



Performance of wastewater treatment plants in emission of greenhouse gases

Ezio Ranieri ^{a,*}, Gianfranco D’Onghia ^{a,1}, Francesca Ranieri ^b, Luigi Lopopolo ^a, Sarah Gregorio ^a, Ada Cristina Ranieri ^{c,d}

^a Università degli Studi di Bari, Dipartimento di Bioscienze, Biotecnologie ed Ambiente, Bari, Italy

^b Università degli Studi di Foggia, Dipartimento di Dipartimento di Economia, Management e Territorio, Italy

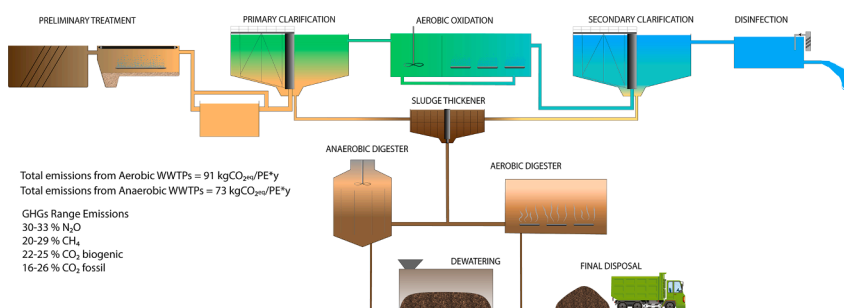
^c Politecnico di Bari, Dipartimento Interateneo di Fisica, Bari, Italy

^d Università Internazionale Telematica Uninettuno, Roma, Italy

HIGHLIGHTS

- CO₂, N₂O, CH₄, have been assessed in each treatment step in 183 Italian WWTP.
- Total emissions for aerobic digestion WWTP amount to 91 kgCO_{2eq}/PE*y as average.
- Total emissions for anaerobic digestion WWTP amount to 73 kgCO_{2eq}/PE*y as average.

GRAPHICAL ABSTRACT



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ABSTRACT

The present work has estimated greenhouse gas emissions in aerobic and anaerobic Wastewater Treatment Plants in Southern Italy. Greenhouse gases emissions from each treatment unit were calculated based on emission factors related to Chemical Oxygen Demand removal for biogenic CO₂ and CH₄ assessment and on Nitrogen removal for N₂O. N₂O, biogenic CO₂, and CH₄ emissions vary for aerobic and anaerobic-based WWTPs respectively from 73 kgCO_{2eq}/PE*y for anaerobic plants to 91 kgCO_{2eq}/PE*y for aerobic plants. In aerobic and anaerobic digestion systems WWTPs the contributions to CO_{2eq} total emissions from N₂O, CH₄, biogenic CO₂, and fossil CO₂ are 30 %–33 %, 20 %–29 %, 22 %–25 %, and 26 %–16 %, respectively. N₂O emissions from biological processes were found the most contributing sources of greenhouse gases while in the physical processes higher contribution is indirect carbon dioxide related to energy consumption. Compensatory measures are reported to reduce greenhouse gases emissions.

* Corresponding author.

E-mail address: ezio.ranieri@uniba.it (E. Ranieri).

¹ Consorzio Nazionale Interuniversitario per le Scienze del Mare CoNISMa, Italy.

1. Introduction

Wastewater treatment plants (WWTPs) are a significant source of Greenhouse Gases (GHGs), (Shahabadi et al., 2009; Daelman et al., 2013). In many European countries, the urban water cycle accounts for 1–3 % of the total electric energy consumption (Longo et al., 2016) and 3–10 % of the Global Warming Potential (GWP) by contributing towards GHG emissions into the atmosphere, both as direct and indirect footprints (Samuelsson et al., 2018). Different technologies for wastewater treatment are directly correlated to the amount of GHGs emissions (Ranieri et al., 2023). Electric energy consumed in the WWTPs is also a relevant GHGs source (Ranieri et al., 2021; Menduni et al., 2023). In addition, recently, an average increase in the energy requirements in WWTPs has been perceived due to technological upgrades for treatment to meet the more rigorous environmental standards (Van Lienden et al., 2010; Gandiglio et al., 2017). While fossil CO₂ emission in WWTPs is directly linked to the production of the energy required for the WWTP operation, in the biological wastewater treatment processes are emitted biogenic carbon dioxide (CO₂), methane (CH₄), and nitrous oxide (N₂O) (Cakir and Stenstrom, 2005; Xiuhong, et al., 2008; UNFCCC, 2018; Wang et al., 2022). The strength of wastewater and the degree of organic substances removal influence the GHGs emissions. So, the wastewater treatment process can reduce GHG emissions by up to 30 % under the controlled COD and N conditions (Yapıcıoğlu and Demir, 2021). The GHGs emissions correlated to the WWTPs processes may be directly reduced by appropriately selecting the treatment technology or enhancing the process and energy efficiency of the WWTPs (Ranieri et al., 2017). Usually, WWTP CH₄ emission is associated with anaerobic conditions (Monteith et al., 2005), while N₂O is produced mainly by biological treatment specifically within an activated sludge basin and aerobic digestion sludge (Valkova et al., 2021). Biogenic CO₂ is emitted generally in secondary biologic treatment and the aerobic sludge stabilization basin similar to N₂O emission due to bacterial metabolism or organic substances oxidation (Valkova et al., 2021; Ranieri et al., 2023), indeed fossil CO₂ emission is correlated to the electric energy consumption because production is principally based on fossil fuels (Larsen et al., 2015). In addition, CH₄ and N₂O have a 100-year global warming

potential (GWP) of 30 and 300 respectively (Ranieri et al., 2023), indicating that 1 kg of CH₄ released in the atmosphere equals 30 kg of CO₂ and 1 kg of N₂O released in the atmosphere 300 kg of CO₂. For municipal wastewater GHGs emissions in WWTPs range from 0.5 to 2.2 kg CO₂eq/m³ (Chen and Kuo, 2016; Chen, et al., 2019). Thereby, the adoption of more stringent treatments, requiring higher consumption of reagents and energy (Cardoso et al., 2021), resulting in increased emissions of climate-changing gases both direct and indirect from the integrated water service (Bakhshi and Demonsabert, 2012). Therefore, it becomes necessary to consider the energy and environmental aspects instead of capital and operative costs to develop more and more sustainable treatment wastewater treatment (Ranieri et al., 2023; Ranieri et al., 2021). Many studies have monitored and analysed total GHG emissions from wastewater plants, but the literature appears to be lacking regarding singular GHG for each unit of the plant due to a lack of data. Current GHGs quantification often doesn't consider differences in treatment processes. Many authors use IPCC emission factors which are considered CH₄ and N₂O centralized only into the aerobic and anaerobic process but neglecting the differentiation with other treatments and excluding account of CO₂, leading to large uncertainties of GHG emission factors. (IPCC, 2019). Meanwhile, the possibility to make wastewater management energy-neutral (or even energy-positive) has attracted considerable attention on different aspects (Menduni et al., 2020; Sharawat et al., 2021), and it should be possible to reduce the GHGs emissions from wastewater treatment plants to the aim of achieving climate neutrality concerning similar waste and wastewater treatment (EUDP, 2018; Wang et al., 2022).

The present study is aimed to carry out an environmental analysis of Apulian WWTPs (Fig. 1) based on the assessment of GHGs emissions associated with them.

The general aim of the paper is to estimate the GHGs distribution on the specific unit of aerobic or anaerobic digestion-based WWTP process to individuate where the emissions result higher and most contribute to climate change (Kalimeris et al., 2017). In addition, some technical suggestions will be figured out to understand how each GHG source could be reduced improving the sustainability of the wastewater treatment systems (Capodaglio et al., 2016). All this would result in

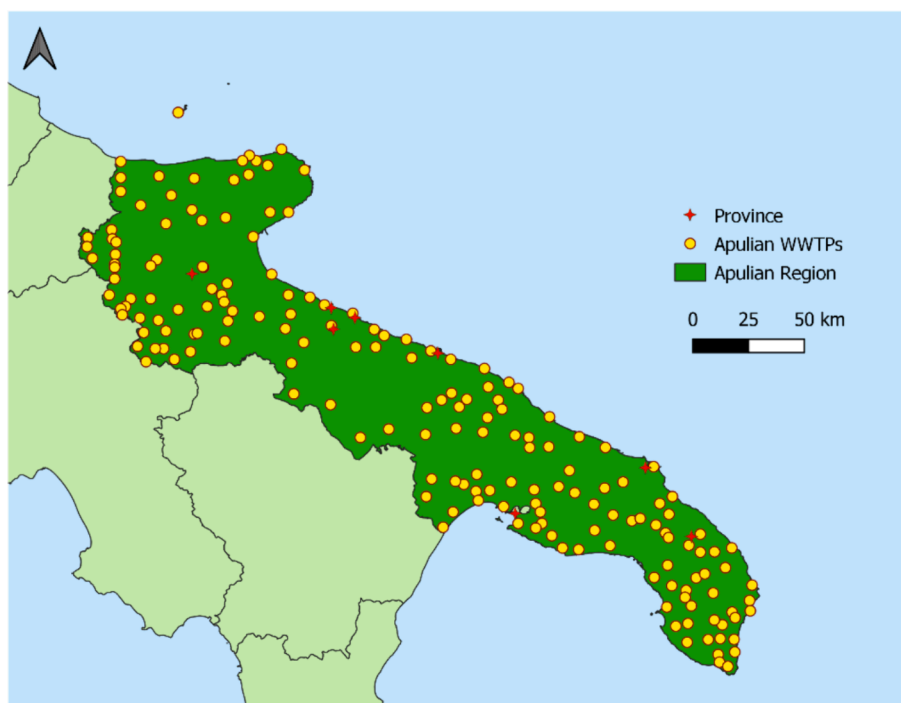


Fig. 1. Apulian WWTP analysed.

decreased energy consumption, treatment costs, and environmental impact (Petrella et al., 2016).

Therefore, the specific objectives of this paper are:

- To assess the COD and N removal in each wastewater treatment section of a conventional aerobic and anaerobic digestion-based WWTP
- To evaluate GHGs emitted in the pre-treatment section, biological section, secondary sedimentation, and sludge treatment
- To define what process measures should be done to reduce CO₂, N₂O, and CH₄ emissions.

2. Materials and methods

All the 183 WWTPs analysed for the present investigation are found throughout the Apulian region. They are managed by one of the largest Italian water management companies – Acquedotto Pugliese S.p.A. (AQP). 140 WWTPs are based on the aerobic process for sludge management while 43 are equipped with anaerobic digestion sludge (Ranieri et al., 2023).

2.1. Design plants compared

The typical configuration of aerobic plants is characterized by three steps to the water line and three steps to the sludge line, following reported. The first step is preliminary treatments of which only the grit tank was considered significant to analyse and quantify. It's constituted from an open tank that receives raw influent. The next treatment is based on Conventional Activated sludge (CAS), an open and ventilated tank to abatement biodegradable organic substances, and a circular settler to separate clarified water from the sludge (biomass generated by bacterial metabolism). The sludge from the biological treatment is collected, thickened, and transferred in a centrifuge unit for dewatering before being disposed of in a landfill. Each of them is an open tank and considered a source of emissions Anaerobic plants represent the comparison scenario where the first step is the same as an aerobic process. After these, in some cases, the grit tank follows a primary clarification before the biological process for the water treatment line. While, the sludge is thickened, and stabilized in anaerobic digestion and dewatering. Tertiary treatments: filtration and disinfection of the effluent before being discharged into the surface body are not included in the boundary system due lack of data in the literature to compare. Water in the outlet isn't reused within the plants or in urban and agricultural fields. Neither the sludge is reused nor the potential biogas, in the anaerobic scenario, isn't recovered but burned on the industrial torch.

2.2. Dataset of investigation

All starting data are average value refer to five years of investigation (from 2018 to 2022) as shown in Table 1. Aerobic WWTPs serving each an average population of about 10,543 PE, an average capacity of 1473 m³/d, and an average daily consumption of 1668 kwh/d. The raw sewage presents average influent of 1175 kgCOD/d and 115 kgN/d. On the other side, anaerobic WWTPs described previously, are larger, indeed serving each an average population of about 87,700 with average capacity plants of 11,646 m³/d and an average daily consumption of 6,501 kwh/d. The raw sewage presents an average influent of 10,330 kgCOD/d and 873 kgN/d.

To account for the emission from different scenarios and steps of

Table 1
Average value for Anaerobic and Aerobic WWTPs.

Average value	PE	kwh/d	m ³ /d	COD (kg/d)	N (kg/d)
Anaerobic	87,700	6,501	11,646	10,330	873
Aerobic	10,543	1,668	1,473	1,175	115

treatment, the CO₂eq from CH₄, N₂O, and CO₂ have been calculated with GHG Emission Factors (EF) in relationship to % of COD remotion and N remotion and their kg per day removed for each unit. Principally, emission factors of CH₄ and N₂O to biological treatments, thereby, aerobic oxidation and sludge digestion in aerobic and anaerobic processes have been taken from the IPCC, 2019 averaged with supplementary emission factors found in the literature. Table 2 shows the GHG emission inventory of wastewater facilities.

As reported by Wang et al. (2022), each Emission Factor (EF) result is specific for each WWTP. Thereby, in the EF analysis, it has been considered, wherever possible, similar EF where the same WWTP technology occurs. Thus, a range of values of emission factors have been considered to estimate emissions from each treatment.

Mass balance on carbon removal and N removal is based on knowledge of AQP facilities and wastewater samples analysis at the exit of each treatment section. Similar WWTP mass balances have been also considered (Mininni et al., 2015; Garrido et al., 2013; Mannina et al., 2009) with the aim of critically analyse the COD and N distribution in wastewater, sludge and air. Thus, the amount of each GHGs for all units of treatment is calculated using Eqs. (1), (2) and (3):

$$kgCH_4 = EF_{CH_4} (kgCH_4 / kgCOD_{removed}) \times kgCOD_{removed} \quad (1)$$

$$kgN_2O = EF_{N_2O} (kgN_2O / kgCOD_{removed}) \times kgN_{removed} \quad (2)$$

$$kgCO_{2biogenic} = EF_{CO_2} \times kgCOD_{removed} \quad (3)$$

Where: the EF is defined as the ratio of kilograms of greenhouse gas (GHG) emitted per kilogram of chemical oxygen demand (COD) or nitrogen (N) removed.

The kg COD removed is determined by multiplying the kg COD in the influent by the percentage removal of carbon at each station. Similarly, the kg N removed is calculated by multiplying the kg N in the influent by the percentage removal of nitrogen at each station. The multiplication of these emission factors and the kilograms of COD or N removed from each unit allows for the calculation of GHG emissions.

To convert the obtained kg GHG to kg CO₂ equivalent, the emissions of CH₄, N₂O, and CO₂ are multiplied by 30, 300, and 1, respectively, based on their global warming potential (GWP). The amount of fossil CO₂ is calculated using Eq. (4):

$$EF_{Electricconsumption} \quad (4)$$

Where: EF of electric energy is reported in the report of Acquedotto Pugliese (AQP, 2021).

2.3. Statistical analysis

A statistical analysis has been conducted. After identifying the outliers using the Generalized Extreme Value Distribution test from the software Past 4.13, they were removed from the dataset, this rigorous approach ensured the robustness of the analysis by excluding extreme values that could potentially bias the results. Following outlier removal, the Mann-Whitney U test was conducted to compare greenhouse gas emissions between aerobic and anaerobic wastewater treatment plants. Results indicated a significant difference (p < 0.05) in emissions, highlighting the impact of treatment methods on greenhouse gas outputs.

3. Result and discussion

The estimation of emissions by each treatment station related to AQP plants was based on COD and N removals, reported in flowcharts below, and based on experimental values collected on field and emission factors found in literature for GHGs emissions reported in Table 2.

As reported in the flow diagrams for aerobic (Fig. 2) and anaerobic plants (Fig. 3), it is shown that the removal of Chemical Oxygen Demand

Table 2
Emission factors to GHG for each treatment in aerobic/anaerobic WWTPs.

UNITS FOR AEROBIC AND ANAEROBIC WWTPs					
Emission factors	N ₂ O	CH ₄	CO ₂ biogenic	Notes	References
UNITS process PRELIMINARY TREATMENTS					
Oxidation ditch	0.2 gN ₂ O	0.9 kgCH ₄	2.1 kgCO ₂	7 × 10 ⁴ m ³ /d	Yan et al., 2014
Reversed A ² O	24.6 gN ₂ O	18.3 kgCH ₄	78.3 kgCO ₂	23 × 10 ⁴ m ³ /d	
A ² O	24.6 gN ₂ O	18.3 kgCH ₄	78.3 kgCO ₂	23 × 10 ⁴ m ³ /d	
A ² O			5.25gCO ₂ / m ³	CODin: 397 mg/L	Bao et al., 2014.
AO	//	//	4.38gCO ₂ / m ³	CODin: 384 mg/L	
Oxidation ditch			5.45gCO ₂ / m ³	CODin: 488 mg/L	
Aerated grit tank	1.6 × 10 ³ gN ₂ O/y	5.7 × 10 ⁴ gCH ₄ /y	3.9 × 10 ⁶ gCO ₂ /y	11,000 PE	Czepiel et al., 1993
Non-aerated grit tank	1.6 × 10 ² gN ₂ O/y	9.2 × 10 ⁴ gCH ₄ /y	1.1 × 10 ⁶ gCO ₂ /y	1.1 × 10 ³ L/y	Czepiel et al., 1995
WWTP 18,000 PE		Value Range	Value Range	CODin:318 ton/y	Marinelli et al., 2021
WWTP 22,000 PE	2.6 × 10 ⁻⁴ kg N ₂ O /kgNrem	1.3 × 10 ⁻⁴ –	4.1 × 10 ⁻³ – 0.1 kgCO ₂ / kgCODrem	CODin:444 ton/y	
WWTP10,000 PE		1.5 × 10 ⁻³ kg CH ₄ /kgCODin		CODin:237 ton/y	
		0.0075 kg CH ₄ /kg (CODinfluent – CODsludge)		Load COD influent (kg/ PE/y)	IPCC et al., 2019
	//		//	Load CODin sludge (kg/PE/y)	
UNITS process PRIMARY SETTLER					
A ² O			0.28 gCO ₂ /m ³		Bao et al., 2014
AO	//	//	0.25 gCO ₂ /m ³		
	//	0.34 g CH ₄ /m ³	//		Czepiel et al., (1993)
	//	0.16 g CH ₄ /m ³	//		Wang et al., (2011)
	0.00055 kgN ₂ O/kgNrem	0.00084 kg CH ₄ /kgCOD removed	//		Samuelsson et al., 2018
UNITS process AEROBIC OXIDATION					
Oxidation ditch	4975 gN ₂ O	88 kgCH ₄	4128.3 kgCO ₂	7 × 10 ⁴ m ³ in/d	Yan et al., 2014
Reversed A ² O	6718.1 gN ₂ O	147.7 kgCH ₄	13743.1 kgCO ₂	23 × 10 ⁴ m ³ in/d	
A ² O	9778.8 gN ₂ O	74.4 kgCH ₄	24,878 kgCO ₂	23 × 10 ⁴ m ³ in/d	
A ² O			168.65 gCO ₂ / m ³	CODin: 397 mg/L	Bao et al., 2014
AO	//	//	167.99 gCO ₂ / m ³	CODin: 384 mg/L	
Oxidation ditch			355.87 gCO ₂ / m ³	CODin: 488 mg/L	
Active sludge (15,000 PE)	0.00032 kgN ₂ O-N/ kgNH ₄ -N in	//	//	NH ₄ -Nin:52.4 mg/l	Caniani et al., 2019
Italian CAS	0.027 g N ₂ O-N	//	//	30,000 PE	Gori et al., 2016
Netherlands CAS	0.25 g N-N ₂ O/N	//	//		
Activated sludge (11,000 PE)	3.2 × 10 ⁴ gN ₂ O/L	2.2 × 10 ⁵ gCH ₄ /y	3.6 × 10 ⁸ gCO ₂ /y	1.1 × 10 ³ L/y	Czepiel et al., 1993 Czepiel et al., 1995
WWTP 1–6 (>15,000 PE)	Value range	Value Range	Value Range		Marinelli et al., 2021
WWTP 7–12 (<15,000 PE)	6.7 × 10 ⁻⁸ to 0.02 kg N ₂ O/kgNrem	2.2 × 10 ⁻⁸ to 0.003 kg CH ₄ /kgCODin	1.8 × 10 ⁻⁵ to 3.1 kg CO ₂ /kgCODrem		
	0.025 kg N ₂ O /kgTN	0	//	working efficiently	Noyola et al., 2018
		0.075 kg CH ₄ /kgCOD	//		IPCC, 2019
UNITS process SECONDARY SETTLER					
Oxidation ditch	114.3 kgN ₂ O	0 kgCH ₄	43.4 kgCO ₂	7 × 10 ⁴ m ³ in/d	Yan et al., 2014
Reversed A ² O	829.2 kgN ₂ O	0 kgCH ₄	181.7 kgCO ₂	23 × 10 ⁴ m ³ in/d	
A ² O	240.1 kgN ₂ O	0 kgCH ₄	211.4 kgCO ₂	23 × 10 ⁴ m ³ in/d	
A ² O			0.52 gCO ₂ / m ³	CODin: 397 mg/L	Bao et al., 2014.
AO	//	//	0.41 gCO ₂ / m ³	CODin: 384 mg/L	
Oxidation Ditch			2.08 gCO ₂ / m ³	CODin: 488 mg/L	
UNITS process SLUDGE THICKENER TANK					
Oxidation Ditch	//	//	0.07 gCO ₂ /m ³	CODin: 488 mg/L	Bao et al., 2014
UNITS process AEROBIC STABILIZATION					
11,000 PE	1.7 × 10 ³ gN ₂ O/L	6.3 × 10 ⁴ gCH ₄ /y	2.1 × 10 ⁷ gCO ₂ /y	1.1 × 10 ³ L/y	Czepiel et al., 1993 Czepiel et al., 1995
WWTP 6 (<15,000 PE)	8.9 × 10 ⁻⁸ kg N ₂ O/kgTS	3.8 × 10 ⁻⁷ kg CH ₄ / kgTS	1.3 × 10 ⁻³ kg CO ₂ /kgTS	TS unspecified	Marinelli et al., 2021
	//	0.15 g CH ₄ /PE-d	//		Daelman et al., 2013
PE > 5000	0.001 kg N ₂ O-N/kg N	//	//		Valkova et al. (2021)
	0.00024 kg N ₂ O/kg N	0 kgCH ₄ /kgCOD	//		IPCC, 2019
UNITS process ANAEROBIC DIGESTION					

(continued on next page)

Table 2 (continued)

UNITS FOR AEROBIC AND ANAEROBIC WWTPs					
Emission factors	N ₂ O	CH ₄	CO ₂ biogenic	Notes	References
	//	0.34 gCH ₄ /PE·d			Daelman et al., 2013
	//	3.44 g CH ₄ /m ³	//		Wang et al., 2022
	0	0.2	0.38 kgCO ₂ /kgCOD		IPCC, 2019

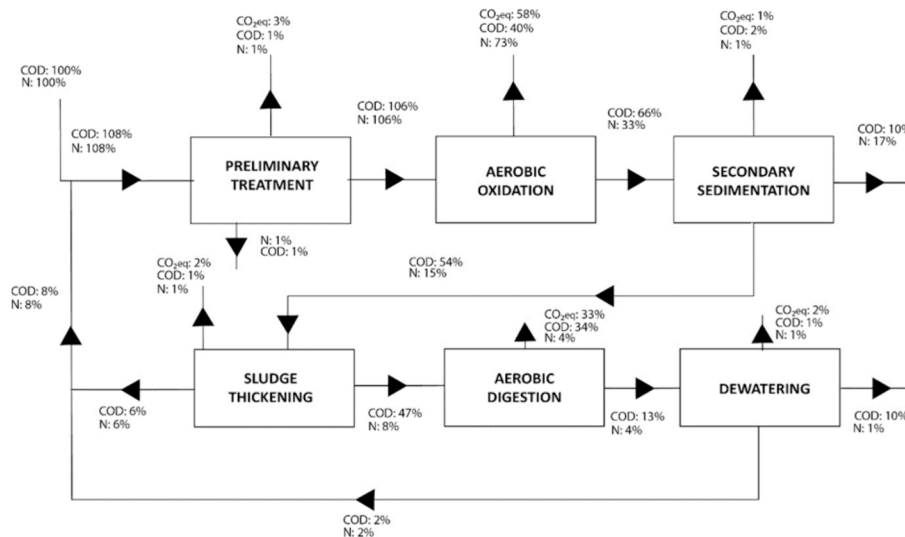


Fig. 2. Mass balance of Aerobic Wastewater Treatment Plant in terms of COD, Ntot, and CO₂eq.

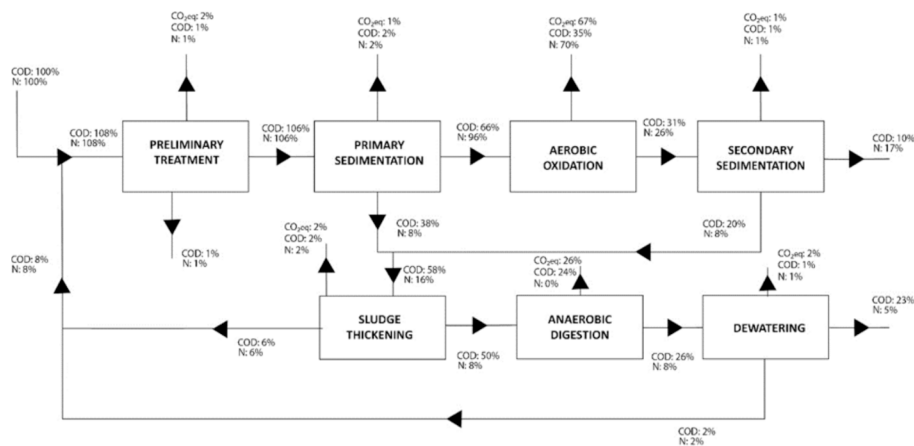


Fig. 3. Mass balance of Anaerobic Wastewater Treatment Plant in terms of COD, Ntot, and CO₂eq.

(COD) and Nitrogen (N) predominantly occurs in biological oxidation and sludge line digestion. In the aerobic WWTPs, aerobic oxidation reduces COD by 40 % and N by 73 % with 58 kg CO₂eq emitted while aerobic digestion removes 34 % of COD and 4 % of N with 33 kg CO₂eq released. These values are near to the scenario hypothesized by Garrido et al. (2013), particularly analysing COD removal efficiency in the digester sludge systems. The varying organic substance percentages in sludge highlight the potential benefits of concentrating carbon in sludge, both for its soil amendment properties and the reduction of greenhouse gas emissions. While aerobic digestion plant sludge exhibits 10 % COD and 1 % N, anaerobic digestion plant sludge shows higher concentrations at 23 % COD and 5 % N. This difference suggests the potential for enhanced carbon sequestration and reduced atmospheric greenhouse gas emissions in anaerobic digestion systems.

Indeed, in the case of the anaerobic WWTPs, aerobic oxidation

removes COD by 35 % and N by 70 %, while anaerobic digestion removes 24 % of COD.

As illustrated in Fig. 3, COD and N content in sludge is higher when derived from the anaerobic plant, due to the presence of primary settler, into account that it contributes around 30 % of the influent BOD on the sludge (Metcalf and Eddy, 2003). This outcome in the CO₂eq comes from the operations of anaerobic plants being lower compared to that of aerobic plants.

Fig. 4 shows direct GHGs contributions in each section of treatment both aerobic and anaerobic plants.

As higher rates of COD and N removal in biological processes have been found, the higher contribution of emissions in these phases has been relatively quantified.

The total annual emissions are displayed in Fig. 4 and resulted in 91 kgCO₂eq/PE*Y (Person Equivalent per Year) in aerobic WWTPs equal to

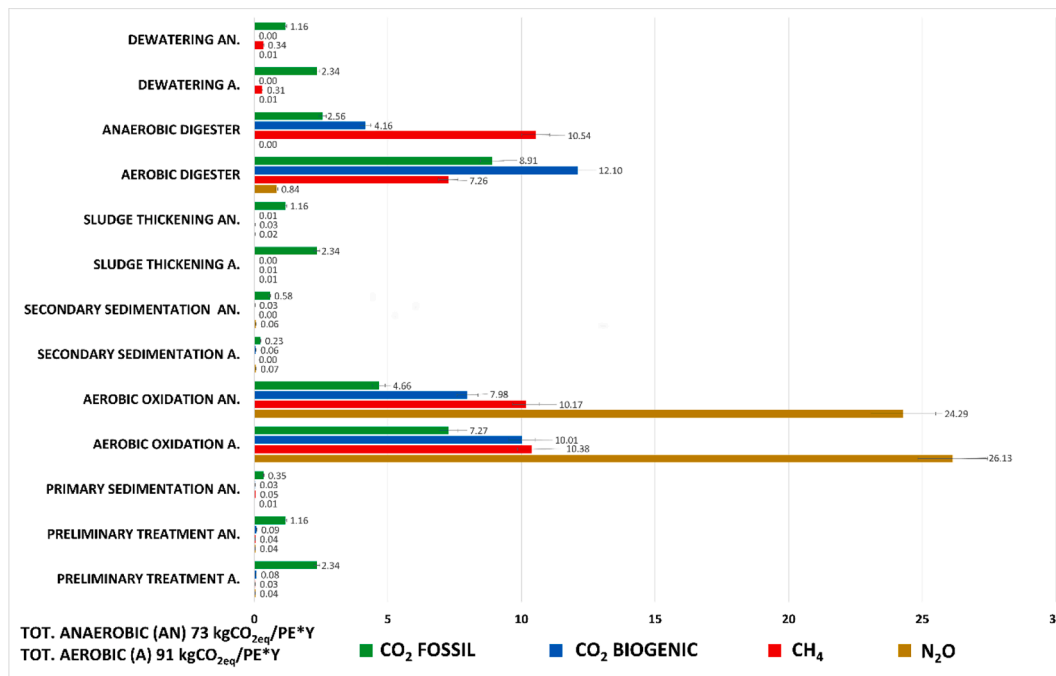


Fig. 4. Emissions in kgCO₂eq for each section of the anaerobic and aerobic plant arising from N₂O, CH₄, biogenic CO₂, and fossil CO₂.

1.8 kg CO₂eq/m³ and 73 kgCO₂ eq/PE*Y in anaerobic WWTPs equal to 1.4 kg O₂eq/m³.

In aerobic WWTPs have been estimated total annual emissions of 91 kgCO₂ eq/PE*Y (Person Equivalent per Year) equal to be 1.8 kg CO₂eq/m³.

According to Yan et al., 2014, the aerators and circulating flow of dissolved N₂O in the biological basins had a great impact on total GHG emission, which resulted in a discrepancy between the GHG generation and GHG emission amount.

Aerobic oxidation has resulted N₂O contribute, as average, by 26 kgCO₂eq/PE*Y, CH₄ contribute by 7 kgCO₂eq/PE*Y, biogenic kgCO₂ contribute by 22 kgCO₂eq/PE*Y and fossil CO₂ by 23 kgCO₂eq/PE*Y. In aerobic digester the N₂O contribution has been estimated to be lower than 1 kgCO₂eq/PE*Y, CH₄ contributes approx. 7 kgCO₂eq/PE*Y, biogenic kgCO₂ contribute 12 kgCO₂eq/PE*Y and fossil CO₂ approx. 9 kgCO₂eq/PE*Y.

These values obtained from this simulation have resulted higher than those measured by Caniani et al., 2019 which presented a smaller plant with scarce efficiency in the aeration system and utilised several emission factors. For instance, the N₂O fraction was calculated with an emission factor of 0.00032 corresponding to 0.032 % of influent TKN (Total Kjeldahl Nitrogen) and resulted in 70 gN₂O/day from the aeration tank. Moreover, Marinelli et al., (2021) highlight that the emission factor values were inversely proportional to the WWTP size, resulting in higher specific values for the smallest WWTP plant (<15,000 PE) about 0.27 kg N₂O/kgTNrem.

In addition, the COD/TKN ratio significantly influences direct GHG emissions and specifically N₂O emissions. A rapid increase in TKN concentration led to an increase in N₂O emissions in the aerobic reactors (Mannina et al., 2019).

Foley et al., (2010) and Law et al. (2012) found an inverse proportionality in the considered WWTPs between high levels of nitrogen removal and N₂O emitted.

Nitrous oxide emissions from wastewater treatment plants vary substantially between plants, ranging from negligible to substantial, depending on the operability of the system (He et al., 2023). Kampschreur et al., (2009) and Massara et al., (2017) evidenced that N₂O release in the atmosphere is regulated by the slow growth of denitrifying

bacteria, low chemical oxygen demand to nitrogen (low C/N ratio), low dissolved oxygen, low temperature, and low SRT. According to these findings, some compensatory measures have been introduced in Apulian WWTPs (D’Onghia et al., 2024).

In anaerobic WWTPs have accounted for total annual emissions of 73 kgCO₂eq/PE*Y equal to 1.4 kg CO₂eq/m³ with N₂O contributing by 24 kgCO₂eq/PE*Y, CH₄ contributing by 21 kgCO₂eq/PE*Y, biogenic CO₂ contributing by 16 kgCO₂eq/PE*Y and fossil CO₂ by 11 kgCO₂eq/PE*Y showing that the presence of the primary sedimentation step, before the aeration tank, does not interfere with the N₂O emissions released in the aeration tank and there is not much difference in terms of emissions released into the atmosphere in this step. It is evident that anaerobic digestion doesn’t emit significant N₂O emissions but results in high emissions of CH₄ and CO₂.

Cakir and Stenstrom, 2005 in their study shown how at higher wastewater strengths there is sufficient CO₂ and CH₄ production to reduce the nitrogen concentrations to the low levels usually observed in anaerobic digesters.

The emission of GHGs produced in the considered Apulian in terms of CO₂eq has been estimated as reported in Table 3:

In both typologies of plant, the most impactful units were biological treatment (aerobic oxidation and sludge digestion) with a contribution of 58 % and 33 % on the total CO₂eq emitted respectively to aerobic plants and 67 % and 26 % to anaerobic plants. This is probably due to the decay rate of the substance.

Shahabadi et al., (2009) show that emissions from the oxidation tank increase sharply with increasing decay rate and that they had significant effects on the total amount of GHGs emissions, up to 62 % as total.

Table 3

GHGs Emission (in kgCO₂eq/PE*Y) produced by Apulian wastewater treatment plants.

TOTAL EMISSIONS	N ₂ O (SD)	CH ₄ (SD)	Biogenic CO ₂ (SD)	Fossil CO ₂ (SD)
AEROBIC PLANTS	27 (1.21)	18 (0.82)	22 (0.92)	23 (0.98)
ANAEROBIC PLANTS	24 (1.05)	21 (0.97)	16 (0.75)	11 (0.52)

Concerning fossil CO₂ emission, in the biological treatments is due to the electricity consumption of air blowers, and in the remained physical treatments is due to the electricity consumption of pumps in both aerobic and anaerobic plants. It can be seen that aerobic ones are more energy-intensive.

In Fig. 5 the percentages of each GHGs contribution per treatment unit are shown, respectively for aerobic and anaerobic WWTPs.

The highest fluxes of GHGs refer to N₂O followed by CH₄, biogenic CO₂ in biological steps while in physical steps the largest contribution is due to fossil CO₂.

Most of the N₂O was released from the nitrification process in the aerobic oxidation tank and the N₂O emission factor significantly affected the contribution of N₂O emission to the total GHGs production. Higher N₂O emissions from aerobic oxidation tanks have been shown by Yan et al. (2014) and He et al., 2023. Czepiel et al. (1993), based on an annual wastewater flow of 1.1×10^9 L/y, reported annual fluxes to be 5.6×10^9 gCH₄/y from primary treatment and 7.9×10^9 gCH₄/y from

secondary activated sludge treatment. The IPCC Guidelines (2006) reported that the highest CH₄ emission occurs in aerobic oxidation, sludge digestion, and primary settler and established that a well-managed treatment facility using conventional activated sludge normally produces little or no CH₄. The high contribution that has been found in both plants could be due to low dissolved oxygen concentration (<0.2 mg/l) in aerobic oxidation and dissolved methane in aerobic digestion and dewatering unit as reported by Wang et al., (2011), indeed the methane emission factor is much higher than those values reported by Yan et al., (2014) and Czepiel et al. (1993). In anaerobic plants, especially in primary sedimentation, CH₄ emissions can be formed as a result of inadequate underflow removal leading to deep sludge blankets (Monteith et al., 2005) and in the anaerobic digester step, partly emitted as fugitive CH₄ from scruffy pipes, and partly in flare and converted into CO₂. On the basis of the mass balance reported in Fig. 3, in terms of the initial COD percentage, the average theoretical production of methane in Apulian anaerobic digestion is 1.287 kg CH₄/AE*y. The average

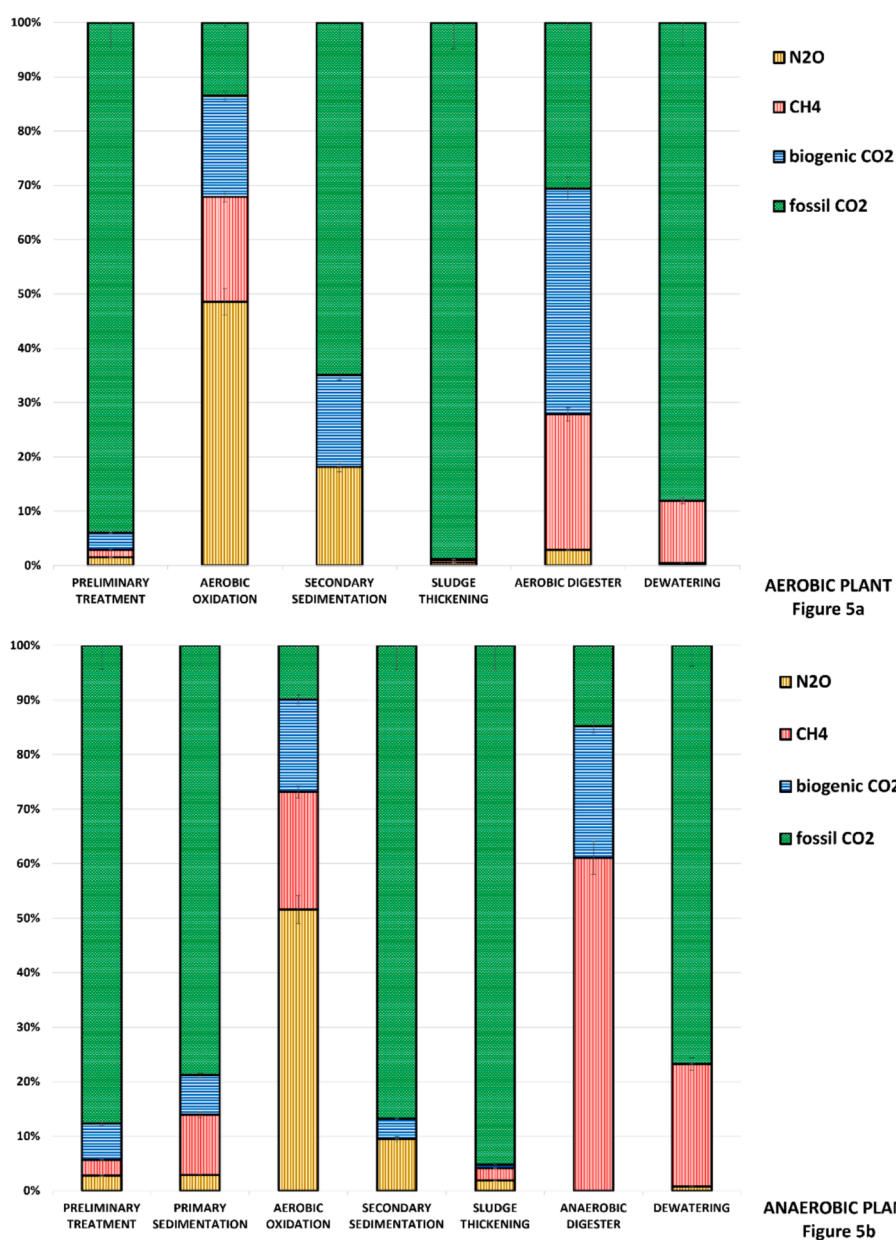


Fig. 5. (a) Percentage contribution to the total emission of CH₄, N₂O, biogenic, and fossil CO₂, for each section of the aerobic plant. (b) Percentage contribution to the total emission of CH₄, N₂O, biogenic, and fossil CO₂, for each section of the anaerobic plant.

measured methane production in all plants is 1.222 kgCH₄/AE*y that reveal a methane loss of 0.065 kg CH₄/AE*y as average, equal to approx 5.1 % of the total CH₄ production in the anaerobic based WWTPs and 18.5 % of the total GHGs emission from the anaerobic digester, in terms of kg CO₂/AE*y, as average (Fig. 6). CH₄ fugitive emissions values are slightly higher than others reported in similar experiences (Liebetrau et al., 2010; Tauber et al., 2019).

Yoshida et al., (2014) reported that the fugitive emissions represent between 2 and 10 % of the total methane emissions that characterize biogas and if there are failures in the biogas production and transport these values could become even higher.

Methane can be produced, in a low quantity, less than 1 kgCO_{2eq}/PE*y, also in grit tanks and preliminary treatments, depending on biological nutrient decomposition processes in the sewer systems (Guisa-sola et al., 2008, Yan et al., 2014).

Finally, it can be seen that biogenic CO₂ characterizes mainly aerobic digesters differently from anaerobic digesters.

Cakir and Stenstrom (2005) in their study showed how CO₂ emission from an aerobic digester could be produced ranging from 1 to 10 tons/day as a function of the BOD while in an anaerobic digester, it could be assumed up to zero if CH₄ it would have recovered. Caniani et al., (2019), also considering the same emission value to measure indirect emission released from air diffusers, found 35,8 tCO₂/y (for each treatment line) and 4.8 kgCO₂/year/inhabitants. Marinelli et al., (2021) quantified biogenic CO₂ in 25 % of the impact on total carbon footprint and indirect emissions due to energy consumption ranging from 10 to 40 % as a function of the carbon and nitrogen removed loads in the different WWTPs.

Possible compensatory measures for reducing N₂O emissions concern new sludge line with the recirculation flow from the sludge thickener directly in the anoxic section of the biological compartment to increase the C/N ratio and to limit O₂ presence in this anoxic basin (D'Onghia et al., 2024) and the use of covers for stations are also potential strategies. This strategy has been recently implemented in the upgrading of three Apulian wastewater treatment plants connecting a by-pass line from the sludge thickener direct to the denitrification step determining a N₂O emission reduction of approx. 38 % than in configuration previous the upgrade.

Possible compensatory measures for reducing CH₄ emissions may include preventing biogas leaks from digesters, in anaerobic plants. In some anaerobic digestion plants, biogas is currently incinerated, producing CO₂. Recovering and utilizing this biogas for on-site electricity generation could significantly reduce environmental impact, mitigating greenhouse gas emissions and enhancing overall energy efficiency.

Possible compensatory measures for reducing CO₂ emissions may include the reduction of electrical consumption by using artificial intelligence to control and optimize the biological process and to enhance operational efficiency, particularly for pumping stations and recirculation in aerobic and anaerobic wastewater treatment systems.

4. Conclusions

N₂O emissions are the most significant in terms of their contribution to the overall carbon footprint, especially in secondary biological treatments, in both aerobic and anaerobic plants, ranging from 24 kgCO_{2eq}/PE*y for anaerobic plants to 27 kgCO_{2eq}/PE*y for aerobic plants. The flow varies depending on various operating parameters as well as plant characteristics and technologies and this proves that N₂O may be mitigated through proper functionality of the system.

The total emissions for aerobic digestion plants amount to 91 kgCO_{2eq}/PE*y, whereas for anaerobic digestion plants is 73 kgCO_{2eq}/PE*y.

CRediT authorship contribution statement

Ezio Ranieri: Project administration, Conceptualization.

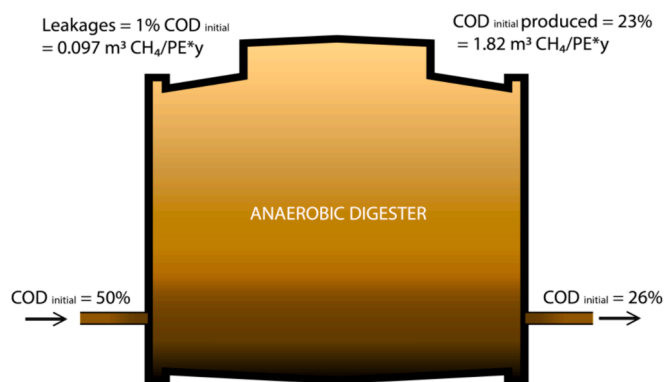


Fig. 6. Methane production and fugitive emission. COD initial Mass Balance in the anaerobic digester. Average values.

Gianfranco D'Onghia: . **Francesca Ranieri:** Formal analysis. **Luigi Lopopolo:** Validation. **Sarah Gregorio:** Investigation. **Ada Cristina Ranieri:** Data curation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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References

- Acquedotto Pugliese (AQP), 2019-21. Social budget document: wastewater treatment plant data.
- Bakhshi, A.A., Demonsabert, S.M., 2012. Estimating the carbon footprint of the municipal water cycle. *J. Am. Water Works Ass.* 104 (5), E337–E347.
- Bao, Z., Sun, S., Sun, D., 2014. Characteristics of direct CO₂ emissions in four full-scale wastewater treatment plants. *Desalin. Water Treat.* <https://doi.org/10.1080/19443994.2014.940389>.
- Cakir, F.Y., Stenstrom, M.K., 2005. Greenhouse gas production: a comparison between aerobic and anaerobic wastewater treatment technology. *Water Res.* Oct 39 (17), 4197–4203. [10.1016/j.watres.2005.07.042](https://doi.org/10.1016/j.watres.2005.07.042).
- Caniani, D., Caivano, M., Pascale, R., Bianco, G., Mancini, I., Masi, S., Mazzone, G., Firouzian, M., Rosso, D., 2019. CO₂ and N₂O from water resource recovery facilities: Evaluation of emissions from biological treatment, settling, disinfection, and receiving water body. *Sci. Total Environ.* 648, 1130–1140.
- Capodaglio, A.G., Ranieri, E., Torretta, V., 2016. Process enhancement for maximization of methane production in codigestion biogas plants. *Manag. Environ. Qual.* 27 (3), 289–298. <https://doi.org/10.1108/MEQ-04-2015-0059>.
- Cardoso, B.J., Rodrigues, E., Gaspar, A.R., Gomes, A., 2021. Analysis of Specific Energy Consumption of Wastewater Treatment Plants in the North of Portugal. In: *International Conference on Water Energy Food and Sustainability*. Springer International Publishing, Cham, pp. 361–369.
- Chen, Y.C., Kuo, J., 2016. Potential of greenhouse gas emissions from sewage sludge management: a case study of Taiwan. *J. Clean. Prod.* 129, 196–201.
- Chen, X., Mielczarek, A.T., Habicht, K., Andersen, M.H., Thornberg, D., Sin, G., 2019. 431 Assessment of full-scale N₂O emission characteristics and testing of control concepts in an 432 activated sludge wastewater treatment plant with alternating aerobic and anoxic phases. 433. *Environ. Sci. Technol.* 53 (21), 12485–12494.
- Czepiel, P.M., Crill, P.M., Harriss, R.C., 1993. Methane emissions from municipal wastewater treatment processes. *Environ. Sci. Technol.* 27 (12), 2472–2477.

- Czepiel, P., Crill, P., Harriss, R., 1995 Sep 1. Nitrous oxide emissions from municipal wastewater treatment. *Environ. Sci. Technol.* 29 (9), 2352–2356. <https://doi.org/10.1021/es00009a030>.
- Daelman, M.R.J., van Voorhuizen, E.M., van Dongen, L.G.J.M., van Loosdrecht, M.C.M., Volcke, E.I.P., 2013. Methane and nitrous oxide emissions from municipal wastewater treatment – results from a long-term study. *Water Sci. Technol.* 67 (10), 2350–2355.
- D’Onghia, G., Ranieri, E., Ranieri, F., Lopopolo, L., Gregorio, S., Ranieri, A.C., 2024. Compensatory measures to reduce GHGs in wastewater treatment plants in Southern Italy. *J. Water Process Eng.* 60, 105128.
- EUDP, 2018. EUDP 14-II. J.nr. 64014-0565, pp. 1–50.
- Foley, J., de Haas, D., Yuan, Z., Lant, P., 2010. Nitrous oxide generation in full-scale biological nutrient removal wastewater treatment plants. *Water Res.* 44, 831–844.
- Gandiglio, M., Lanzini, A., Soto, A., Leone, P., Santarelli, M., 2017. Enhancing the energy efficiency of wastewater treatment plants through co-digestion and fuel cell systems. *Front. Environ. Sci.* 5, 70.
- Garrido, J.M., Fdz-Polanco, M., Fdz-Polanco, F., 2013. Working with energy and mass balances: a conceptual framework to understand the limits of municipal wastewater treatment. *Water Sci. Technol.* 67 (10), 2294–2301.
- Gori, R., G. Bellandi, and C. Caretti, 2016. “Experience, progresses and perspectives of off-gas testing in wastewater treatment: From aeration efficiency towards CFP assessment.” In *Proc., SIDISA 2016*. Roma: DEI Tipografia del Genio Civile.
- Guisasola, A., de Haas, D., Keller, J., Yuan, Z., 2008. Methane formation in sewer systems. *Water Res.* 42 (6–7), 1421–1430.
- He, X., Li, Z., Xing, C., Li, Y., Liu, M., Gao, X., Ding, Y., Lu, L., Liu, C., Li, C., Wang, D., 2023. Carbon footprint of a conventional wastewater treatment plant: An analysis of water-energy nexus from life cycle perspective for emission reduction. *J. Clean. Prod.* 429, 139562.
- IPCC (2019) Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories.
- Kalimeris, A., Ranieri, E., Founda, D., Norrant, C., 2017. Variability Modes of Precipitation along a Central Mediterranean Area and Their Relations with ENSO, NAO, and Other Climatic Patterns. *Atmos. Res.* 198, 56–80. <https://doi.org/10.1016/j.atmosres.2017.07.031>.
- Kampschreur, M.J., Temmink, H., Kleerebezem, R., Jetten, M.S., van Loosdrecht, M.C., 2009. Nitrous oxide emission during wastewater treatment. *Water Res.* 43 (17), 4093–4103.
- Liebetrau, J., Clemens, J., Cuhls, C., Hafermann, C., Friehe, J., Weiland, P., Daniel-Gromke, J. (2010). Methane emissions from biogas-producing facilities within the agricultural sector (Vol. 10, No. 6, pp. 595–599). Weinheim: WILEY-VCH Verlag.
- Longo, S., d’Antoni, B.M., Bongards, M., Chaparro, A., Cronrath, A., Fatone, F., Hospido, A., 2016. Monitoring and diagnosis of energy consumption in wastewater treatment plants. A state of the art and proposals for improvement. *Appl. Energy* 179, 1251–1268.
- Mannina, G., Rebouças, T.F., Cosenza, A., Chandran, K., 2019. A plant-wide wastewater treatment plant model for carbon and energy footprint: model application and scenario analysis. *J. Clean. Prod.* 217, 244–256.
- Marinelli, E., Radini, S., Foglia, A., Lancioni, N., Piasentin, A., Eusebi, A.L., Fatone, F., 2021. Validation of an evidence-based methodology to support regional carbon footprint assessment and decarbonisation of wastewater treatment service in Italy. *Water Res.* 207, 117831 <https://doi.org/10.1016/j.watres.2021.117831>.
- Massara, T.M., Malamis, S., Guisasola, A., Baeza, J.A., Noutsopoulos, C., Katsou, E., 2017. A review on nitrous oxide (N₂O) emissions during biological nutrient removal from municipal wastewater and sludge reject water. *Sci. Total Environ.* 596, 106–123.
- Menduni, G., Sgobba, F., Russo, S.D., Ranieri, A.C., Sampaolo, A., Patimisco, P., Giglio, M., et al., 2020. Fiber-coupled quartz-enhanced photoacoustic spectroscopy system for methane and ethane monitoring in the near-infrared spectral range. *Molecules* 25 (23). <https://doi.org/10.3390/molecules25235607>.
- Menduni, G., Zifarelli, A., Kniazeva, E., Dello Russo, S., Ranieri, A.C., Ranieri, E., Patimisco, P., Sampaolo, A., Giglio, M., Manassero, F., Dinuccio, E., Provolò, G., Wu, H., Lei, D., Spagnolo, V., 2023. Measurement of methane, nitrous oxide and ammonia in atmosphere with a compact quartz-enhanced photoacoustic sensor. *Sens. Actuators B* 375, 132953.
- Mininni, G., Laera, G., Bertanza, G., Canato, M., Sbrilli, A., 2015. Mass and energy balances of sludge processing in reference and upgraded wastewater treatment plants. *Environ. Sci. Pollut. Res.* 22, 7203–7215.
- Monteith, H.D., Sahely, H.R., MacLean, H.L., Bagley, D.M., 2005. A rational procedure for estimation of greenhouse-gas emissions from municipal wastewater treatment plants. *Water Environ. Res.* 77 (4), 390–403.
- Noyola, A., Paredes, M.G., Güereca, L.P., Molina, L.T., Zavala, M., 2018. Methane correction factors for estimating emissions from aerobic wastewater treatment facilities based on field data in Mexico and on literature review. *Sci. Total Environ.* 639, 84–91.
- Petrella, A., Mascolo, G., Murgolo, S., Petruzzelli, V., Ranieri, E., Spasiano, D., Petruzzelli, D., 2016. Photocatalytic oxidation of organic micro-pollutants: pilot plant investigation and mechanistic aspects of the degradation reaction. *Chem. Eng. Commun.* 203 (10), 1298–1307. <https://doi.org/10.1080/00986445.2016.1188292>.
- Ranieri, E., Ionescu, G., Fedele, A., Palmieri, E., Ranieri, A.C., Campanaro V., 2017. Sampling, characterisation and processing of solid recovered fuel production from municipal solid waste: An Italian plant case study. *Waste Manag. Res.* Aug;35(8):890–898. doi: 10.1177/0734242X17716276.
- Ranieri, E., Giuliano, S., Ranieri, A.C., 2021. Energy consumption in anaerobic and aerobic based wastewater treatment plants in Italy. *Water Pract. Technol.* 16 (3), 851–863. <https://doi.org/10.2166/wpt.2021.045>.
- Ranieri, E., D’Onghia, G., Lopopolo, L., Gikas, P., Ranieri, F., Gika, E., Spagnolo, V., Ranieri, A.C., 2023. Evaluation of greenhouse gas emissions from aerobic and anaerobic wastewater treatment plants in Southeast of Italy. *J. Environ. Manage.* 337, 117767.
- Samuelsson, J., Delre, A., Tumlin, S., Hadi, S., Offerle, B., Scheutz, C., 2018. Optical technologies applied alongside on-site and remote approaches for climate gas emission quantification at a wastewater treatment plant. *Water Res.* 131, 299–309.
- Shahabadi, M.B., Yerushalmi, L., Haghight, F., 2009. Impact of process design on greenhouse gas (GHG) generation by wastewater treatment plants. *Water Res.* 43 (10), 2679–2687.
- Sharawat, I., Dahiya, R., Dahiya, R.P., 2021. Analysis of a wastewater treatment plant for energy consumption and greenhouse gas emissions. *Int. J. Environ. Sci. Technol.* 18, 871–884.
- Tauber, J., Parravicini, V., Svardal, K., Krampe, J., 2019 Nov. Quantifying methane emissions from anaerobic digesters. *Water Sci. Technol.* 80 (9), 1654–1661. <https://doi.org/10.2166/wst.2019.415>.
- UNFCCC, 2018. UN Framework Convention on Climate Change: Climate Change Annual Report.
- Valkova, T., Parravicini, V., Saracevic, E., Tauber, J., Svardal, K., Krampe, J., 2021. A method to estimate the direct nitrous oxide emissions of municipal wastewater treatment plants based on the degree of nitrogen removal. *J. Environ. Manage.* 279, 111563.
- Van Lienden, C., Shan, L., Rao, S., Ranieri, E., Young, T.M., 2010. Metals removal from stormwater by commercial and non-commercial granular activated carbons. *Water Environ. Res.* 82 (4), 351–356. <https://doi.org/10.2175/106143009X12487095236874>.
- Wang, D., Ye, W., Wu, G., Li, R., Guan, Y., Zhang, W., Hubacek, K., 2022. Greenhouse gas emissions from municipal wastewater treatment facilities in China from 2006 to 2019. *Sci. Data* 9 (1), 317.
- Wang, J., Zhang, J., Xie, H., Qi, P., Ren, Y., Hu, Z., 2011. Methane emissions from a full-scale A/A/O wastewater treatment plant. *Bioresour. Technol.* 102 (9), 5479–5485.
- Xiuhong, L., Yi, P., Changyong, W., Takigawa, A.K.I.O., Yongzhen, P.E.N.G., 2008. Nitrous oxide production during nitrogen removal from domestic wastewater in lab-scale sequencing batch reactor. *J. Environ. Sci.* 20 (6), 641–645.
- Yan, X., Li, L., Liu, J., 2014. Characteristics of greenhouse gas emission in three full-scale wastewater treatment processes. *J. Environ. Sci.* 26 (2), 256–263.
- Yapıcıoğlu, P., Demir, Ö., 2021. Minimizing greenhouse gas emissions of an industrial wastewater treatment plant in terms of water-energy nexus. *Appl. Water Sci.* 11 (12), 180.
- Yoshida, H., Mønster, J., Scheutz, C., 2014. Plant-integrated measurement of greenhouse gas emissions from a municipal wastewater treatment plant. *Water Res.* 61, 108–118.