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A study on the carbon footprint contributions from a large wastewater treatment plant

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Abstract

The present work analyses aspects of the carbon footprint of a large wastewater treatment plant in central Italy. The plant mainly consists of a traditional activated sludge system along with an anaerobic digester providing a partial contribution of energy to the management. An integrated approach was adopted to evaluate the environmental sustainability of the treatment plant in terms of carbon footprint. For the assessment different sources of greenhouse gas emissions such as nitrous oxide and carbon dioxide were considered: effluent, production and transport of natural gas, energy consumption, boiler, co-generator, substrate and endogenous decays. According to the methodology adopted, energy consumption, production and transport of natural gas and N_2O emissions from the effluent were found the most contributing sources of greenhouse gases. Based on this, these sources are suggested as the most relevant ones on which wastewater treatment plant managers should pay more attention when taking actions for carbon footprint mitigation. Considerations on the role of CO_2 of biogenic origin (specifically the one in the biogas) in terms of sequestration options demonstrate that the analysis in this field should not be limited to the calculation and comment of non-fossil contributions to the overall balance.

1. Introduction

The main cause of climate change has been strictly linked to increased greenhouse gases (GHGs) in the atmosphere [1–3]. Based on this, with the growing concern for global warming, several European countries have

been tasked with achieving carbon neutrality by 2050 [4]. Although wastewater treatment plants (WWTPs) are fundamental technologies to run cities safely and hygienically, they can contribute significantly to overall GHG emissions [5–7].

Wastewater treatment processes mainly involve the removal of carbon-based substrates and nutrients such as nitrogen and phosphorus from wastewater [8–10]. In general, biological carbon-based substrates removal can be achieved through anaerobic or aerobic treatment technologies. Influent nitrogen, coming in the forms of ammonium and as organically bound chemical, is conventionally removed via nitrification and denitrification. These technologies generally generate a large amount of sludge, which needs to be properly treated before final disposal. Sludge treatments traditionally include thickening, stabilization, dewatering, and drying. Sludge stabilization is necessary to drastically reduce or eliminate the potential for putrefaction. Anaerobic and aerobic digestions (AD and AeD, respectively) are commonly applied for this purpose [11–17]. AD reduces sludge volume and generates methane for energy production. It is preferably adopted in large WWTPs. In comparison, AeD is more applied in small WWTPs due to its low capital cost, suitability for small amounts of less degradable sludge, and simple operation, despite an energy consumption approach. Sludge disposal is commonly carried out according to several techniques such as composting, landfilling, agriculture/land reuse, and incineration among others. Previous studies consistently reported that conventional wastewater technologies could lead to significant levels of GHG emissions not only deriving from direct production during the treatment processes, but also indirectly generated from the production of energy required by the various equipment and from the handling of sludge [18–24].

In several studies quantifying greenhouse gas emissions from WWTPs, there are still gaps with respect to the various contributions that should be considered [24–27]. The focus has been so far on the emissions of nitrous oxide (N_2O) and on the electrical energy consumption. However, other potentially important GHG sources such as sludge handling processes and effluent flows are often not considered. Furthermore, the creation of a database of experiences on different kind of technologies adopted in WWTPs can help start the use of a sustainable approach in the decisions from the stakeholders involved. Similarly, the contribution by sludge storage processes, including sludge drying and short-term storage (STS), are rarely included in previous carbon footprint analyses [28,29].

The various treatment technologies as well as the related different sizes could lead to different amounts of sludge production (e.g., aerobic technologies produce three-to-four times of sludge than anaerobic counterpart) and, in turn, different amount of indirect production of greenhouse gases.

In this work, a study on the carbon footprint of a large urban WWTP is presented. The study is meant to provide a complementary tool for the evaluation of the environmental impact of a newly built infrastructure on human activities and natural resources. It can help evaluating the environmental sustainability both on a local and global scale, compatibly with what is outlined by the European Community rules. The study aims at elucidating how all the different GHG sources can actually contribute to the overall carbon footprint of WWTPs. This potentially plays a key role in directing plant managers and designers' actions for GHG minimization towards the most contributing sources.

2. Materials and methods

The plant considered in this study is classified as large. Details are given in the next sections. The plant is mainly composed of a conventional activated sludge system with an anaerobic digester contributing to the overall energy requirements of the plant.

2.1. Green house gas emissions and legislation framework

WWTPs are well-known potential sources of greenhouse gases. Studying their emissions to mitigate and control them is the starting point to make these plants as sustainable as possible from the point of view of atmospheric emissions. The carbon footprint is a measure that expresses the total emissions of GHGs, directly or indirectly associated with a product, organization or service, in CO_2 equivalent. In accordance with the Kyoto Protocol, the greenhouse gases to be included are: carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFCs), sulphur hexafluoride (SF6) and perfluorocarbons (PFCs). As presented in Table 1, the CO_2 equivalent (t_{CO_2e}) is used to express the overall greenhouse effect produced by these gases in reference to the greenhouse effect of CO_2 only equal to 1.

Table 1. Potential greenhouse effect of the main gases [1].

GHG	Radiative force (W/m^2)	Greenhouse potential 100-years	Concentration in atmosphere (ppb)
CO_2	0.000018	1	370,000
CH_4	0.00037	25	1,750
N_2O	0.0032	298	314

Where: Radiative forcing is an absolute measure of the strength of a GHG over a volume base, while GWP (Global Warming Potential) is a relative measure, based on mass, over a time horizon.

The measurement of the carbon footprint of a product or process requires the specific identification and quantification of the consumption of raw materials and energy in the selected phases of its life cycle. With this regard, the experience of recent years suggests that the carbon footprint label is perceived by consumers as an indicator of the quality and sustainability of companies. In addition to conducting the analysis and accounting of CO_2 emissions, companies define a carbon management system aimed at identifying and implementing economically-efficient interventions reducing CO_2 emissions. Offset of emissions (carbon neutrality) can be achieved by the implementation of reduction measures, such as planting of trees or producing renewable energy ("Ministry of the Environment, 2015").

Regarding the reference legislation, the fundamental standards for Carbon Footprint analysis are the GHG Protocol, ISO 14064, ISO 14067 and PAS 2050. The acronym ISO identifies a series of regulations or guidelines developed by the International Organization for Standardization. These are tools for conducting business processes, improving their effectiveness and efficiency in the creation of a product. PAS 2050 (Publicly Available Specification) drawn up in England are guidelines based on ISO standards with the aim of assessing and reducing greenhouse gas emissions through Life Cycle Assessment (LCA) analysis. The GHG Protocol is an international tool mostly used by business leaders and governments to understand, quantify and control greenhouse gas emissions, evaluating four different standards:

- *Product Life Cycle Accounting and Reporting Standard* involves understanding the greenhouse gas emissions over the product life cycle, including the raw materials used, manufacturing, distribution and disposal similar to an LCA product.
- *Business Value Chain Accounting and Reporting Standard* is intended for organizations or businesses to assess the entire value chain and calculate the environmental impacts of greenhouse gas emissions. The standard also provides for the identification of possible ways to reduce greenhouse gas emissions.
- *Project Assessment Protocol and Guidelines* are used to assess greenhouse gas emission reductions by any project.
- *Corporate accounting and reporting standards* are roughly the same as an organizational LCA. It is intended for organizations/companies and is used to assess greenhouse gas emissions from their activities.

Thus, a carbon footprint value can be assigned to a product, a manufacturing plant, an organization or a company. In particular, the LCA analysis systematically evaluates the environmental impacts of a product, activity or process along the entire life cycle of that product, activity or process. The Carbon Footprint is therefore a subset of a complete LCA. The basic standards of the LCA are ISO 14044 and ISO 14040. Just like the carbon footprint, the LCA can be created for a product, a service, a project and an organization. The different assessment categories include impacts on natural resource depletion, climate change, ecosystem degradation and human health. In addition to GHGs, the LCA analysis takes into account environmental emissions and all other material inputs throughout the life cycle and evaluates all potential direct and indirect impacts on the environment. Therefore, it is a "Multi-Criteria" analysis that evaluates multiple factors. On the other hand, the carbon footprint is basically a "mono-criteria" analysis since it focuses only on one environmental impact, i.e. the climate change caused by greenhouse gas emissions.

2.2. Carbon footprint in treatment plants

The carbon footprint of WWTPs can be categorized into three components: (i) direct emissions, (ii) indirect emissions, and (iii) derived or involved emissions. Direct emissions refer to GHG emissions deriving directly from wastewater treatment processes. Specifically, they comprise nitrous oxide (N_2O), methane (CH_4) and carbon

dioxide (CO_2), which are produced during wastewater and sludge biological treatment and consequently strip to the atmosphere. N_2O and CH_4 have respectively a global warming potential (GWP) about three hundred times and twenty-five times that of CO_2 and, consequently, even a small amount of these two gases emitted can significantly contribute to the carbon footprint of a WWTP. In literature it was estimated that 1% of nitrogen loading converted to N_2O could increase the total carbon footprint of WWTP by 30% [30]. Indirect emissions are GHG emissions deriving from energy consumption by various mechanical systems such as mixing equipment, aeration systems, pumping systems, dewatering systems, etc. [11]. Derived or involved emissions are GHG emissions from sources not under WWTP management but from the handling processes of the various wastewater treatment end products such incineration of sludge and final disposal of wastewater effluents [12].

The composition of wastewater makes treatment processes a potential source of greenhouse gases. Biological processes are capable of potentially producing large quantities of GHG, transforming organic carbonaceous and nitrogen compounds into carbon dioxide, methane and nitrogen oxides. Therefore, evaluating their production potential is necessary to mitigate and control them. CO_2 is produced directly in biological processes. Another CO_2 source is linked to the production (also self-production) of energy necessary to power all the plant machineries. N_2O is currently the most powerful greenhouse gas and participates to the catalytic cycle of ozone destruction, producing NO and NO_2. The emissions that occur in the aerated areas of the plants depend on the nitrogen load, the volumetric stripping and the activity of ammonia and nitrite oxidizing bacteria [31]. N_2O is formed in the liquid phase during nitrification and denitrification. It accumulates in the water volume and is subsequently released into the atmosphere according to its stripping capability, directly linked to the aeration regime. A low air supply regime leads to higher N_2O accumulation in water compared to higher air supply operational regimes.

With regards to CH_4, although its production in aerobic reactors does not occur, dissolved methane can be carried in the plant through influent wastewater. As a matter of facts, the anaerobic processes occurring in the sewer system can produce a discrete amount of methane, which in turn accumulates in the sewage carried to the treatment plant. Once entered the WWTP, it can strip to the atmosphere or can be biologically oxidized in stagnation areas. In some sections of the plant mainstream where anaerobic conditions can evolve, such as grid-based pre-treatments, CH_4 can be generated. Furthermore, in anaerobic digestion processes, biogas is produced and, although these reactors are closed, direct gas leaks to the atmosphere can accidentally occur.

Compared to an experimental approach, the theoretical one adopted in this study has the possibility to estimate the emissions of a treatment plant independently from the measurements. Based on literature data, this approach makes it possible to estimate emissions through suitable conversion coefficients. These factors are calculated on a stoichiometric basis, considering the chemical and biological reactions that take place in the reactors. They provide a more immediate but certainly less site-specific approach. In fact, the ability to know and evaluate emissions depends solely and exclusively on the polluting load at the entrance and on the operating conditions of the plant.

The main sources of greenhouse gas production will be analysed in the next sections in order to evaluate their contribution in terms of emissions.

2.2.1. Direct CO_2 emissions

A conventional activated sludge treatment system consists of a biological reactor and a secondary clarifier with a recirculation of a fraction of excess sludge. To evaluate the emissions, we refer to the readily biodegradable substance (BOD_5 or soluble biodegradable COD), considering the growth of biomass and endogenous decay. Furthermore, to carry out an appropriate mass balance about the reactor, it is necessary to consider the quantity of solids removed from the primary and secondary settler and the quantity of sludge recirculated on top of the reactor itself. In this way, taking into account the actual operating conditions, it is possible to estimate the production of GHGs within the activated sludge system.

The kinetics of endogenous growth and decay play a fundamental role within these systems. In fact, the production of CO_2 directly depends on the rate at which these reactions take place. At the same time, it is necessary to know the operating conditions of the nitrification and denitrification process in order to evaluate the production of N_2O.

Regarding the emissions deriving from any anaerobic reactors in the sludge line due to biogas production or from cogeneration plants, it is important to know the operating conditions of the systems. In this way, once the inlet flows of biogas added from the outside and the production of biogas from the stabilization reactors are known, it is possible to estimate the production of CO_2 resulting from combustion processes or accidental gas leaks.

To estimate the production of carbon dioxide produced in aerobic biological reactors, reference will be made only to two conditions [32]: oxidation of the organic substance (or degradation of the substrate), and endogenous decay. Regarding the degradation of the substrate, we can consider the following reaction [33]:

$$2\ C_{10}H_{19}O_3N + 25\ O_2 \rightarrow 20\ CO_2 + 16\ H_2O + 2\ NH_3 \tag{1}$$
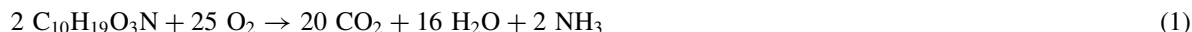
The conversion factor FC_S describing the amount of CO_2 emitted per O_2 employed for organic carbon oxidation can then be computed according to Eq. (2).

$$FC_s = \frac{(44 \times 20)\ \text{kg CO}_2/\text{mol}}{(25 \times 32)\ \text{kg O}_2/\text{mol}} = 1.1\ \text{kg CO}_2/\text{kg O}_2 \tag{2}$$

To estimate the oxygen consumption, the amount of oxygen removed in the treatment needed for bacterial growth, and the amount of oxygen purged must be both considered. The estimate can be made through Eq. (3) from Bridle Consulting [34], as follows:

$$r_{O_2} = Vr_s \times (\frac{1}{f} - 1.42 \times Y) \tag{3}$$

In Eq. (3), r_{O_2} is the oxygen removal rate (g O_2/d), Vr_s is the BOD_5 removed (kg BOD_5/d), f is the ratio between BOD_5 and BOD_{end} (equal to 0.68 according to [35]), and Y is the cell growth yield (kg VSS/kg BOD_5).

On the other hand, the stoichiometry of the reaction for the contribution related to endogenous respiration is as follows:

$$C_5H_7O_2N + 5\ O_2 \rightarrow 5\ CO_2 + 2\ H_2O + NH_3 \tag{4}$$

$C_5H_7O_2N$ represents the new cellular material produced. Considering the molecular weights of the biomass produced and CO_2 (113 and 44 g/mol, respectively), it is possible to obtain the conversion factor for endogenous respiration (FC_{end}) in a similar way to what was done previously, as expressed in Eq. (5).

$$FC_{end} = \frac{(44 \times 5)\ \text{kg CO}_2/\text{mol}}{(113)\ \text{kg } VSS/\text{mol}} = 1.947\ \text{kg CO}_2/\text{kg } VSS \tag{5}$$

Based on a mass balance in the reactor or on real data from the plant, it is necessary to know the load of volatile suspended solids influent into the reactor. In this way, by multiplying this data by the substrate conversion factor, it is possible to know the CO_2 contribution deriving from the endogenous respiration of the biomass.

Besides CO_2 production, biological nitrogen removal processes are a potential source of N_2O. N_2O production must be constantly monitored given its high global warming potential. During biological processes, the incoming nitrogen is converted into nitrites and nitrates (nitrification) under aerobic conditions, while nitrites and nitrates are converted into dinitrogen gas under anoxic conditions (denitrification). N_2O is produced during the denitrification phase as an intermediate product. Furthermore, several research works have demonstrated that also during nitrification accumulation of intermediate compounds such as hydroxylamine (NH_2OH) and NO_2^- under specific operating conditions such as very low oxygen levels can induce ammonia-oxidizing bacteria to produce N_2O as an end product in the aerated tanks [36]. A simplified overview of the different N_2O producing pathways in wastewater biological tanks according to [37] and Hiatt and Grady [38] is depicted in Fig. 1.

The guidelines proposed by the IPCC 2006 [39] consider emission factors for N_2O based on the nitrogen load entering the plant, the population served and on a series of correction factors. This approach allows evaluating the emissions both during the treatment processes in the plant, and as indirect emissions of the effluent, which will be discussed later. The quantity of N_2O emitted by the plant (N_2O_{Imp}) in g N_2O/y is expressed in Eq. (6).

$$N_2O_{Imp} = P \times U \times F_{IND-COM} \times EF_{imp} \times \frac{28}{44} \tag{6}$$

In Eq. (6), EF_{imp} is the N_2O emission factor, P is the number of equivalent inhabitants (inhab), U is the plant utilization factor (equal to 1 if the plant is in operation all year round), and $F_{IND-COM}$ is the industrial and commercial protein production factor (Default 1.25, [35]). The value for EF_{imp} proposed by the IPCC is equal to 3.2 g N_2O inhab^{-1} y^{-1}. This value was determined based on data from several pilot plants in the United States [40]. In reality, the N2O emission factor fluctuates in a wide interval, as shown in Table 2.

Boiocchi et al. [41] identified N2O emission factors within the same range. It is important to point out that the value of N_2O_{Imp} obtained through Eq. (6) is only an estimate that does not consider the processes and operating conditions, which could sensibly change the emission factors [24,42]. Nonetheless, it provides a good method for preliminarily assessing the order of magnitude of N2O emissions.

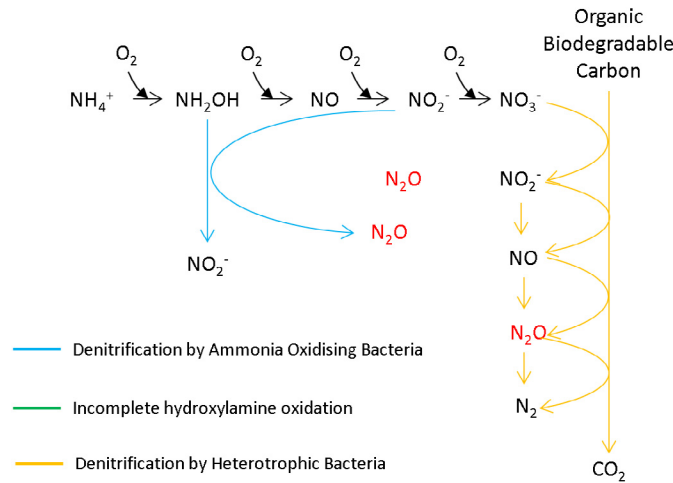**Fig. 1.** Simplified overview of the N_2O producing pathways in wastewater biological systems.

Table 2. Value used for the determination of direct N_2O emissions [39].

Parameter (Notation)	Unit	Default	Range
Emission factor (EF_{imp})	g N_2O/inhab/year	3.2	2–8
Equivalent inhabitants (P)	Inhabitants	Specific	Specific
Plant utilization Factor (U)	–	Specific	Specific
production factor ($F_{IND-COM}$)	–	1.25	1–1.5

2.2.2. Indirect emissions

In this study, only anaerobic digestion was analysed for the evaluation of indirect greenhouse gas emissions. This process is widely used in wastewater treatment plants and this in turn enables different alternatives for sludge reuse. The biogas produced can be exploited for energy recovery (sometimes it results sufficient to satisfy the energy needs of the plants). All the biogas produced is assumed to be sent to the cogeneration unit for the production of electrical and thermal energy used either externally or internally to keep stabilization process inside the digesters under either mesophilic or, less commonly, thermophilic conditions (i.e. 30–40 °C or 45–55 °C, respectively). It can be assumed that all incoming methane is thereby converted and transformed into CO_2 and H_2O. Therefore, in terms of greenhouse gas contribution, biogas is not emitted as it is, but its contribution is in the form of CO_2 generated from the combustion process, which takes place according to the reaction in Eq. (7).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{7}$$

Based on Eq. (7), the ratio between the molecular weight of methane and carbon dioxide is then used to estimate the combustion conversion factor (FC_{comb}), as presented in Eq. (8):

$$FC_{comb} = \frac{44 \text{ kg } CO_2/\text{mol}}{16 \text{ kg } CH_4/\text{mol}} = 2.75 \text{ kg } CO_2/\text{kg } CH_4 \tag{8}$$

The conversion factor for combustion multiplied by the methane from the biogas produced yields the quantity of CO_2 produced from methane combustion. Alternatively, based on the type of plant and the type of fuel, emission factors provided by ISPRA on TERNA data source can be used [43]. It is important to take into account the fact that the amount of biogas generated from anaerobic digestion is not always sufficient to satisfy the energy demand. To meet both the energy needs of the plant and the demand for electricity and heat of the users close to the plant, cogenerators are generally sized for higher amounts of fuel. The fuel typically added is natural gas, which in this study is assumed to be 100% methane. In this way, the quantity of CO_2 produced by the combustion of the biogas and natural gas will be output as CO_2 from the cogenerator, plus the CO_2 that enters the cogenerator from the biogas, which is not altered by the combustion process. This concept is mathematically described in Eq. (9).

$$CO_2^{energy} = CO_2^{comb_{biogas}} + CO_2^{comb_{natgas}} + CO_2^{biogas} \tag{9}$$

In Eq. (9), CO_2^{energy} is the CO_2 emitted for the production of all energy used in the WWTP, $CO_2^{comb_{biogas}}$ is the CO_2 emitted from the combustion of CH_4 coming from the biogas produced in the anaerobic digester of the WWTP, $CO_2^{comb_{natgas}}$ is the CO_2 emitted from the combustion of CH_4 coming from externally-sourced natural gas, CO_2^{biogas} is the CO_2 directly produced during the anaerobic reactions inside the digester and therefore part of the collected biogas.

To better assess the emissions deriving from these sources, it is necessary to know the flow of biogas and natural gas entering both the cogenerator and the boilers. Furthermore, the boilers, being sized only on demand peaks to make up for the production shortages of the cogenerator, are not in operation all year round, so it will be necessary to know or estimate the time in which they come into operation. Once the inlet methane flow rates are known, the calculation of the emissions is done in the same way as for the cogenerator, assuming that the incoming natural gas is composed of 100% methane and that is converted entirely into carbon dioxide. This assumption is suitable considering the low impurities present in the natural gas and the high efficiency of combustion.

To evaluate indirect emissions, it is necessary to know the energy mix of the country where the plant is located, that is Italy in our case [44]. It is of utmost importance to evaluate thermoelectric sources, as they are the ones that are the most emitting. Conversely, renewable energies have substantially no impact on the environment. It is then necessary to proceed with the evaluation of the emission factors. In this study, it was decided to take into consideration the gross emission factors, as they include not only the production but also the transport of electricity. Non-cogenerative plants are those with higher emissions as they do not recover part of the thermal energy produced during combustion. Once the emission factors are known, it is necessary to know the power installed in the system. The analysis was conducted on all machineries in service, evaluating for each the installed power, the number of units and the hours of operation. In this way, the value necessary to appropriately estimate the indirect emission contribution of the plant could be obtained. As expressed in Eq. (10), the calculation of the production of GHG due to energy consumption ($P_{CO_2 \, energy}$) consists in multiplying the overall CO_2 emission factor, obtained as the average of the emission factors of the various energy sources (EF_i) weighted according to the respective percentage of utilization (Per_e, by the value of electricity consumption (C_e) obtained from the analysis of the installed power in the system.

$$P_{CO_2 \, energy} = C_e \times \sum_i (Per_e \times EF_i) \tag{10}$$

At the same time, in virtue of what has been said previously on the incoming flows to the co-generator, it is necessary to evaluate the emission factor of natural gas imported from outside to meet the energy demand. In fact, once the natural gas flow rate (Q_{NG}) to be added is known and the gross emission factor for natural gas (EF_{NG}) is known, it will be sufficient to multiply the two factors to know the production of GHG from natural gas usage ($P_{CO_2 \, NG}$), as shown in Eq. (11). For the natural gas emission factor (EF_{NG}), a value of 1.956 kg $CO_{2equiv.}/Nm^3$ was used.

$$P_{CO_2 \, NG} = Q_{NG} \times EF_{NG} \tag{11}$$

The total indirect emissions $P_{CO_2 TOT}$ of $CO_{2 \, equiv.}$ deriving from added natural gas and energy consumption will therefore be given by the sum of the two contributions.

$$P_{CO_2 \, TOT} = P_{CO_2 \, energy} + P_{CO_2 \, NG} \tag{12}$$

2.2.3. Derived emissions

In this section, the methods according to which emissions originated from the pollutants discharged into water bodies receiving wastewater effluents are estimated are described. The effluent wastewater pollutants considered are soluble BOD_5 and nitrogen. When the organic matter is oxidized, biomass growth can be assumed to be 0.422 g_{VSS}/g_{BOD_5} and the CO_2 emitted thereby can be assumed 0.33 g_{CO_2}/g_{BOD_5}. Furthermore, the oxidation of VSS produces 1.56 g_{CO_2}/g_{VSS} based on the stoichiometric relationship. Based on this, the CO_2 emissions resulting from the degradation of BOD in the effluent can be calculated as follows:

$$\left[\left(0.422 \frac{g \, VSS}{g \, BOD_5} \times 1.56 \frac{g \, CO_2}{g \, VSS} \right) + 0.33 \frac{g \, CO_2}{g \, BOD_5} \right] \times Q_e \times BOD_{5,eff} = 0.986 \times Q_e \times BOD_{5,eff} \tag{13}$$

The necessary condition for the oxidation of organic matter to occur is that the concentration of dissolved oxygen in the receiving water body is stoichiometrically enough. In real conditions, the dissolved oxygen concentration is not

always sufficient to oxidize all organic matter. Nevertheless, in this study it was not considered as a limiting factor. This assumption is precautionary as it overestimates CO_2 emissions in the effluent. It is also true that alternative electron acceptors such as nitrates can be used to oxidize organic carbon in receiving water bodies.

For the estimation of N_2O emissions from wastewater effluent nitrogen (N_2O_{Eff}), in light of the IPCC guidelines [39], Eq. (14) was used.

$$N_2O_{Eff} = N_{Eff} \times EF_{Eff} \times \frac{44}{28} \tag{14}$$

In Eq. (14), EF_{Eff} is the N_2O emission factor for the effluent stream while N_{Eff} is the effluent nitrogen load. The latter is calculated according to Eq. (15).

$$N_{Eff} = (P \times Prot \times F_{NPR} \times F_{NON-COM} \times F_{IND-COM}) - N_R \tag{15}$$

In Eq. (15) P is the number of equivalent inhabitants (inhab), $Prot$ is the annual per capita consumption of protein (kg Protein/inhab/y), F_{NPR} is the fraction of nitrogen in proteins (Default 0.16 kg N/kg proteins, [35], $F_{NON-COM}$ is the factor for non-consumed proteins delivered to the wastewater, $F_{IND-COM}$ is the industrial and commercial protein production factor (Default 1.25, [35]. N_R is the nitrogen removed with sludge, set to 13.4% of the influent TN load in virtue of the findings by Boiocchi et al. [41]. The influent TN load is calculated based on the typical per capita N load of 12 g N/ inhab/d. All these parameters are corrective factors to best estimate the contribution of nitrogen present in the wastewater. The values used are reported in Table 3. As can be seen, the emission factor is the only parameter fluctuating in fairly wide interval while the other parameters are more constrained. The choice of the default value was based on literature data.

Table 3. Typical ranges and values of indirect emissions [35].

Parameter (Notation)	Unit	Default	Range
Emission Factor (EF $_{eff}$)	kg N_2O/kg $_N$	0.005	0.0005–0.25
Inhabitants		Specific	Specific
Factor of protein consume ($F_{NON-COM}$)	–	1.3	1–1.5
Production factor (F $_{IND-COM}$)	–	1.25	1–1.5
Nitrogen fraction in proteins (F_{NPR})	kg $_N$/kg $_{Proteins}$	0.16	0.15–0.17

2.3. Input parameters

For the assessment of the carbon footprint, literature data and some operating parameters of existing plants were used to best apply the model to a real case. The input parameters used in the evaluation are presented in Table 4 grouped as follows: influent wastewater, sludge treatment line, energy recovery, boiler and effluent. Regarding the sludge line it was assumed the use of two anaerobic digesters.

3. Results and discussions

The results of the emissions are reported in terms of tons of $CO_{2equiv.}$ on an annual basis. The estimation of emissions was made in the most severe operating conditions for the plant.

3.1. CO$_2$ emissions

The results of direct CO_2 emissions are shown in Fig. 2, while Fig. 3 shows the results for indirect CO_2 emissions. Fig. 2 shows comparable GHG contributions among endogenous decay, substrate degradation and heater sources. However, the CO_2 contribution by the heater shows up to be the most impacting on the direct CO_2 emissions, contributing of almost a half, while endogenous decay is the least contributing source. This has important positive implications in virtue of the fact that CO_2 emissions by the heater can be more easily contained and/or minimized, for example through the implementation of CO_2 capturing technologies, compared to the CO_2 produced by the endogenous decay which is a naturally occurring process difficult to control.

With regards to indirect and derived CO_2 emissions, it can be observed from Fig. 3 that the energy consumption deriving from both the cogenerator and the production and transport of natural gas contributes predominantly to

Table 4. Input data.

| Parameter/Notes	Value	Unit
Influent Wastewater		
Inhabitants	800,000	inhab.
Flow (Q_{in})	640,000	m^3/d
VSS (VSS_{inf})	0.150	kg VSS/m^3
BOD_5 (BOD_{5inf})	0.102	kg BOD_5/m^3
Total Nitrogen (TN)	0.033	kg NH_4^+-N/m^3
Temperature ($T_{wastewater}$)	15	°C
Annual consumption of protein/capita * (Protein)	53	kg/inhab/y [45]
Sludge Treatment Line		
Number of digesters (n)	2	–
Production rate biogas (GPR)	0.90	Nm^3/kgVS$_{rem}$
Volume % CH_4 (g_{CH4})	65	% [35]
Volume % CO_2 (g_{CO2})	35	% [35]
Temperature biogas (T_{biogas})	305	K
Accidental losses	0.00	d
Non-operative days	0	d
Energy recovery		
Installed electric power (kW $_{einput}$)	15	MW
Flow of natural gas to the co-generator (Q_{co})	44,335	Nm^3/d
Volume % CH_4 (g_{CH4})	65	% [35]
Volume % CO_2 (g_{CO2})	35	% [35]
Biogas temperature (T_{biogas})	340	K
Biogas pressure (P_{biogas})	1	atm
Methane lower heating value (LHV_{CH4})	34,500	kJ/Nm^3
Biogas lower heating value (LHV_{biogas})	21,500	kJ/Nm^3
Natural gas added to co-generator (GEF-co)	119,994	Nm^3/d
Boiler		
Installed thermic power kW $_{tinput}$	10	MW
day of use (day)	365	d
Flow of biogas to the boiler (Q_{bo})	0	Nm^3/d
Volume % CH_4 (g_{CH4})	0	%
Volume % CO_2 (g_{CO2})	0	%
Biogas temperature (T_{biogas})	340	K
Biogas pressure (P_{biogas})	1	atm
Methane lower heating value (LHV_{CH4})	34500	kJ/Nm^3
Biogas lower heating value (LHV_{CH4})	21,500	kJ/Nm^3
Biogas added to the boiler (GEF-bo)	42260	kg CH_4/d
Effluent		
BOD_5 (BOD_{5eff})	23.24	g BOD_5/m^3

indirect and derived CO_2 emissions, while CO_2 emission from the effluent contribute only marginally. It must be pointed that these results are affected by the various assumption adopted. The sizing on the cogenerator was decided so that it would provide sufficient electricity consumption to system. Furthermore, it was assumed that the cogenerator worked only with natural gas, but other plant configurations also allow the recovery of biogas produced by the digesters. Variations in the demand for electricity significantly affect both the emission values from this source and the flow of natural gas to be added from the outside, while also modifying the emissions for the production and transport of the latter. The contribution of the boiler, on the other hand, was considered only in relation to the thermal needs of the system. In fact, the biogas produced, for example, can partly serve to heat the digester, and to satisfy the thermal demand of a possible sludge drying plant.

3.2. N_2O emissions

For N_2O emissions, the greenhouse effect potential of N_2O is used, which is equal to 298 times that of CO_2. This value is used to convert emissions into equivalent CO_2 terms (Fig. 4).
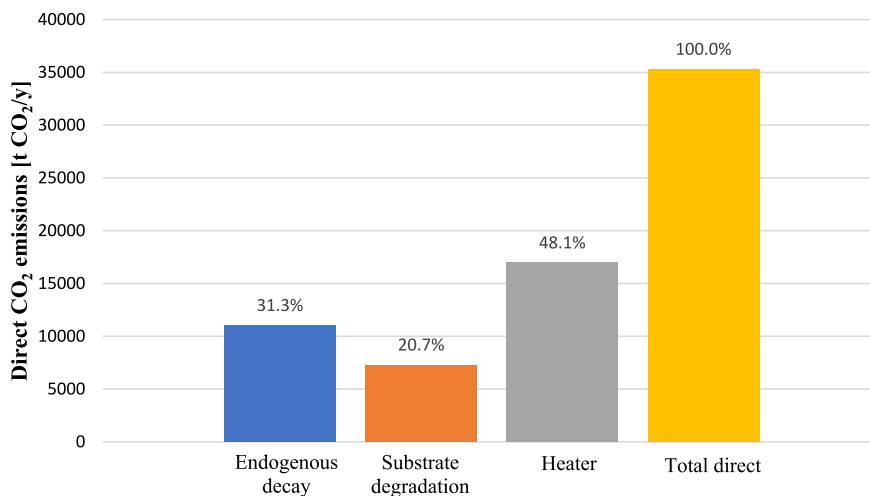
Fig. 2. Direct CO_2 emissions.
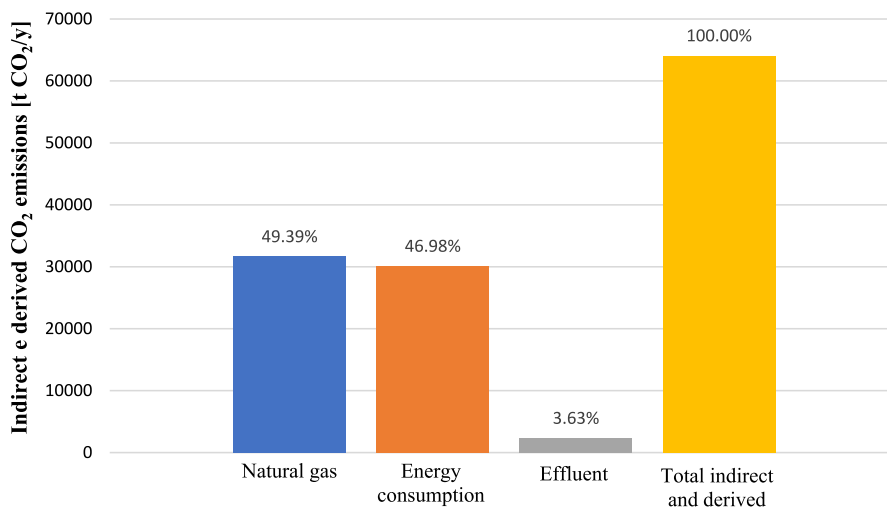
Fig. 3. Indirect and derived CO_2 emissions.

The contribution of the effluent source results much greater compared to the contribution from the biological reactors due to the calculation method used [39]. It is also important to point out the reported three-order-of-magnitude uncertainty on the N_2O emission factor for the effluent contribution. This uncertainty propagates to the final N_2O emissions estimated. Indeed, these results highlight the importance of studying more in detail the N_2O emission potential from effluent. At this aim, in situ measurements are necessary, as there is no standardized theoretical methodology to assess their contribution with certainty. While a lot of research work has been carried out for N_2O modelling and control in biological wastewater treatment systems [5,24,31,41,46], these results should encourage more research on the N_2O emission originated from wastewater discharges.

3.3. Overall greenhouse gas emissions

The assessment of the overall carbon footprint reported was carried out in terms of CO_2 equivalent on an annual time scale. The contributions deriving from CO_2 and N_2O were summed up together to evaluate the overall emission. Additionally, it has to be emphasized that the greenhouse gases that have been considered are only N_2O and CO_2, as it is assumed that the direct emissions of methane into the atmosphere are modest (in trace) in a wastewater
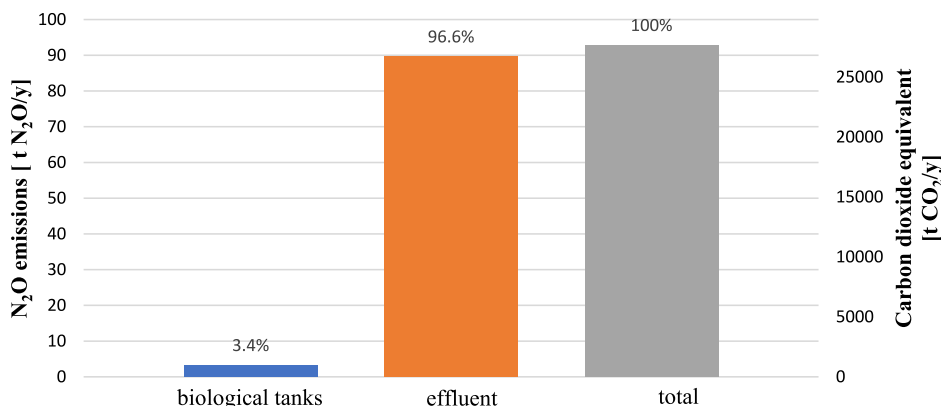
Fig. 4. N_2O production and relative corresponding CO_2 contribution.

treatment plant. The results obtained thereby are shown in Fig. 5. It can be observed that the major contributions to the overall carbon footprint of WWTPs result linked to the production and transport of natural gas, to the energy consumption and to the N_2O emissions from the effluent. Notably, the contribution by N_2O emissions from the biological reactors is found negligible. However, it is important to point out that results about the N_2O emissions here reported are subject to several uncertainties and that the emissions factors proposed by the IPCC might actually underestimate the actual potential N_2O emissions from WWTP biological reactors. It is here important to highlight that in the future CO_2 emissions from different sources may need to be considered distinctively based on whether CO_2 capture technologies can be applied or not. While the CO_2 generated from some wastewater sources cannot be captured before delivery to the atmosphere, the CO_2 generated from other sources such as from biogas combustion and heater can, thus not contributing to the overall WWTP carbon footprint if sequestration technologies are applied. In light of an increasing push towards more sustainable technologies, the adoption of CO_2 capturing technologies may widespread in the future in WWTPs and this will need to be properly accounted.
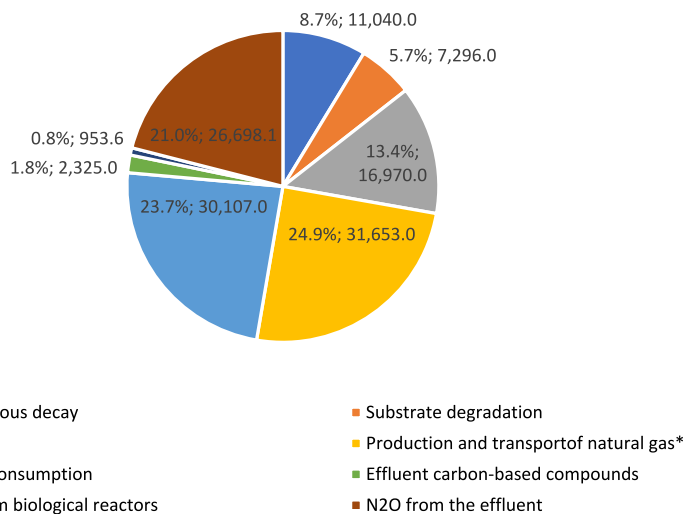

Fig. 5. GHG emissions (in tons of CO_2 equivalent per year) and relative percentage contributions.

4. Conclusions and future perspectives

In this study, a large WWTP was used as a case study to develop a preliminary carbon footprint assessment based on literature data. The results of the emissions are studied in terms of tons of $CO_{2equiv.}$ on annual basis. The estimation of emissions was made in the most severe operating conditions for the plant.

Contrary to several previous research on the same topic, the present work studies more comprehensively the possible wastewater sources of GHGs. This allowed to estimate thoroughly the relative contributions by these sources and to identify the most impactful ones.

Specifically, the energy consumption, the production and transport of natural gas and N_2O emissions from the effluent were found as the most contributing sources. Based on this, it can be suggested that WWTP managers focus their core actions for carbon footprint minimization towards optimizing energy consumptions, reducing the need for natural gas and avoiding the accumulation of N_2O and other N compounds in the liquid effluents.

Employment of renewable energy can represent an important asset for the improvement of WWTP environmental sustainability. It is also due to keep in mind that the results here presented were achieved based on several assumptions that need confirmation with more site-specific investigations.

In future perspective, it is important to discriminate between GHG emissions that can be captured from those that cannot and avoid limiting the analysis on their origin. As a matter of facts, there are some available technologies allowing to capture and remove the CO_2 produced, thus preventing the GHGs to accumulate in the atmosphere not depending on the origin of CO_2. If these technologies were applied, some GHG sources in WWTPs may not be considered when computing the overall plant carbon footprint and the plant could be seen as an opportunity to contribute to the lowering of CO_2 emitted at national level.

Moreover, the assessment of derived emissions demonstrated that the issue of CO_2 emission originated from discharged pollutants should be necessarily included in the balances of the WWTPs. However, to this concern, the literature should evolve towards a more detailed approach for assessing that contribution.

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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