- production, might contribute to a major part of the loss of ammonium in the form of NO and N_2O [14]. However, the wide range of N_2O emission concentrations measured in the WWTPs and reported in literature (0.017–80 mg_{N_2O} /L) underlines that the mechanisms involved in the N_2O formation are not completely known [5,6]. Other studies are needed to better understand the mechanisms of emissions of N_2O from non-aerated zones (*i.e.*, secondary settles and dewatering units). Kampschreur *et al.* [5] and Law *et al.* [6] reported a very large range of N_2O emissions from full-scale WWTP, expressed in percentage of the nitrogen influent load (0%–14.6% and 0%–25% respectively). In recent years, studies concerning N_2O emission from the anammox process were published. Indeed, the partial nitritation-anammox (PNA) process constitutes an alternative for nitrogen removal than conventional nitrification-denitrification over nitrate, since it requires up to 63% less aeration energy, does not require the addition of an external carbon source and the production of sludge and CO_2 emissions are minimal [15]. Given that N_2O is not involved in the anammox metabolism [16], it is generally accepted that anammox bacteria do not contribute to N_2O emissions.

2.2. Methane Production

Methane (CH_4) is an important GHG with a GWP of 25 over a 100-year period [4]. CH_4 is produced during the decomposition of a wide range of organic matter in the absence of oxygen (anaerobic decomposition). Typically, 40 to 45 percent of volatile matter contained in the feed sludge of an anaerobic digester is converted into CH_4 and carbon dioxide. A large part of the processes related to management and treatment of domestic and industrial wastewater has been identified as an important source of CH_4 [17]. During the anaerobic decomposition of organic substrate (activated by methanogenic bacteria), the produced CH_4 (the main component of the biogas) is recovered and used in a combined heat and power system to generate electricity and heat the feed sludge [18]. A small part of this CH_4 can be released to the atmosphere through the surface of the opened tanks (fugitive gas emissions). CH_4 can be also emitted in the sewer system [5]. Large amounts of CH_4 can be produced also from the disposal of raw sewage sludge to landfill, with smaller but still significant levels produced from the disposal of digested sludge to landfill [13].

2.3. Liquid-Gas Mass Transfer

The emission of GHGs produced in wastewater treatment is influenced by their solubility and by external factors (e.g., stripping effect due to the aeration or the stirrers). CO_2 and N_2O are easily soluble in water. The Henry's law constant, at 25 °C and 0% salinity, of CO_2 and N_2O is 34 and 24 $mM \cdot atm^{-1}$ respectively. The Henry's law constant of the O_2 is equal to 1.3 $mM \cdot atm^{-1}$ (at 25 °C and 0 salinity). Thus, an accumulation of CO_2 and N_2O in the liquid phase can occur especially in absence of external factors (e.g., non aerated tanks). Conversely, CH_4 has the same Henry's law constant as O_2 (1.3 $mM \cdot atm^{-1}$ at 25 °C and 0% salinity). Thus, a large part of the CH_4 produced is emitted into the atmosphere. The main external factors influencing the GHG emission can be summarized as: (1) temperature of the liquid phase; (2) aeration and (3) stirrer effect. Ahn *et al.* [11] have found that N_2O emission is two to three orders of magnitude higher in aerated zones than in non-aerated ones.

3. Description of the Research Project

The activities and the results presented here place to the project "Energy consumption of GreenHouse Gas (GHG) emissions in wastewater treatment plants: a decision support system for planning and management" supported by grant of the Italian Ministry of Education, University and Research (MIUR). The project, which started in 2014 and will end in 2017, is carried out by four Research Units (UOs).

The project has the main aim of developing an innovative mathematical platform (Decision Support System—DSS) for the design and management of WWTPs by reducing the environmental impact in terms of both energy costs and emissions. This main aim will be achieved by performing experimental and modeling activities (Figure 2).

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 modeling point of view, the project aims at setting up, for a specific treatment unit, 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.

We are analyzing the main processes that take place in both the water and sludge lines in WWTPs. Both single treatment units and their interactions are being analyzed. 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 [19]. An innovative mathematical model platform for the design and management of WWTPs is going to be set up (Figure 3) to achieve the main goal of the project. As shown in Figure 3, the decision support system will be implemented by using the results of the simple (inner circle of Figure 3) and detailed modeling (outer circle of Figure 3) of the biological processes. The platform could be used both for conventional and advanced biological treatments.

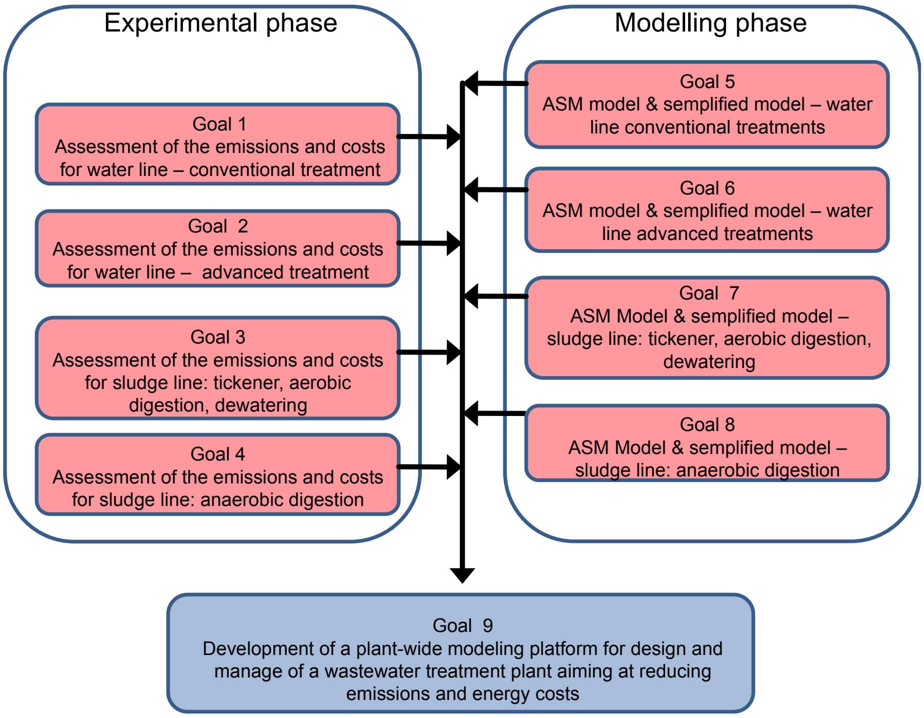


Figure 2. Scheme of the project goals.

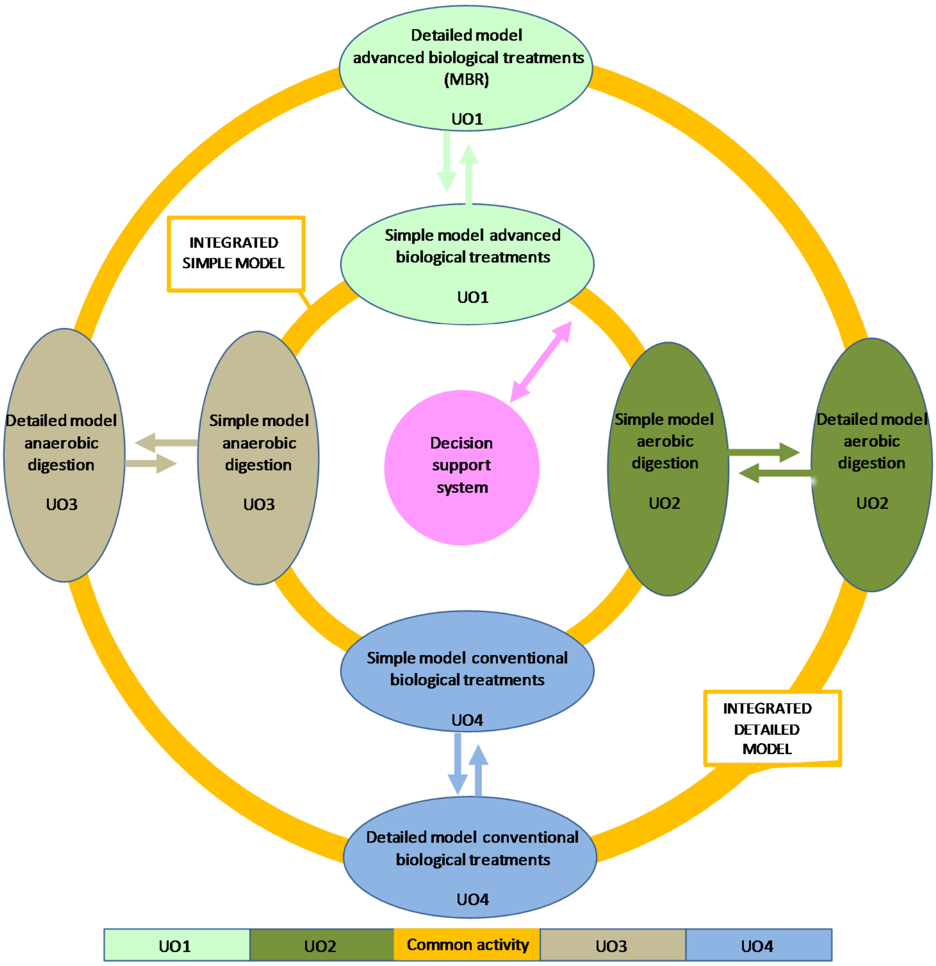


Figure 3. Integrated model layout of the WWTP with indication of the contribution provided by each research unit (UO).

4. Activities of the Research Units

The project is constituted by four research units (UOs): University of Palermo (UO1), University of Basilicata (UO2), University of Cassino and Southern Lazio (UO3) and University of Florence (UO4).

All UOs perform both experimental and modeling activities. The expertise of each UO concerning specific topics has been shared among all the other UOs in order to achieve the final objectives of the project. Therefore, each UO carries out both transverse activities, *i.e.*, in cooperation with all UOs, and individual activities, in relation to the different specific skills of each UO. All activities are carried out through methodologies which have been discussed, set-up and shared during dedicated meetings among the UOs in order to have uniform approaches. The activities of the UOs are highly integrated and synergistic. Both pilot plant and full-scale studies are carried out in order to get a complementarity of the results aimed at a better interpretation of the processes.

In detail, UO1 has expertise on Membrane Bioreactors (MBRs) as well as on advanced modeling of WWTPs. 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 set-up an extensive database useful for phenomena interpretation and raising knowledge about some aspects that are still in need of further investigation. UO1 is analyzing 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. Sensitivity analysis, calibration, validation and uncertainty analysis will be carried out for all the implemented models.

In order to deepen the chemical/physical/biological phenomena of thickening and aerobic digestion more effectively, UO2 has designed, built and operated a pilot scale plant for such treatment units. The pilot plant is used to investigate the GHG emissions from the different pilot plant units, which are measured in different operating conditions, by using the tool developed by the UO4. An extensive 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 new model Aerobic Digestion Model Greenhouse Gas 1, AeDMG1, has been developed [20]. The proposed AeDMG1 model simulates the aerobic digestion processes including also GHG emissions. The fractionating COD and N obtained from the settler underflow was used as input of the AeDMG1. The model has been developed on the ASMN basic concepts. Furthermore, simulations of aerobic digestion processes at elevated sludge retention time were conducted. Finally, the model was validated on experimental measurements at pilot scale. The UO2 is using data from field activities and from the ASM type model to develop simplified models, which increase the possibility of applications in comparison to the more complex models.

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 modeling 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 has defined a detailed protocol for the measurement of oxygen transfer efficiency from processes units and for GHG measurement. Such a protocol has been proposed as a standard and is one of the main results of the project. The UO4 has supported the other UOs in measuring GHGs emissions from plants (both pilot and full scale) investigated. The UO4 has carried out experimental activities on both conventional and innovative plants. Similarly to the other UOs, data gathered from experimental activities are collected in a database in order to increase knowledge and develop models (both detailed and simplified) able to properly predict observed phenomena. Particular attention has been given to the influence of operative conditions on GHGs emissions.

5. Development of a New Protocol for Field Measurement of GHG Emissions

The proposed protocol [19] set up materials and methods for measuring GHG direct and indirect emissions. In particular, the protocol allows us the measurement of CO_2, CH_4 and N_2O from the water treatment line (*i.e.*, primary settler oxidation tank, secondary settler and/or MBR) and from the sludge treatment line (*i.e.*, thickening, digestion and dewatering) and indirect emissions from the energy consumption due to aeration (oxidation tank and aerobic sludge treatment, if present).

Direct emissions from aerated tanks can be measured using online as well as offline methods. Indirect internal emissions caused by aeration can be predicted by using the off-gas method, in those WWTPs where power consumption of blowers is not logged.

Figure 4 shows the layout of the proposed device, that is a floating hood able to capture the off-gas leaving the tank surface. A hot wire anemometer measures the flow rate. The system is also equipped with a dissolved oxygen (DO) probe in the liquid phase, required for correcting the Oxygen Transfer Efficiency (OTE) to standard conditions (*i.e.*, αSOTE). A PVC column (h = 0.255 m, d = 0.025 m) filled with silica gel ensures moisture removal at the end of the captured stream, which is sent to specific sensors for analyzing the concentration of O_2 and CO_2.

The hood should be positioned in different points of the aerated surface so that at least 2% of the tank surface in the end has been covered by the floating device [21].

In this protocol we propose online monitoring carried out with a portable micro gas chromatograph (micro-GC), which have many useful specifications for the application to online GHG measurements. Alternatively, in case of plants with low concentration of N_2O in the off-gas, online monitoring of N_2O emission can be carried out with an InfraRed-Photoacustic (IR) multigas monitor instrument, which has a lower limit of detection with respect to micro-GC. The proposed protocol also covers aspects concerning the analysis of the biogas composition in order to properly assess GHG emission offset from biogas energy recovery and its potential effect on emission from biogas combustion. More details concerning the protocol can be found in [19].

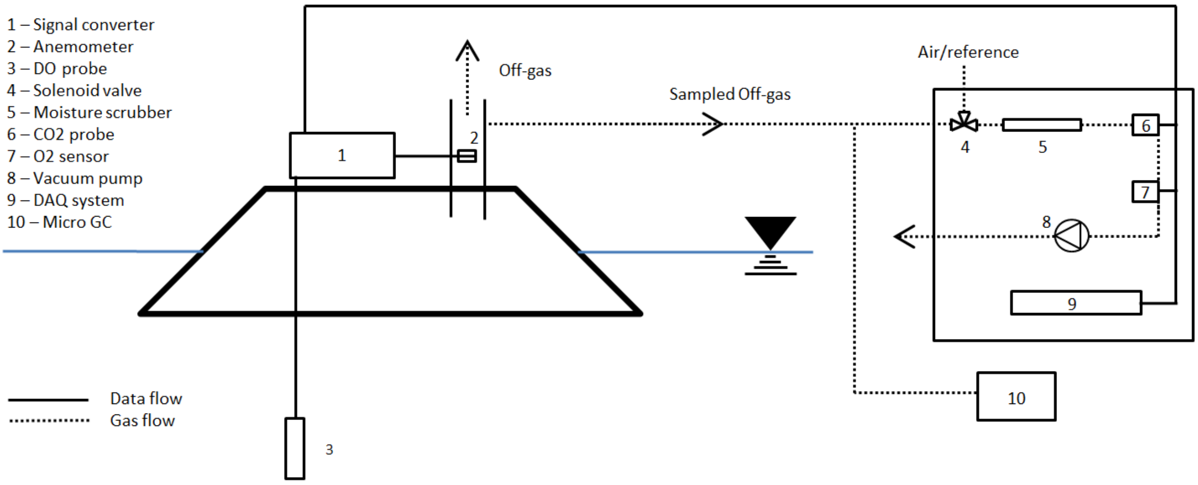


Figure 4. Scheme of the Off-gas analyzer [19].

6. Preliminary Results

Experimental results of the UO1 are reported in Figure 5, which shows the N_2O concentration in the off-gas withdrawn from the aerobic and anoxic tank for an MBR pilot plant.

As reported in Figure 5, the N_2O concentration is higher in thee anoxic tank than the aerobic one for the phases I and II. Thus, showing that treating industrial wastewater under specific nitrification or denitrification conditions, N_2O is mostly produced during the denitrification process. Conversely, in case of civil wastewater (phase III), the effect of the low C/N leads to the increase of N_2O production during the nitrification process. Further details can be found in the literature [22,23].

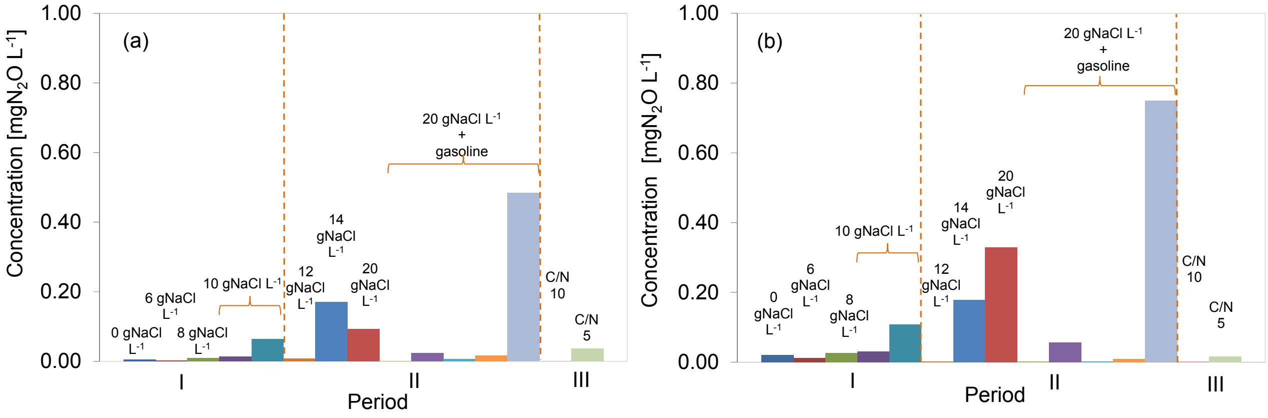


Figure 5. N_2O concentration in the off-gas of the aerobic (**a**) and anoxic tanks (**b**) for each experimental period. Phase (I) Filling Sequential—Batch Membrane Bioreactor (SB-MBR) with anoxic and aerobic tanks, testing the effect of the salinity increase from 0 to 10 g $NaCl{\cdot}L^{-1}$ (86 days) [22,24]; Phase (II) Pre-denitrification MBR, testing the effect of the salinity increase from 12 to 20 g $NaCl{\cdot}L^{-1}$ and the hydrocarbon (gasoline) dosing (88 days) [23]; Phase (III) University Cape Town (UCT)—MBR, testing the effect of the C/N ratio (C/N = 10; C/N = 5) (40 + 40 days).

Regarding the modeling activities, UO1 performed a global sensitivity analysis and uncertainty analysis on a plant-wide mathematical model developed in previous studies [25,26], by using the Extended-FAST method [27]. The plant wide model, which has been coded in Visual Fortran, is able to quantify the carbon and energy footprint of an integrated conventional activated sludge.

Results of the sensitivity analysis are reported in Figure 6. More precisely, results of Figure 6 are related to the CO_2 produced during the biomass respiration (CO_{2_resp}) and the biogas combustion (CH_{4_comb}), the CH_4 produced during the sludge dewatering ($CH_{4\_dewatering}$) and the equivalent CO_2 due to the power use (power requirements).

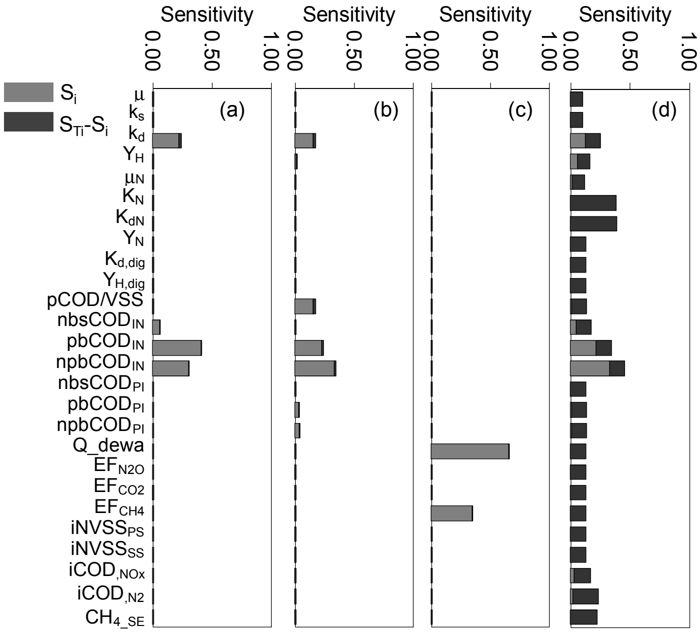


Figure 6. Sensitivity (S_i) and interaction ($S_{Ti} - S_i$) of all factors for (**a**) CO_{2_resp}; (**b**) CH_{4_comb}; (**c**) $CH_{4\_dewatering}$ and (**d**) Power requirements.

UO1 proposed a mathematical model (ASM2d–SMP–GHG) that couples the integrated ASM2d–SMP model introduced by Cosenza *et al.* [28] with the GHG model of Hiatt and Grady [29,30]. The ASM2d–SMP–GHG model is able to quantify GHG emissions in terms of carbon dioxide (CO_2) and N_2O for an MBR plant.

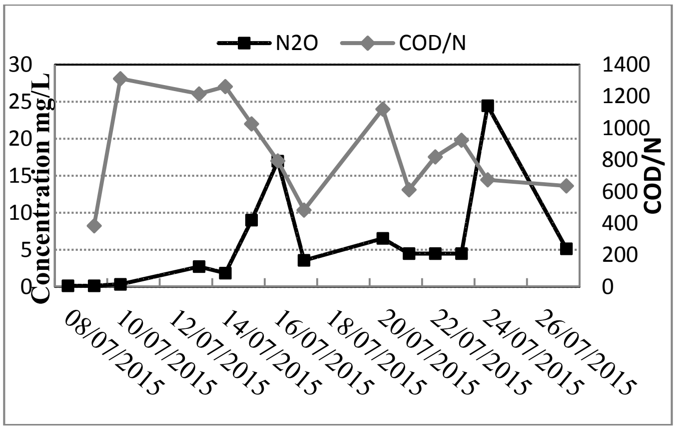
ASM2d–SMP–GHG model was used to identify the key factors and sources of uncertainty affecting GHG modeling by adopting the Extended-FAST and a Monte Carlo based method. The model was applied to an UCT-MBR pilot plant.

The results reveal that model factors related to nitrogen transformation and membrane separation processes play a central role in the uncertainty of GHG estimation. Model factors that are associated with physical processes exhibit large first-order and total-order effects, which emphasizes the importance of a holistic approach that jointly considers biological and physical processes.

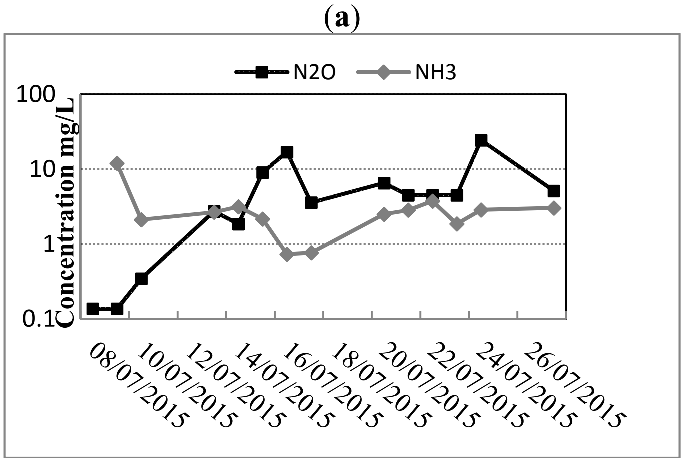
Preliminary results of experimental activities of UO2 concern the measure of N_2O concentration in the off-gas of a pilot-scale aerobic digester.

At the beginning of the experiment, the sludge, coming from a conventional activated sludge treatment plant, had a sludge retention time of 20 days. The digestion lasted 20 more days, during which fresh sludge from the WWTP was added to the digester every day. Mixed liquor dissolved oxygen ranged from 1.5 to 4.7 mg/L and temperature ranged from 18.1 to 23.0 °C. At the end of the experiment, sludge was stabilized, with a reduction of VSS equal to 40% and a ratio VSS/TSS equal to 0.5. Gaseous N_2O sampling was carried out every day for a period of two hours, filling eight tedlar bags (one every 15 min), from which the daily average concentration was calculated.

Figure 7 shows the N_2O concentration in the off-gas withdrawn from the aerobic digester and NH_4 concentration in the reactor. 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 [31]. N_2O concentration in the off-gas increase with the increase of sludge stabilization. COD/N ratio in the reactor seems to have an effect on N_2O emission. As already found in the literature for the activated sludge process [32], during denitrification, 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 7b), 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.



(**a**)



(**b**)

Figure 7. (**a**) N_2O concentration in the off-gas of the aerobic digester and COD/N ration in the reactor; (**b**) N_2O concentration in the off-gas of the aerobic digester and NH_3 concentration in the reactor.

The preliminary results obtained by UO3 are related to the comparison of membrane Bio-Reactor (MBR) and Conventional Activated Sludge (CAS) systems in terms of biomethanation potential (BMP) of the produced sludge.

Among the several advantages of MBR compared to traditional CAS systems is often reported the higher stability of the MBR sludge due to higher sludge retention time (SRT). This advantage is evident in the case of CAS systems that are upgraded to MBR since the upgrading allows us to increase the microorganisms concentration in the biological reactor, resulting in a higher total biomass and therefore a higher SRT. However, this is not always the case for new built MBR facilities that can be designed with lower SRT values similar to the typical values for CAS systems.

This is confirmed by the results of UO3, obtained testing four different sludges collected from two different MBR treatment plants located in Marina del Cantone (Naples—Italy) (MBR sludge 1) and Capri (Naples—Italy) (MBR sludge 2) respectively and from two CAS treatment plant located in Nola (Naples—Italy) (CAS sludge1) and Massa Lubrense (Naples—Italy) (CAS Sludge2) (Table 1).

Table 1. Operational Parameters of the treatment plants where the sludges were collected.

WWTP	HRT (h)	Flow Rate (m^3/h)	SRT (d)	COD (mg/L)	N-NH_4^+ (mg/L)	Membrane
MBR1	20	12	30	450	40	Hollow fiber
MBR2	24	65	35	350	35	Plain
CAS1	7	3300	40	310	22	--
CAS2	18	100	15	350	35	--

Such results [33] are summarized in Figure 8 showing the specific cumulative methane production of the four studied sludges. The methane production per VS mass unit for CAS sludge was higher compared to the MBR sludge, with the following order CAS2>CAS1>MBR1>MBR2. This was partially unexpected as based on the SRT of the four sludges (Table 1) and previous studies [34,35], the expected order was CAS2>MBR1>MBR2>CAS1. This seems to indicate that the SRT is not the sole parameter influencing the sludge BMP. However, a quite high BMP of MBR sludges (244 and 186 NmL/gVS for MBR1 and 2 respectively) was obtained, that is in both cases less than 1/3 lower than the BMP of CAS sludges (304 and 342 NmL/gVS for CAS1 and CAS2 respectively).

As preliminary results of the UO4, main results of a campaign aimed at evaluating GHGs emission from a large WWTP located in Italy, are here reported.

The off-gas measurement campaign was carried out in a conventional denitrification-nitrification activated sludge plant treating approximately 60,000,000 m^3/year of municipal wastewater. The aeration tank is equipped with fine-bubble diffusers (ABS, PIK300) with EPDM membranes. At present, the airflow rate is automatically regulated through a cascade ammonia-DO controller with an ammonia set point in the range of 0.5–1.5 mg/L.

Experimental results showed that the nitrous oxide concentration trend in the off-gas of the aeration tank is variable during the day, with lower values during the morning and at night, and higher values during the afternoon. The nitrous oxide trend follows those of N-NH_4 and N_{tot} concentrations in the influent. In agreement with the data in literature, the N_2O concentration was higher for lower values of the dissolved oxygen in the oxidation tank.

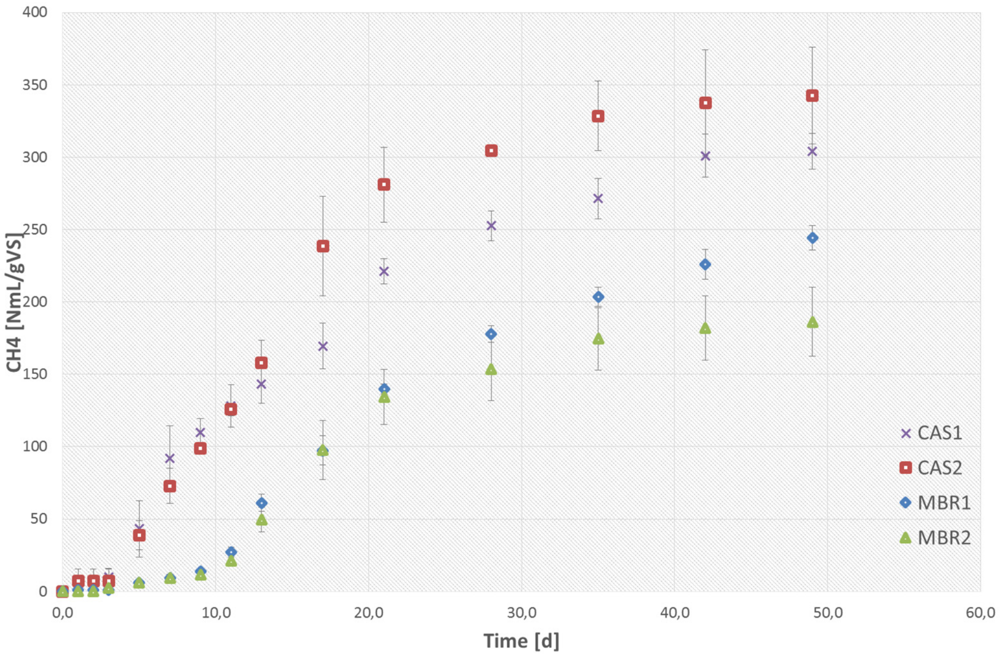


Figure 8. Cumulative specific methane productions of membrane bioreactor (MBR) sludge and Conventional Activated Sludge (CAS).

Moreover, not only were the trends similar, but the values obtained with the different procedures were also within the same range (differences lower than 0.5 ppm were always registered). Table 2 shows the nitrous oxide concentrations in the gaseous phase. The value of the nitrous oxide concentration monitored in the ambient air during the day varied between 0.2 and 0.4 ppm.

Table 2. Nitrous oxide concentration in the gaseous phase.

N_2O (ppm)	Online IR
Maximum	6.26
Minimum	2.81
Average	3.39

Considering the off-gas flow rate, the average nitrous oxide production was 8900 mg/h, while the maximum and the minimum values were 22,950 and 4450 mg/h.

On average, nitrogen emitted as N_2O from the oxidation tank represents 0.025% of the total inlet nitrogen. This value is in agreement with the data in literature [36]. Table 3 shows the average values of the nitrous oxide concentration in the gaseous and liquid phases during the afternoon.

Table 4 shows the CO_2 and the CH_4 concentrations measured in the off-gas. The average concentrations of CO_2 and CH_4 in the atmosphere monitored during the day were 635 and 1.77 ppm respectively.

Table 3. Nitrous oxide concentration in the gaseous (instantaneous off-line sampling) and in the liquid phase.

Nitrous Oxide Concentration	Gaseous Phase (ppm)	Liquid Phase (mg/L)
14:30–16:00	5.11	0.032
16:00–17:30	4.68	0.016
17:30–19:00	4.81	0.026

Table 4. CO_2 and CH_4 concentrations measured in the off-gas.

Off-Gas Flow Rate	CO_2 (ppm)	CH_4 (ppm)
Maximum	22129	4.72
Minimum	19364	0.54
Average	20889 (*n* = 244)	3.27 (*n* = 244)

Considering the off-gas flow rate, the average methane production was 0.03 kg CH_4/h.

By considering the CO_2 concentration data measured and the off-gas flow rate, the average CO_2 production is 9871 kgCO_2/d. The specific CO_2 emission is therefore 0.911 kgCO_2/kg$COD_{oxidized}$. The calculated value for the monitored WWTP is slightly lower than the specific CO_2 emission (1.1 kgCO_2/kg$COD_{oxidized}$) which is calculated by taking the general domestic wastewater formula ($C_{10}H_{19}NO_3$) into account. Considering the mass of CO_2, CH_4 and N_2O emitted and the respective global warming potential, the emission of GHGs from the whole WWTP is due to CO_2 for 94.8%, N_2O for 5.1% and CH_4 for 0.1%.

7. Conclusions

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, 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.

The aim of the experimental activities is to identify design and operational variables that have an important role both in energy consumption and GHG production, while maintaining a high quality of liquid effluents.

The main preliminary conclusions are the following:

- During the treatment with MBR of industrial wastewater, N_2O is mostly produced during the denitrification process. Conversely, in case of civil wastewater, the effect of the low C/N leads to the increase of N_2O production during the nitrification process.
- Concerning the modeling of the MBR treatment, the role of phosphorus in the contribution of accumulating organisms during the modeling of GHGs production should not be neglected. Furthermore, the uncertainty in the emission factors for CO_2 is higher than the uncertainty in the emission factors for N_2O.
- N_2O concentration in the off-gas of an aerobic digester increases with the increase of sludge stabilization. Nitrification plays an important role in N_2O emissions during aerobic digestion.
- Biomethanation potential (BMP) tests conducted on MBR and traditional CAS systems show that the SRT is not the sole parameter influencing the sludge BMP.
- All the measures have been carried out by following the same protocol, developed during the project. The proposed protocol [19] set up materials and methods for measuring GHG direct and indirect emissions of CO_2, CH_4 and N_2O from the water treatment line (*i.e.*, primary settler oxidation tank, secondary settler and/or MBR) and from the sludge treatment line (*i.e.*,

thickening, digestion and dewatering) and indirect emissions from the energy consumption due to aeration (oxidation tank and aerobic sludge treatment, if present).

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Author Contributions

All the authors designed the study and carried out the research activities. In particular, Donatella Caniani is the coordinator of the UO2, Giovanni Esposito is the coordinator of the UO3, Riccardo Gori is the coordinator of the UO4, and Giorgio Mannina is the coordinator of the UO1 and the Principal Investigator of the project. Donatella Caniani wrote the first draft of the manuscript, and all the authors made the revisions.

Conflicts of Interest

The authors declare no conflict of interest.

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